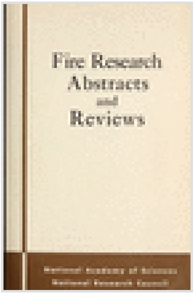

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FOREWORD

A publication of great significance to the furtherance of fire research in the United States has been published.* I urge the readers of this journal to obtain a copy and study its contents. It is a pleasure to reprint the "Conclusions and Recommendations" from this publication in the following pages. If the recommendations are implemented, a major forward step will have been taken. Professor Howard W. Emmons, chairman of the summer study, deserves great credit for the conception and brilliant execution of this difficult undertaking.

The Ninth Symposium (International) on Combustion to be held at Cornell University, August 27-September 1, 1962, will include several papers of direct interest to fire research. One part of the colloquium on "Modelling Principles," organized by Professor D. B. Spalding, Imperial College, London, will deal specifically with free-burning fire problems. Detailed information on the technical program, housing, etc., can be obtained from the Combustion Institute, Union Trust Building, Pittsburgh 19, Pennsylvania.

W. G. Berl,
Editor

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* NAS-NRC Publication 949, "A Study of Fire Problems" (A study held at Woods Hole, Massachusetts, July 17 to August 11, 1961, under the guidance of the Committee on Fire Research of the National Academy of Sciences-National Research Council). Available from the Printing and Publishing Office, National Academy of Sciences-National Research Council, Washington 25, D.C. ($2.00 per copy).

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A STUDY OF FIRE PROBLEMS

(A Study held at Woods Hole, Massachusetts, July 17 to August 11, 1961, under the guidance of the Committee on Fire Research of the National Academy of Sciences-National Research Council, Division of Engineering and Industrial Research.)

Conclusions and Recommendations

During the course of the summer study on hostile fire, certain features of the over-all fire problem have been clarified in the minds of the participants; the purpose of this section is to discuss these features briefly.

The problems of fire suppression and prevention have been under study for a great number of years by a wide variety of private and governmental organizations, and at the present time some 20 million dollars are spent annually in fire-related research and development work in the United States. However, most of this effort is applied work, a good deal of which is directed toward problems of satisfying code requirements and finding remedies for very specific problems. In addition, because the effort is supported by a wide variety of organizations, the direction of the total effect is diffuse, and areas of economic interest to the whole nation are often of insufficient interest, to any one group, to produce a desirable over-all level of attention.

The consensus of the summer study group is that a fire group should be established within the structure of the Federal Government to ensure that the national effort is a balanced one. This group would have as its prime functions the following:

1. The continuous assessment of the complete program of fire prevention and suppression, including the fire-related research and development work being carried out in the nation.

2. Based on the assessment of the national effort, the group should arrange for the execution of work not adequately supported. Where possible, this arrangement should take the form of encouragement and/or financial support to the private and public organizations already carrying out work in the deficient areas. Where necessary the fire group should actively support new work either by contract with existing organizations or by work within the organization of the fire group itself.

To carry out these functions effectively, the fire group should consist of a staff of technical people who devote full time to the project. Although the use of consultants and advisory committees may be desirable, the existence of a permanent organization with full-time director and technical staff is necessary. Of equal importance is the assurance of a budget which would permit a sustained effort.

An attempt has been made to estimate a reasonable budget for the fire group. It is felt that an initial annual expenditure of about three million dollars would be required. Of this sum, approximately one-third would be spent on fundamental research problems, one-third on problems associated with obtaining information of a fundamental and applied nature from large-scale controlled or natural burns, and one-third on studies of fire-related problems in the areas of economic and operational research. As the program develops, greater effort in these areas would be possible, and problems of an applied nature could be attempted in following years. The sustained effort required to support this fire group work may become as great as three times the initial effort.

It should be emphasized that the study group was aware of the efforts presently being made in industry and by government groups to support and to encourage fire-prevention and -suppression work. One of the major functions of the proposed fire group should be to stimulate such work; and where feasible, the resources of these organizations should be used in carrying out the proposed program.

The purview of the fire group should include all aspects of the fire problem. Thus, the group should be free to sponsor investigations of any problem which, in its judgment, is critical. These investigations should specifically include fundamental research problems in the pertinent fields of science, applied and developmental problems, operations research, economic analysis of problems at various levels of government, and educational problems.

The summer study group feels that a number of specific programs are required and should be initiated as soon as possible by the proposed fire group. These suggested programs reflect the potentially broad scope of the work of the fire group. General areas of interest will be discussed in the following paragraphs; specific recommendations for action are given later in this chapter.

At the present time there exists a great body of knowledge concerning fire-prevention and -suppression activities. This information includes areas such as techniques for good public educational programs, good fire-fighting tactics, and good professional training programs. Such information is used well in some areas and not at all in others. One of the important actions of the fire group should be to search for ways and means of achieving the adoption by state and local fire authorities of the best techniques available. Similarly, the fire group should also encourage the dissemination of fire-prevention information through the available communications media, to reach the general public, and through the support of regular and continuing programs in schools, to reach the young people of the nation.

In any study of fire problems, from the point of view of operations research or economics, it immediately becomes apparent that a tremendous amount of information is available but that this material is often incomplete, nonuniformly reported, or inaccurate, and that pertinent corollary data are often not collected at all. In order to facilitate the useful collection of data, two programs should be initiated. First, sufficient studies of the important economic and operational problems should be carried out to identify the desired information, and second, this information must be increasingly accurate, collected in a consistent and uniform manner.

The economic problems of importance certainly include the determination of the best level and distribution of expenditures for fire-prevention and -suppression measures at national, urban, and personal levels, and the examination of the economic incentives which operate to reduce fire costs. In the latter category, the determination, allocation, and regulation of fire costs, including insurance and taxes, should be studied.

Both the economic and the operations-research studies should be directed at the problem of establishing the best use of fire-fighting funds. For example, there is at present no rational way of determining the relative value of funds spent on fire-prevention work and on fire-fighting equipment. The fact that a great diversity of practices exists in the fire departments of the United States suggests that the best practices may be sorted out by the correct operational analysis. In any event, the techniques of operational analysis should be used to extract as much information as possible from the fires which annually destroy about 1.5 billion dollars worth of property.

Available techniques should be used to construct model fires and educational "games" for the training of firemen and for the evaluation of new fire-fighting practices.

Controlled burning of condemned structures or selected forest areas can be used to obtain quantitative information of interest in operational research and fundamental and applied research. Information obtained from controlled burns can be an invaluable supplement to information which can also be obtained from hostile fires. A major effort should be made to develop appropriate instrumentation and necessary techniques for this type of investigation.

The fire group should investigate the present national effort in applied research and should support needed work. Because most of the work being done in this field is supported by industrial concerns with immediate objectives in mind, the summer study group feels that supplementary efforts will be necessary.

Finally, the summer study group feels that the present effort in fundamental research is relatively weak. The fire group should support work on fundamental problems covering the entire purview of the group. For example, studies are needed on such fire-related phenomena as pyrolysis, ignition, fire spread, atmospheric interactions, fuel properties, effects of moisture, and extinguishment. These projects should be supported by direct contracts, where possible, but where necessary, should be carried out by the staff of the fire group.

The fire group should also have the responsibility of translating the results of basic studies, as far as possible, into useful fire-suppression tools. Thus, the ill-defined area between "fundamental" and "applied" work should receive particular attention.

As a principal part of the translation mentioned in the last paragraph, the fire group should be responsible for increasing the dissemination of information at all technical levels. The group should hold meetings and support publications with the purpose of bringing the fire problem to the attention of the engineering and scientific community, increasing the exchange of information between scientists, engineers, and professional fire people. Although a technical journal devoted to fire problems may be inappropriate at this time, an abstracting journal such as the Fire Research Abstracts and Reviews serves a very useful function.

In the foregoing discussion, the general problems falling within the purview of the proposed fire group are discussed in general terms. More specific recommendations follow.

Recommendations

I. A fire group should be established within the Federal Government to take over-all responsibility for the fire problem. This fire group should note and encourage work now in progress as supported by diverse public and private units; assess progress continually; seek, encourage, and develop new ideas on fire control; arrange for the execution of work not now adequately supported.

For these purposes, the fire group should:

1. consist of a director with an adequate staff of full-time personnel,
2. be given authority and have responsibility to contract for necessary

work with universities and nonprofit research groups, industrial concerns, and government organizations, and
3. be provided with a budget adequate for the work.

A first year budget of $3,000,000 is suggested. Perhaps three times this sum will be needed as the program develops. The fire problem, costing society $5,000,000,000 per year, deserves to be considered along with other national problems of this magnitude at the highest levels—the Departments and Congress. The fire group should, therefore, have authority at this level.

II. The fire group should make use of existing public and private organizations in carrying out its program.

III. The program of the fire group should include the following important activities:

1. Search for ways and means of achieving universal adoption by state and local fire authorities of the best techniques which have been developed by the more progressive states and communities. These include fireman training, prevention measures, and prefire planning.
2. Support public education in fire-prevention measures and fire consciousness. Additional study will be needed to develop specific measures.
3. Collect, organize, analyze, and disseminate data on fires. The most urgent need is a quantitative evaluation of the relative importance of organizational and operational factors in fire control, and their economic consequences. To be useful, pertinent data of adequate accuracy must be collected in a consistent and uniform manner. This will involve state and municipal organizations, and urban and forest fires.
4. Study the economic aspects of fire, including common-pool problems and cost-benefit relationships.
5. Study the effect on total fire cost of the variable factors of fire-control organization and response. These factors include leadership, fire-fighting tactics, prefire planning, and personnel training. To carry through this study, a scale of "fire hazard potential" for area classification and a general measure of "total fire cost" should be developed.
6. Examine the determination, allocation, and regulation of fire costs including insurance and taxes, required to promote more equitable distribution of costs and to produce an economic incentive to reduce risk.
7. Support a wide variety of fundamental research connected with fire phenomena, such as fuel properties, pyrolysis, ignition, fire spread, atmospheric interactions, effect of moisture, extinguishment, etc.
8. Support those special items of applied research that are of important social consequence but poor economic prospect. These items include special hazards, test methods and standards, and development of new techniques lying between fundamental research and commercial exploitation.
9. Use controlled burning of condemned structures and selected forest areas to acquire data on fundamental fire phenomena and the response of fire to extinguishing agents. Data should also be obtained on the effect of the various organizational and operational factors in (5) above.

10. Develop player-participation games for the training of fire-fighting personnel, for the investigation of fire-fighting techniques, and for the planning of interagency cooperation in fire-suppression activities.
11. Sponsor meetings and publications as required to bring the fire problem to the attention of the scientific and engineering community and to disseminate new knowledge to all interested parties.

PROCEEDINGS OF SYMPOSIUM* ON

FIRE CONTROL RESEARCH

Iron Pentacarbonyl in Methane-Oxygen (or Air) Flames

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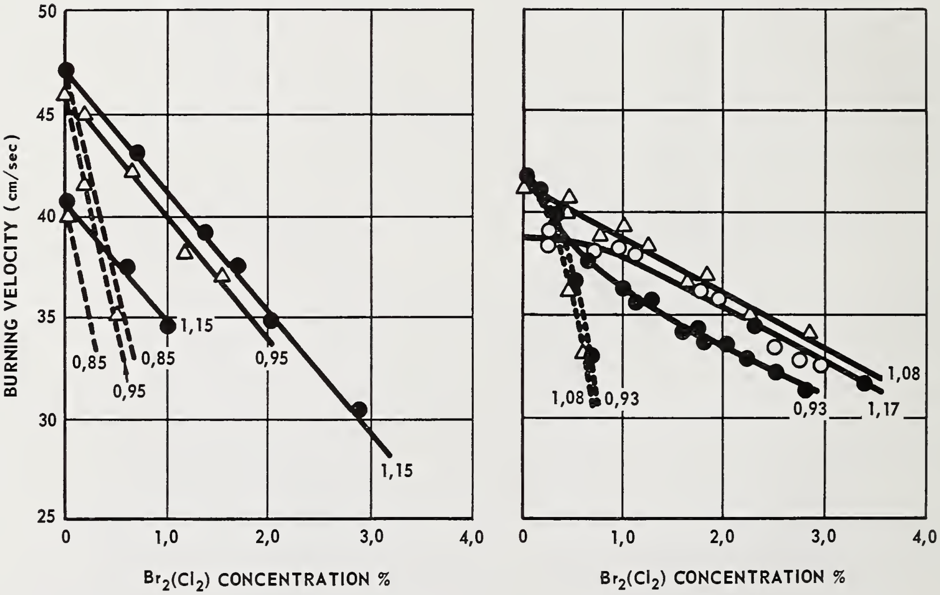
It is known that halogenated hydrocarbons or halogens added to a combustible mixture of hydrocarbon and air, or to some other combustible mixture, reduce the burning velocity of laminar flames. An example is given in Figure 1, where the burning velocity in benzene-air and n-hexane-air mixtures (at three different fuel concentrations) is plotted as a function of the chlorine or bromine content of the mixture. In order to obtain a pronounced decrease of the burning velocity one has to add an amount of additive which is comparable to the fuel concentra-



(*a*) *benzene/air*

(*b*) *n-hexane/air*

Figure 1. Influence of bromine and chlorine concentration on burning velocity. Dotted curves refer to bromine. Numbers alongside curves indicate equivalence ratio (actual fuel/stoichiometric fuel).

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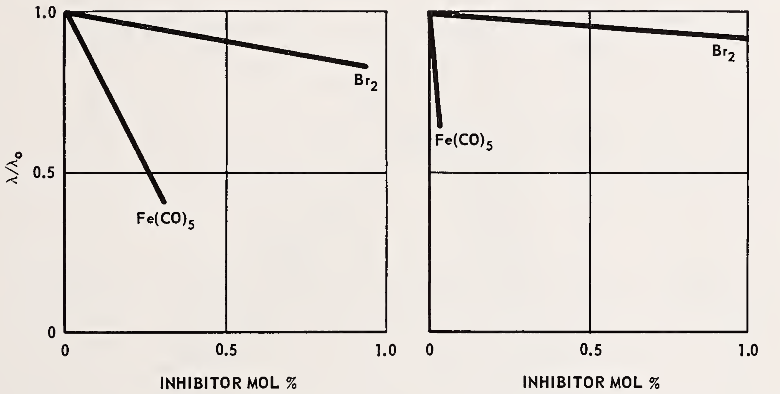
* Jointly sponsored by the Committee on Fire Research, NAS-NRC, and the Division of Fuel Chemistry, American Chemical Society, as a part of the National Meeting of the American Chemical Society in Chicago, Illinois, September 3–8, 1961. The first part of the Proceedings appeared in FIRE RESEARCH ABSTRACTS AND REVIEWS, Volume 3, No. 3 (September 1961). The papers included here conclude the Proceedings.

tion. (Hydrogen-rich fuels very often need more additive than lean mixtures. Iodine is more active than bromine which in turn is more active than chlorine.)

Investigating the influence of additives on the burning velocity, several substances were tested which were much more effective than halogens or phosphorus-containing substances. One of these substances was $Fe(CO)_5$. Figure 2 shows the influence of $Fe(CO)_5$ on the burning velocity of hydrogen-air and n-hexane-air mixtures compared with that of bromine. For mixtures of other hydrocarbons with air the efficiency of $Fe(CO)_5$ is comparable to its influence on n-hexane-air mixtures.



(*a*) *hydrogen (37%)/air* (*b*) *stoichiometric n-hexane/air*

Figure 2. Influence of bromine and iron pentacarbonyl on burning velocity. λ/λ_0 = *fractional reduction in burning velocity*

Measurements of the burning velocity alone do not give detailed quantitative information about the specific kinetic influence of $Fe(CO)_5$ and its products. Therefore, we tried to find the mode of action of $Fe(CO)_5$ in hydrocarbon-air and in hydrocarbon-oxygen flames in the course of our investigation of reaction rates in low-pressure flames. In order to do this, first the pressure dependence of the influence of $Fe(CO)_5$ had to be investigated. Figure 3 shows the influence of pressure on the burning velocity of methane-oxygen flames as a function of concentration. Contrary to observations of other authors, the burning velocity for "stoichiometric" methane-, acetylene-, and ethane-oxygen flames is practically independent of pressure in a range from 0.1 to several atmospheres. Below 0.1 atm, their burning velocity seems to increase with decreasing pressure (at 0.033 atm, the burner diameter was 3 cm, the diameter of the pressure vessel was 18 cm, and the height 35 cm).

Figure 4 gives the influence of iron pentacarbonyl on the burning velocity of the stoichiometric methane-oxygen mixtures at several pressures. (The $Fe(CO)_5$ concentration is given in volume per cent of the entire mixture.) Small inhibitor concentrations have a distinct but not strong influence. The influence decreases with decreasing pressure (the $Fe(CO)_5$ concentration is proportional to pressure). In methane-air mixtures (Figure 5) as well as in other hydrocarbon-air-mixtures, the influence of $Fe(CO)_5$ is much more pronounced. 0.01 per cent of $Fe(CO)_5$

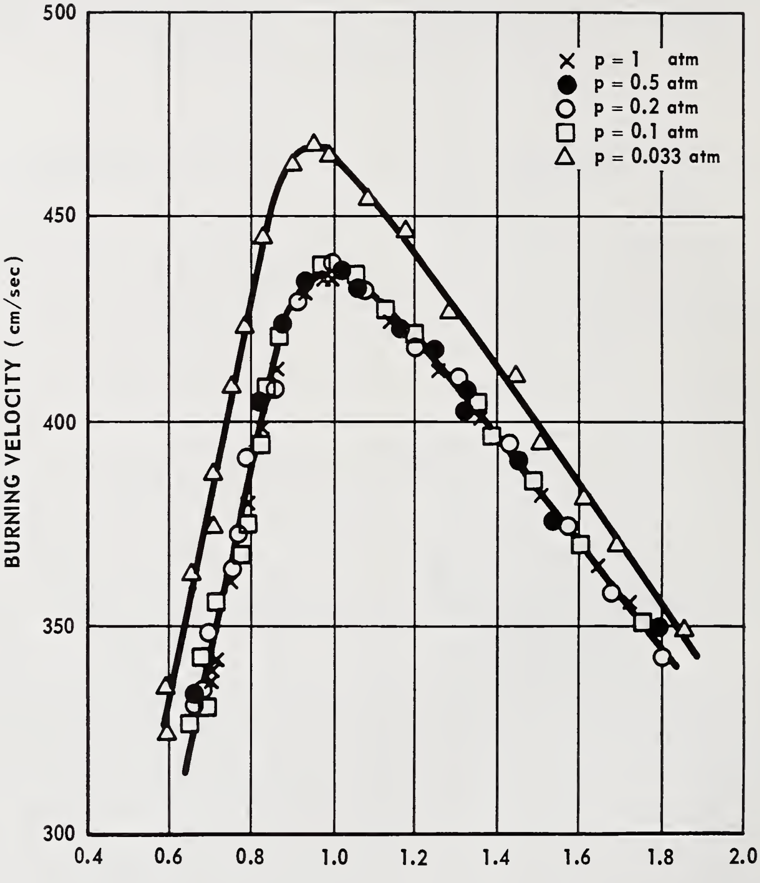


Figure 3. Influence of mixture composition and pressure on the burning velocity of methane/air flames. λ = actual oxygen content/stoichiometric oxygen content.*

causes a decrease in burning velocity of 25 per cent at atmospheric pressure. If one compares the influence of $Fe(CO)_5$, not in volume per cent of the total mixture but in volume per cent of the fuel, it still remains three times more active in mixtures with air than with oxygen. This is true as long as the absolute $Fe(CO)_5$ concentration (in molecules per cm^3) remains the same. As in methane-oxygen the additive becomes less active with decreasing pressure.

In a pressure range sufficiently low to allow a detailed investigation of the reaction zone of the flame the effect of $Fe(CO)_5$ is very small. Therefore, one cannot obtain direct information about the inhibition of $Fe(CO)_5$. Nevertheless, the investigation of low-pressure flames with $Fe(CO)_5$ added seemed to be useful for learning something about the specific action of the inhibitor on the chemical reaction. The following results should be considered as preliminary.

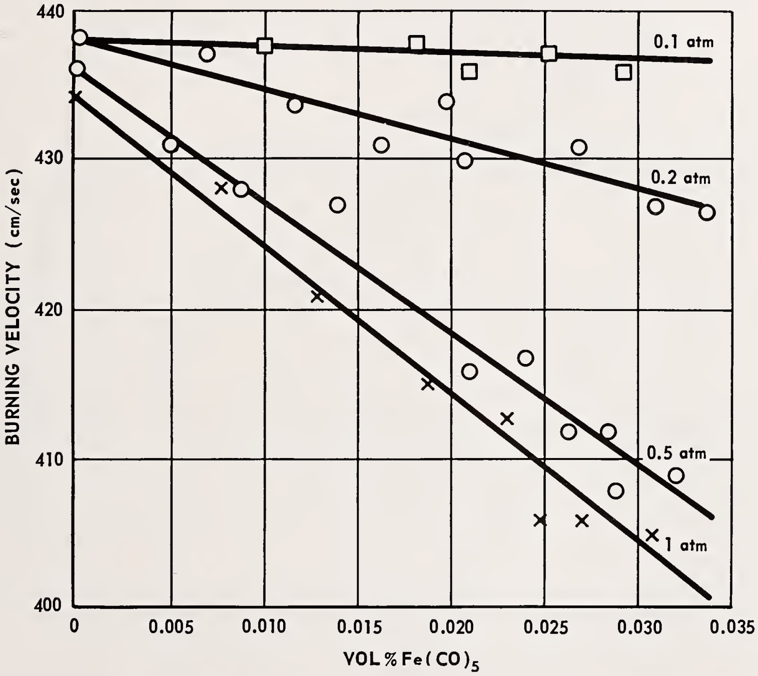


Figure 4. Influence of iron pentacarbonyl concentration and pressure on the burning velocity of stoichiometric methane/oxygen flames.

Methane-air flames were investigated in some detail with and without additives. The flames were burning on flat-flame burners of 12- and 20-cm diameters, mostly at 60 mm Hg pressure. Temperatures were measured by several independent methods: surface-protected platinum-platinum-rhodium thermocouples with compensation for radiation losses, rotational temperatures of OH bands and, occasionally, line-reversal temperatures.

In Figure 6 the flame temperature (thermocouple) is plotted versus height above burner (centimeters) for three different mixtures ($1.1\ CH_4+10$ air, CH_4+10 air, $0.9\ CH_4+10$ air) burning at 60 mm Hg with a burning velocity $v_n=0.33$ m/sec without additive. Flame temperature and burning velocity under

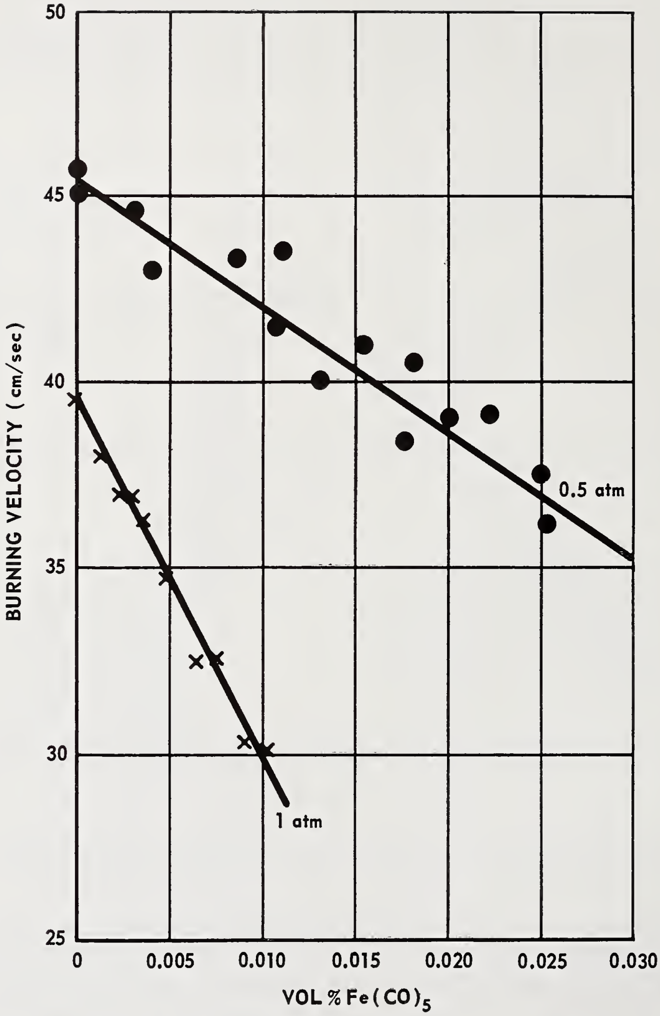


Figure 5. Influence of iron pentacarbonyl concentration and pressure on the burning velocity of stoichiometric methane/air flames.

these circumstances, of course, depend on the flow conditions chosen. For comparison some rotational temperature values determined from the absorption spectrum of OH are plotted in the same graph.

With added $Fe(CO)_5$ (0.001 per cent by volume) the thermocouple measurements are no longer reliable, due to iron oxide deposit. This changes radiation losses, and, in addition, may give rise to heterogeneous reactions (Figure 7). From previous investigations there is little doubt that OH radicals play an important role in the propagation of all flames of hydrocarbons with air or oxygen. In Figure 8 OH concentration and temperature for the stoichiometric methane-air flame are plotted as function of distance from the burner. The decrease of OH concentration in the "burned" gas is partly due to diffusion losses.

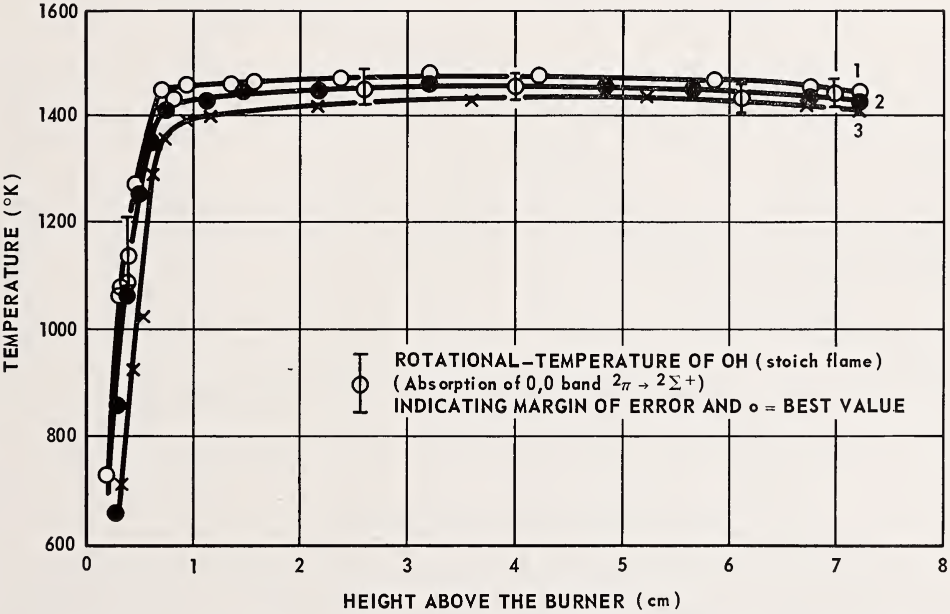


Figure 6. Temperature of methane/air flames as a function of burner height in the absence of iron pentacarbonyl. (1) 1.1 CH_4/10 air (2) 1.0 CH_4/10 air (3) .9 CH_4/10 air (flow rate 280 cm/sec; $v_n = 1/3$ m/sec; $p = 60$ mm).

In Figure 9 the decrease of OH absorption (as measure of concentration, but not corrected for finite optical thickness) in the burned gases is plotted for the pure mixture of methane with air, with 0.001 per cent $Fe(CO)_5$ or 0.005 per cent $Fe(CO)_5$ added to the mixture. Taking corrections into account, the concentration decrease of OH itself would be somewhat steeper. The initial increase in OH concentration and its maximum value are hardly influenced by added $Fe(CO)_5$. Only the position where OH absorption increases is shifted away from the burner with increasing $Fe(CO)_5$ concentration, and the flames become less stable.

From the experimental results obtained we cannot decide whether the decay reaction of OH is homogeneous or heterogeneous, but it seems that at relatively

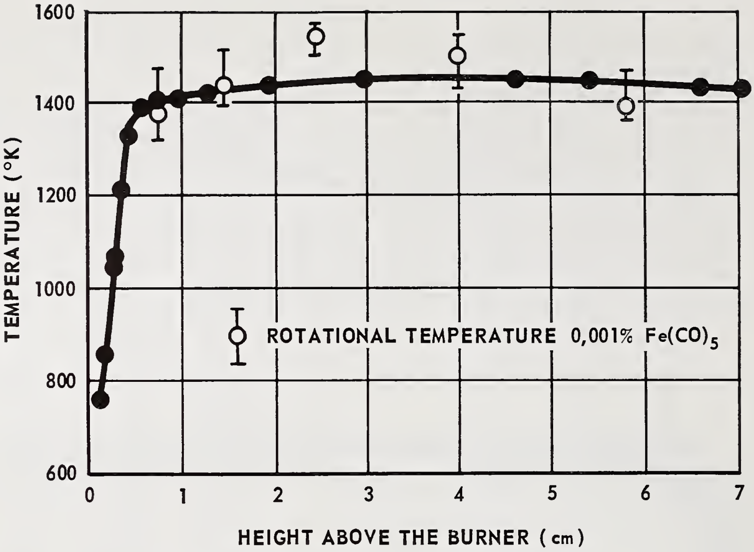


Figure 7. Influence of iron pentacarbonyl on temperature of stoichiometric methane/air flames. Solid curve indicates thermocouple temperature in absence of iron pentacarbonyl. (p=60 mm; v_n=⅓ m/sec.)

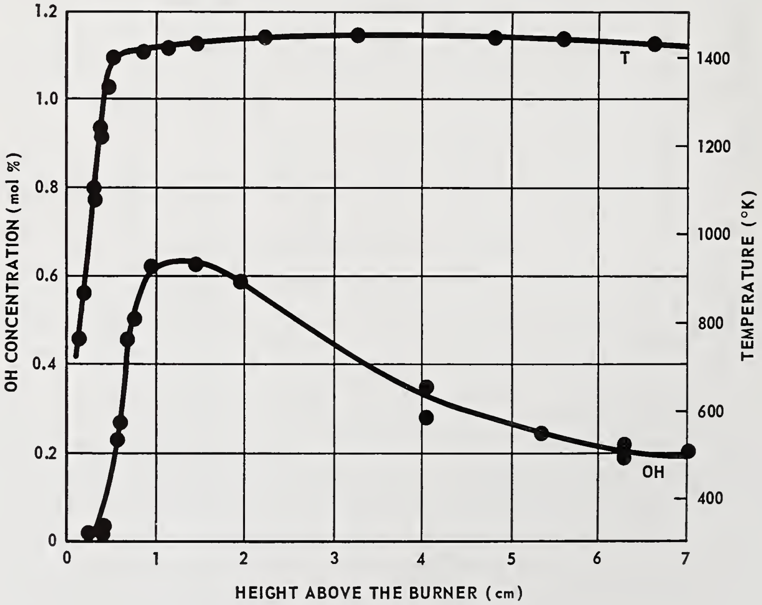


Figure 8. Temperature and OH concentration in a stoichiometric methane/air flame as a function of burner height in the absence of iron pentacarbonyl. (p=60 mm; v_n=⅓ m/sec; flow rate 280 cm^3/sec.)

high $Fe(CO)_5$ concentrations a heterogeneous decay reaction is dominant while at very low concentrations a homogeneous reaction may become important.

In order to obtain further information, spectra of the flames were taken. (The middle of the flame was focused on the slit of the spectrograph.) Figure 10(1) shows the emission of a stoichiometric methane-air-flame at 60 mm Hg around the maximum of OH emission 0.1–0.9 cm above the burner. Figure 10(2) shows the emission of the same flame 2.6–3.4 cm above the burner. Figures 10(3–6) show emission spectra of the flame, but with 0.005 per cent $Fe(CO)_5$ added. Figure 10(3) represents the zone 0.1–0.9 cm above the burner and shows clearly Fe lines below 3064Å. U. The exposure time of all spectra was identical, while in Figures 10(4–6) the weaker spectra correspond to 1/15 of the normal exposure time. In the flames with $Fe(CO)_5$ the emission of FeO is seen, but there is no pronounced continuum emission.

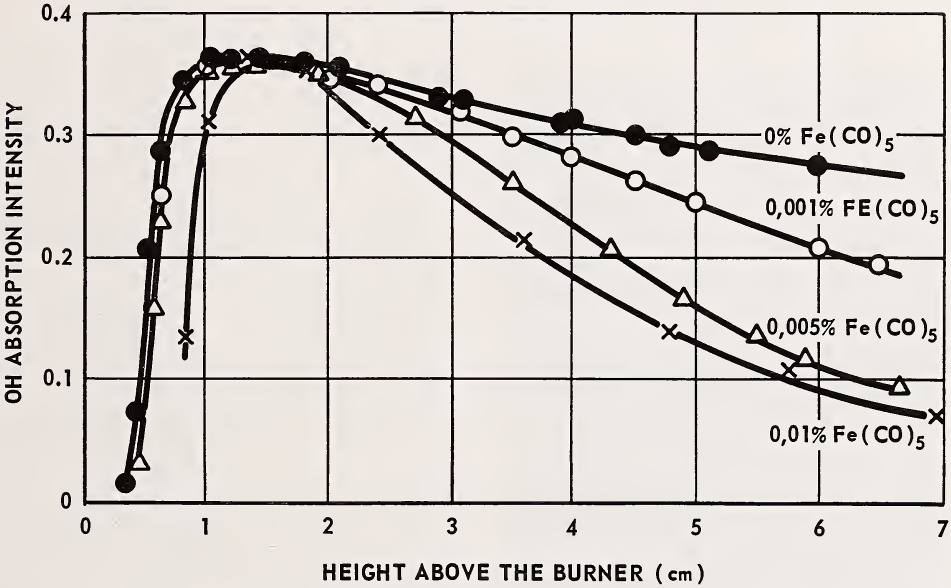
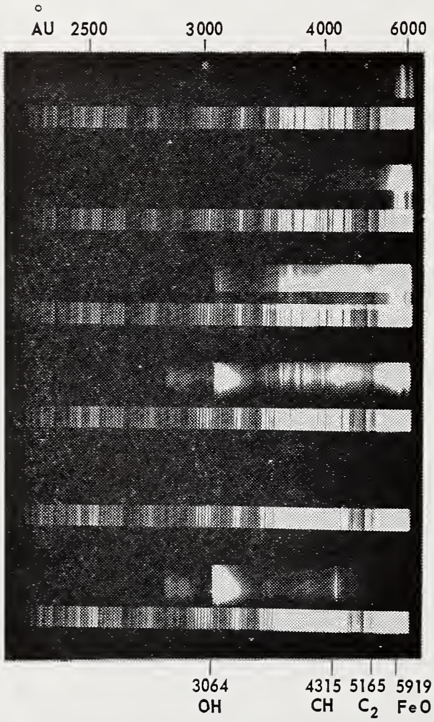


Figure 9. Influence of iron pentacarbonyl on OH absorption intensity as a function of burner height in a stoichiometric methane/air flame. ($p=60$ *mm*; $v_n=1/3$ *m/sec.*)

In Figures 11, 12, 13 the emission of different radicals, measured with a high resolution monochromator, is plotted as function of the height above the burner. Maximum emission of OH, maximum concentration of OH, and maximum emission of C_2 and CH do not coincide at all. The emission maxima, including the first one of FeO, may be linked approximately to a maximum of reaction rate. A measure for the concentration of iron atoms is shown in Figures 13 and 14 where the absorption of the 3859.91 Å iron line is plotted for different $Fe(CO)_5$ concentrations. While in the main reaction zone the emission of OH, C_2, CH and Fe has a pronounced maximum and then decreases very rapidly, the emission of

FeO shows a different behavior. It has a second maximum about 3 cm above the burner, in a zone where OH concentration and Fe absorption decrease rapidly. Iron forms solid oxide particles in the flame, but the decrease in radiation intensity of FeO does not seem to be connected with the decay of FeO concentration. The emission maxima of FeO, seem to be due to chemiluminescence. Measurements of the concentration and formation of solid particles are under way.

These preliminary results, reported without discussion, were made to obtain a first estimate of the mode of action of these very active inhibitors. The investigations are still in progress.



NO.	HEIGHT ABOVE THE BURNER	REMARKS	
6	6.0 – 6.8 cm	FeO	0.005% $Fe(CO)_5$
5	3.1 – 3.9 cm	MAX. OF FeO EMISSION	0.005% $Fe(CO)_5$
4	1.1 – 1.9 cm		0.005% $Fe(CO)_5$
3	0.1 – 0.9 cm	MAX. OF OH EMISSION	0.005% $Fe(CO)_5$
2	2.6 – 3.4 cm		0% $Fe(CO)_5$
1	0.1 – 0.9 cm	MAX. OF OH EMISSION	0% $Fe(CO)_5$

Figure 10. Emission spectra of stoichiometric methane/air flames as a function of burner height.

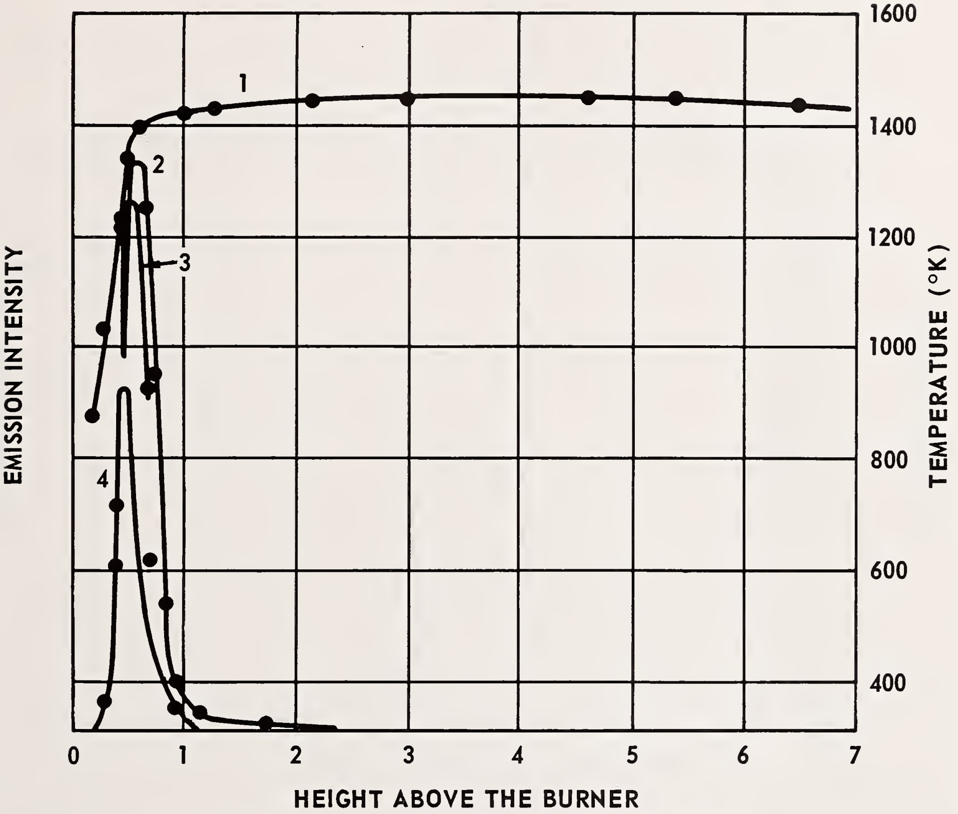


Figure 11. Emission intensity of stoichiometric methane/air flames in absence of iron pentacarbonyl as function of burner height. (1) thermocouple flame temperature (2) emission of OH [3089.86 Å] (3) emission of CH [~4288 Å] (4) emission of C_2 *[~5165 Å]. (*$p=60$ *mm;* $v_n=1/3$ *m/sec.)*

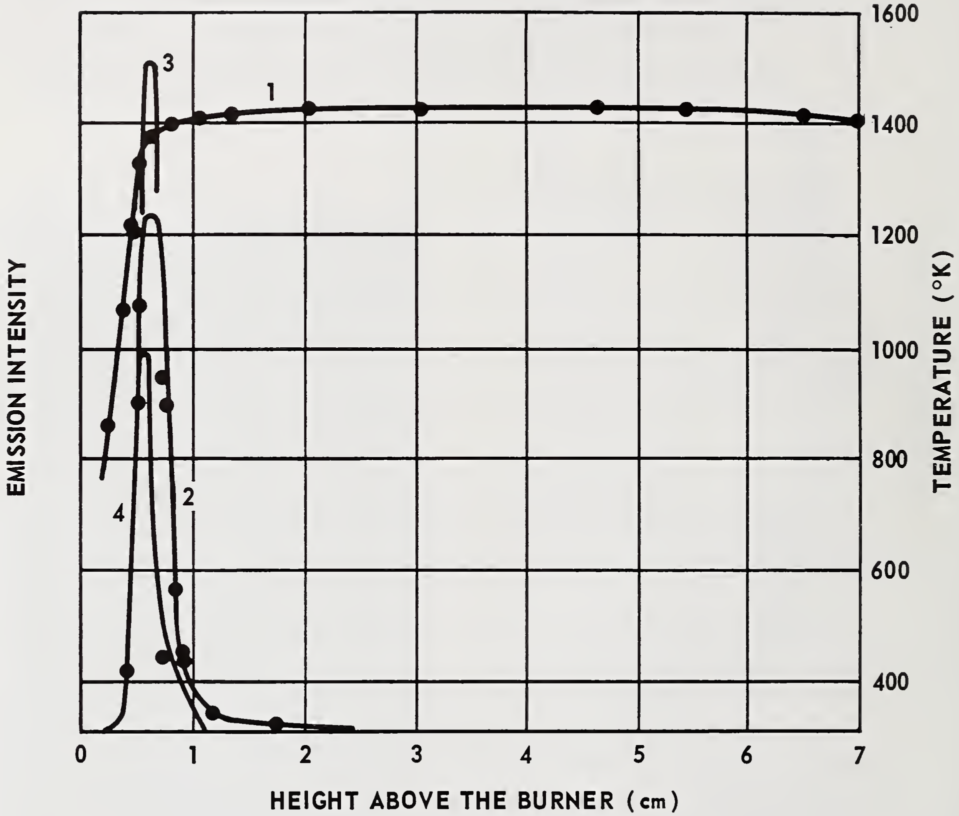


Figure 12. Effect of 0.005% iron pentacarbonyl on the emission intensity of stoichiometric methane/air flames, as a function of burner height (legends and conditions identical to Figure 11).

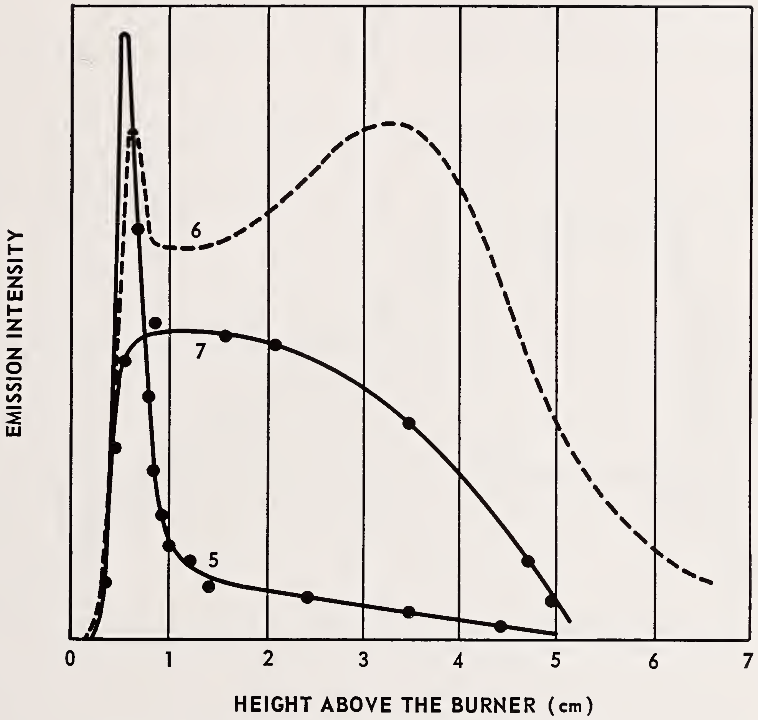


Figure 13. Effect of 0.005% iron pentacarbonyl on the emission (absorption) intensity of stoichiometric methane/air flames as a function of burner height. (5) emission of Fe [5270.360 Å] (6) emission of FeO [5913 Å] (7) absorption of Fe [3859.913 Å].

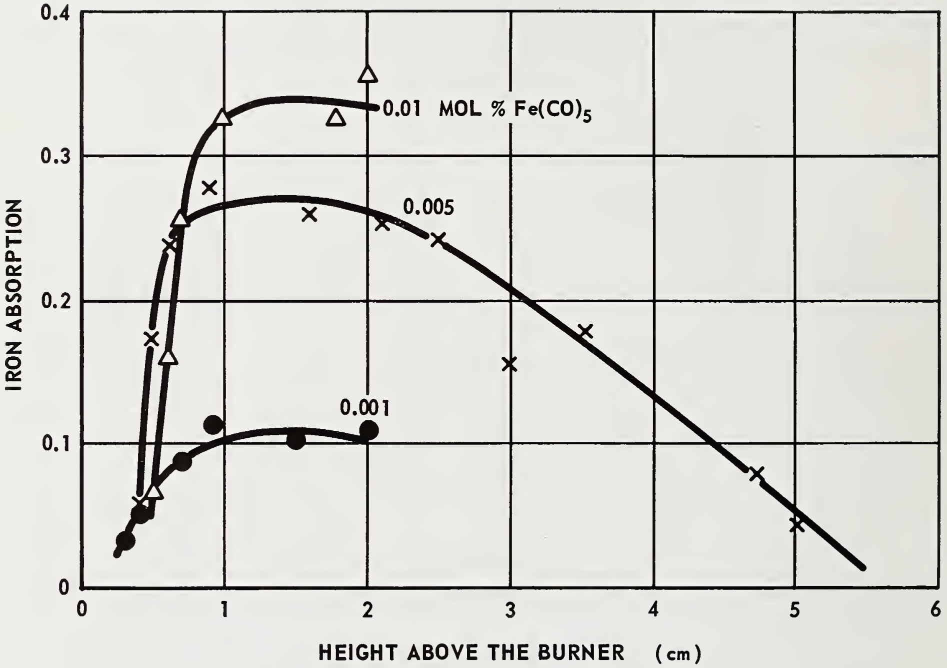


Figure 14. Influence of iron pentacarbonyl on the iron absorption as a function of burner height.

The Effect of Powders on Premixed Hydrocarbon-Air Flames *

W. A. Rosser, Jr., S. H. Inami, and H. Wise

Stanford Research Institute, Menlo Park, California

Abstract

A study was made of the inhibition of premixed flames by finely divided metal salts, some of which were found to be effective inhibitors of hydrocarbon combustion.

The speed with which flames propagated through mixtures of CH_4air-suspended powder was measured. Various powders were used. The course of particle heating and evaporation during transit through a flame was analyzed theoretically. This analysis indicated that a significant degree of evaporation could be expected for those powders which were observed to be effective inhibitors. Conversely, poor inhibitors could not be expected to evaporate.

The experimental measurements and the accompanying analysis of evaporation rates are consistent with a mechanism of inhibition by powders which involves this succession of steps: (a) heating of the powder particles by the hot flame gases, (b) evaporation of the powder particles, (c) decomposition or reaction of the evaporated material to provide metal atoms, and (d) inhibition of the combustion process by the metal atoms. Several reaction mechanisms involving metal atoms are feasible and consistent with the data.

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* Complete paper has been submitted for publication in *Combustion and Flame.*

Study of Various Influences on the Extinction of Methane-Oxygen Detonations by Fine Powders

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Since our last contribution to this subject[1] a considerable impulse has been given, especially in the United States, to the study of flame extinction, inhibition and related phenomena. An important effort has been made to coordinate investigations carried out in this field, to promote further research and to bring to the knowledge of workers throughout the world all possible information on the topic.

The existence of an extensive and exhaustive survey on the action of flame-extinguishing agents by Friedman and Levy[2] together with the publication by the Committee on Fire Research of the National Academy of Sciences-National Research Council of FIRE RESEARCH ABSTRACTS AND REVIEWS[3] permits us to cut short historical development on this subject and refer the reader in search of such information to references 2 and 3.

Experimental

All our experiments were carried out on the mixture CH_4+2O_2 whose detonation velocity is well determined and of the order of 2300 m/s. Whereas previous investigations had been carried out with various mixture concentrations and in some cases with hydrocarbons other than methane, we have this time extensively studied the behaviour of stoichiometric methane-oxygen mixture at atmospheric pressure. The layout of the apparatus allows mixtures to be prepared at constant volume in a mixing vessel where each constituent is introduced under its own partial pressure. Methane is 99 per cent pure and is desiccated before admission. Oxygen is delivered from commercial cylinders and is also treated by phosphorus pentoxide.

The detonation tube is made of perspex, sheathed by a plastic vinyl tubing. This device has proved effective in that the tube is not shattered to pieces as was the case with glass tubes; reproducible and well-defined conditions prevail at each experiment. The tube itself consists of two parts separated by a specially built slide valve which is mechanically triggered open synchronously with the ignition device. The tube is mounted vertically with an inside diameter of 16 mm. The top part is 40 cm long and the bottom part 200 cm. The ignition is started at the bottom by a small detonator and the detonation travels upward.

The slide valve consists in the main of a thin glucinium bronze blade 3/10 mm thick which either shuts the communication between the two tubes or quickly opens the complete aperture. The shutter mechanism has a number of advantages, mainly that, being extremely thin, the sudden opening of the slide introduces little perturbation to the mixture contained in the tube. Also, since the aperture of the valve is exactly equal to the tube diameter, it does not introduce any diameter variation. It has also been possible to use this device to introduce the pulverised material into the mixture by setting the weighed sample on the slide prior to the experiment, allowing the two parts of the tube to be first evacuated (the slide valve being vacuum tight through the use of O rings), and subsequently filled with the combustible mixture at the same pressure. In triggering the valve to open and before getting the ignition started, the powder is free to fall and disperse toward the detonation front travelling upward towards it.

The luminous phenomenon is recorded by the classical rotating drum camera on a Kodak Tri X film and different recordings are given in Figures 1–5. It can be seen in Figure 1, which relates to the detonation of $CH_4+2\,O_2$ mixture without any powder, that the detonation is well-established and stable throughout the propagation and that the slide valve which has been set open at the instant of ignition has not introduced any perturbation.

The pulverized substance under study was potassium bitartrate which had previously proved to be a good inhibitor and which has the advantage of being easily prepared in fine fractions and of not being very hygroscopic.

The sample is first crushed mechanically and then sieved to a fraction passing through 450 mesh. This fraction is further reduced by passing through a Roller Air Elutriator. Two fractions can be obtained in this way, an average diameter $<10\mu$ and an average diameter $<20\mu$. In each case the specific surface area was measured by the Rigden air permeability method.

A relay is able to introduce a delay between the opening of the valve and the ignition of the mixture. This enables the operator either to obtain a simultaneous ignition and opening of the shutter which causes the powder to fall, or to start the powder falling prior to ignition.

In delaying the opening of the valve and the ignition, one alters the dispersion of the sample which is better dispersed if the delay is long. A powder (potassium bitartrate) of average particle size $<10\mu$ is likely to disperse from 0 to 68 cm when the delay varies from 0 to 0.6 sec.

Table 1 summarizes the results obtained with such a sample where r (average radius) is $<10\mu\simeq3.25\mu$ and where S is the specific surface area of the sample (cm²/g); in this case $S=4680$ cm²/g.

TABLE 1

t	0	0.15	0.2	0.3	0.4	0.48	0.5	0.6
m	2015	510	675	1050	1320	1590	1640	1970
n	10.2	2.59	3.43	5.33	6.70	8.07	8.32	10.0
Σ	9430	2390	3160	4910	6180	7440	7680	9220
h	—	10	14	24	37	51	54	68
σ	—	119	112	101	83	73	71	68
ν	—	1.29	1.22	1.10	0.901	0.787	0.767	0.732

where

m = extinguishing mass (mg); i.e., the minimum weight of material to obtain the complete quenching of a detonation

n = millimoles of powder contained in the tube

h = height (cm) attained by the falling powder

σ = the total extinguishing surface area (cm²), (ms)

Σ = the average extinguishing density expressed in surface of the powder per volume unit of the cloud (cm²/cm³) at the extinction point

$\nu=\frac{\Sigma}{V}$, (V = volume of the dust cloud = h. area of the cross section of the tube)

This table shows a number of characteristic features:

1) The minimum quantity in weight necessary for extinction is obtained with a delay of 0.15 sec, after the cloud has dispersed 10 cm downwards; if the

delay is longer, the powder is increasingly more dispersed and the quantity necessary for extinction increases. Thus, a minimum dispersion is necessary and is more effective than none. When dispersion increases beyond this critical value, the density of the cloud becomes smaller and a larger quantity becomes necessary to obtain the same effect.

2) Except in the case where $t=0$, i.e., no dispersion, there exists a relation of the form:

$$m=k\,t$$

between the extinguishing mass and the delay.

The larger particles together with the smaller ones fall with respective velocities v and v′ which are rapidly attained, the height of dispersion of the falling cloud being

$$h=(v-v')\,t$$

$$\therefore\ m=kt \rightarrow \frac{m}{h}=\frac{k}{v-v'}=\text{cte}$$

Therefore, the minimum extinguishing density would be constant.

Using the values of h we have calculated the average extinguishing densities per unit volume of combustible mixture expressed in number of millimoles ν per cc, n being the total number of millimoles of powder contained in the tube.

3) The density σ decreases rapidly when t increases, reaching a limit value.

TABLE 2

t	0	0.15	0.2	0.3	0.4	0.48	0.5	0.6
m	2000	1000	1100	1570	2100	2725	2950	4000
n	10.2	5.08	5.58	7.97	10.7	13.8	15.0	20.3
Σ	3640	1820	2000	2860	3820	4960	5370	7280
h	—	12	14.5	28	38	50	53	72
σ	—	75.4	68.6	50.8	50.0	49.4	50.4	50.3
ν	—	2.11	1.91	1.42	1.40	1.38	1.41	1.40

Table 2 shows the experimental data obtained with a coarser sample $<20\mu$. The average diameter in this case is 8.4μ, the specific area S is 1820 cm²/g.

These results show that the limit value of the density is attained with $t \simeq 0.3$ sec. Comparing Tables 1 and 2 one sees that m increases when h is increased, σ however decreases and tends towards a limit which is more rapidly reached with a coarser particle than with a fine one.

Table 3 deals with a sample passing a 450 mesh sieve without further reduction. The average radius is $r \simeq 10\mu$ and the specific surface area is 1570 cm²/g.

TABLE 3

t	0	0.15	0.2	0.3	0.4	0.48	0.5	0.6
m	3045	1460	2875	3400	4240	4775	4825	5440
n	15.4	7.41	14.6	17.3	21.5	24.2	24.5	27.6
Σ	4780	2290	4510	5340	6660	7500	7580	8540
h	—	13.5	29	48.5	70	79	80	90
σ	—	84.4	77.4	53.7	47.3	47.2	47.1	47.2
ν	—	2.73	2.50	1.74	1.53	1.52	1.52	1.53

Compared with Table 2 this sample which is coarser than sample 2 shows an increase in m, the minimum quantity necessary for extinction. h, the dispersion height, is also greater, σ and ν decrease when t increases, the limit values being reached as early as 0.3 sec.

In order to compare the experimental data obtained, we have calculated the limit velocity of the dust particles, assuming each particle to be spherical and falling independently. This has led us for a delay of 0.6 sec, the greatest possible dispersion, to a value of

$$r \leqq 83\mu$$

in order to attain a point situated 1 m below the shutter in 0.6 sec. The powder, therefore, forms clusters of an average radius of 83 microns.

Discussion

A certain number of useful comments can be made by careful interpretation of the photographic recordings.

Figure 1 shows a detonation free of powder passing through the slide valve (black space at the upper part) without any disturbance. The interval between two black marks at the top represents 10 cm.

Figure 2 shows a detonation with 2000 mg of potassium bitartrate $<10\mu$ and no delay between the opening of the shutter and the ignition. Practically all the powder is still at the level of the slide valve when the detonation front reaches it. An attenuation of the velocity is apparent. Past the valve the detonation resumes its former velocity.

Figure 3 represents similar conditions with 2015 mg instead of 2000 mg. Near extinction is obtained at the valve. A small flame is seen to propagate at a reduced velocity after passage of the valve.

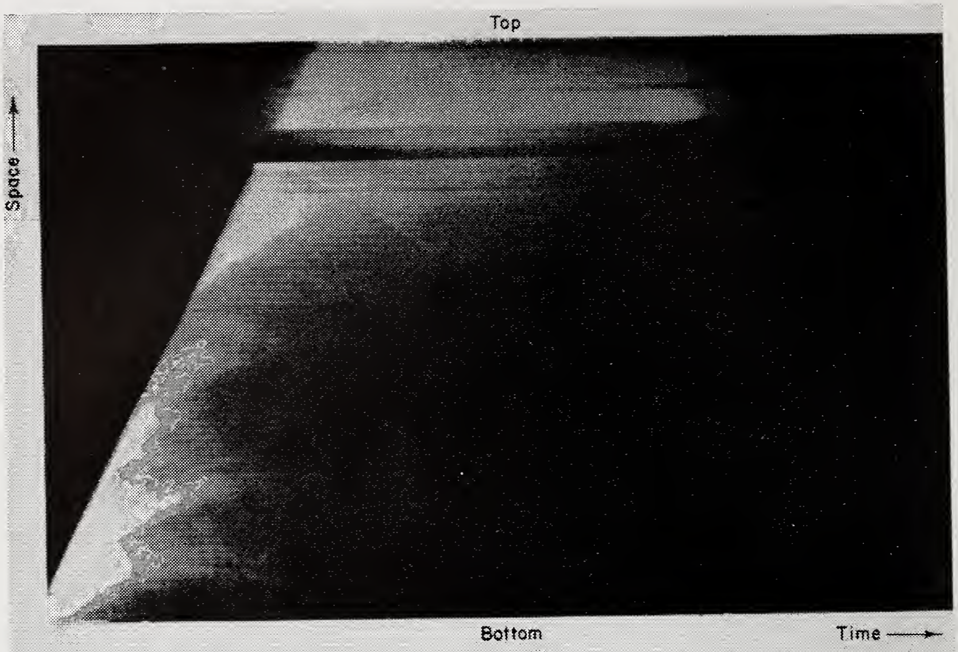
Figure 4 shows a delay 0.3 sec between opening the shutter and ignition, $m = 1040$ mg; the luminous part of the recording immediately before the slide valve coincides with the position of the dust front. This is immediately followed by a dark zone where the velocity is seen to be reduced. The quantity m being less than that necessary for extinction, the wave passes through the shutter and is seen to propagate at the upper part of the tube with a reduced velocity before the detonation is reformed.

Figure 5 shows the same phenomena as used in Figure 4 but with 10 additional mg of powder. Extinction is obtained. The same luminosity and velocity reduction as in Figure 4 are observed.

Conclusions

The general conclusions that can be drawn from the observation of the data are the following:

1) Extinction always proceeds through the same reproducible series of events. A reduction of velocity is always observed after the wave has travelled for some length through the dust cloud. During this propagation a strong excitation of the luminosity is observed. This is immediately followed by an important reduction in luminosity (probably due to the cooling effect). According to whether the dust quantity is sufficient or not to produce extinction, the wave will either proceed with a reduced velocity and reform a detonation further along the tube, or proceed as an unstable deflagration, or else become completely extinguished.



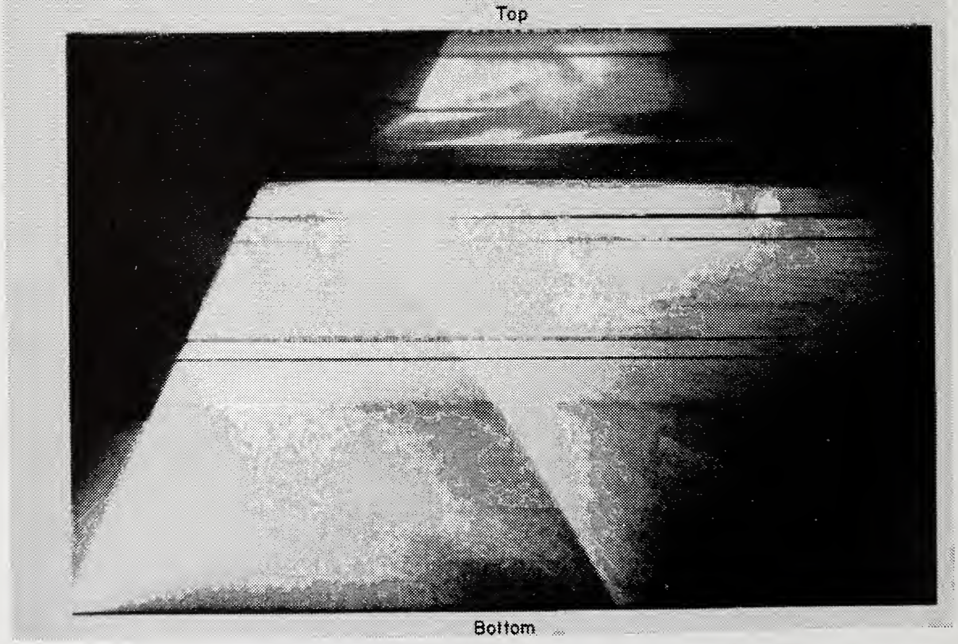


Figure 1. Detonation free of powder passing through slide valve (black space at upper part) without any disturbance. Interval between two black marks at top represents 10 cm.

Figure 2. Detonation with 2000 mg of potassium bitartrate $<10\mu$ and no delay between the opening of shutter and ignition. Practically all the powder is still at the level of the slide valve when detonation front reaches it. An attenuation of the velocity is apparent. Past the valve the detonation resumes its former velocity.

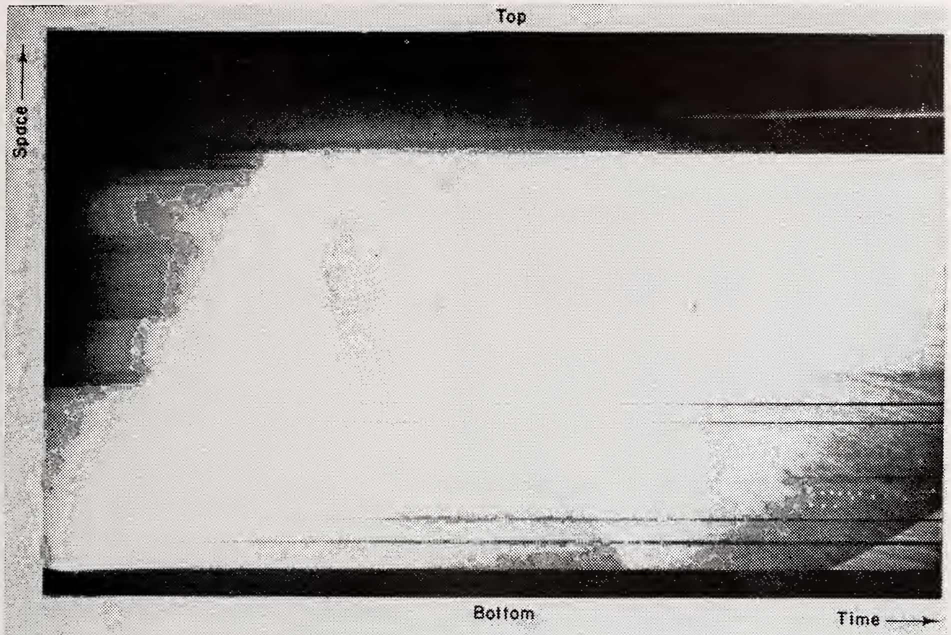


Figure 3. Same conditions as Figure 2 with 2015 mg powder instead of 2000 mg. Near extinction is obtained at valve. A small flame is seen to propagate at a reduced velocity after passing the valve.

Figure 4. Delay 0.3 sec between opening the shutter and ignition, m = 1040 mg; the luminous part of the recording immediately before the slide valve coincides with position of dust front. This is immediately followed by a dark zone where the velocity is seen to be reduced. The quantity m being less than that necessary for extinction, the wave passes through the shutter and is seen to propagate at the upper part of the tube with a reduced velocity before the detonation is reformed.

Figure 5. Same phenomena as Figure 4, but with 10 additional mg of powder. Extinction is obtained. Same luminosity and velocity reduction as in Figure 4 are observed.

These events are perfectly reproducible. The inhibition mechanism is one of dissociation of the combustion and detonation waves, the effect being to reduce the flame velocity, either operating as an important heat sink, reducing the temperature, or by any other mechanism such as chain breaking,[4] to the point where the flame cannot reaccelerate enough to reform the detonation.

2) The effect of dispersion shows that a minimum dispersion is necessary to obtain minimum quantities of material. In the case of our experiments a time lag of 0.15 sec has proved to be optimum. This corresponds to a height of dispersion of 10 cm below the slide valve.

Tables 1, 2, and 3 show that the ratio $\frac{\Sigma}{V}$, the average extinguishing density σ cm^2/cm^3, tends towards a limit value, more or less rapidly attained according to the average particle size.

3) The fine particles remain nearest the slide valve while the coarser ones fall more rapidly. Extinction is only obtained if propagation through the cloud can reach the fine portion of the sample.

We have in this work endeavoured to obtain definite experimental conditions and reproducible results. Studying one mixture and examining the behaviour of one inhibitor (potassium bitartrate), we have limited this paper to the influence of dispersion on the extinguishing phenomenon. Other factors will be studied systematically in the near future.

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The Extinction of Fires by Water Sprays

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Introduction

Water spray has long been widely used for the extinction of fires in both liquid and solid fuels. Although there have been numerous *ad hoc* investigations on the effect of sprays from various nozzles on fires of different types, it is only in recent years that any systematic study has been made using sprays and fires with controlled and measured properties. Work of this nature has been carried out for about ten years at the Joint Fire Research Organization. In this work attention has been paid in particular to the ability of spray to penetrate to the seat of a fire, the mechanism of extinction, and the properties of sprays required to extinguish fires of various types. To some extent the work has also permitted an approach to be made to defining critical heat transfer criteria for extinguishing fire. In this paper these aspects of the problem will be discussed and illustrated by experimental results obtained at the above organization and elsewhere. The results of the experiments also suggest certain broad principles on which fire-fighting operations should be based, and these will be outlined.

Penetration of Spray to the Seat of a Fire

In order for a spray to be able to exert a useful effect on a fire, it is usually necessary for the spray to penetrate to the seat of the fire, particularly to the burning fuel. To do this the spray must be either formed near the fuel or it must have sufficient forward force to prevent too much of the spray being either deflected by or evaporated in the flame and hot gases associated with the fire.

The factors which control the penetration of spray to the seat of a fire are the drop size and thrust of the spray, the thrusts of the flames and wind, gravity, and the evaporation of spray in the flames. When sprays are applied to fires by hand the effects of the thrust of the flames and the wind, and the evaporation of spray in the flames are usually minimized by applying the spray directly through the base of the flames to the fuel from the upwind side of the fire; the reach of the spray, which is determined mainly by gravity and the forward thrust of the spray, usually controls the penetration to the seat of the fire under these conditions. When spray is applied downward to a fire, all the above factors are of importance but particularly the relative thrusts of the spray and the flames. Little information is available from the literature on either of these two factors but work carried out at the Joint Fire Research Organization indicates that they may be estimated from readily measured properties of the spray and the flame. The thrust within a spray is a function of the reaction at the nozzle and the width of the spray; there is also evidence that at some distance from the nozzle it is approximately equal to the thrust of the entrained air current. The latter depends on the flow rate of spray per unit area and the pressure at the nozzles. The thrust of flames is proportional to the buoyancy head. Further information on these relationships is given in the appendix.

Experimental information on the penetration of sprays to burning fuel is available for fires in kerosine burning in a 30 cm diameter vessel using downward application of spray.[1] The results were scattered mainly because the penetration was very sensitive to the pattern of the spray at the fire area, a factor which was very difficult to control experimentally. Broadly, however, the penetration decreased as the pattern of the spray became more peaked in the centre of the vessel and as the thrust and the drop size of the spray decreased. The effect of the latter two factors is illustrated in Figure 1 which refers to sprays in which the peak of the spray distribution was contained in the central half of the vessel but in which not more than one-fourth of the area of the vessel was covered by a flow rate less than one-half of the peak value. In spite of the scatter of the points, the effect of spray thrust, as calculated from the entrained air current, and the drop size on the penetration is clearly seen. There is, however, an indication that at drop sizes greater than about 0.8 mm the penetration was independent of the thrust. If the peak was outside the central area of the vessel the penetration was usually considerably greater.

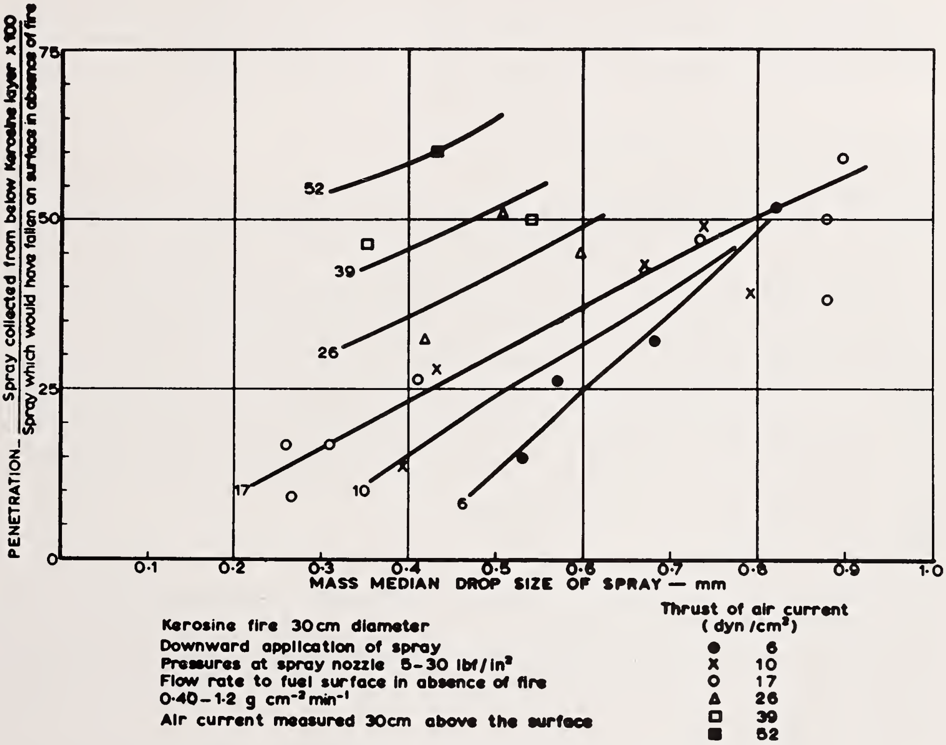

Figure 1. Penetration of spray to the fuel of a fire.

In the tests referred to in Figure 1 the height of the flame as judged visually was 150 cm before the application of spray and was reduced to mean values between 80 and 140 cm during the application of the spray. These heights correspond to upward flame thrusts of 34 and 18–30 dynes/cm² (see appendix). It will be seen from Figure 1 that the thrusts of the spray required to give a 50 per cent penetration for the finer sprays is comparable to these values.

It was observed during the tests that as the thrust of the spray was increased above 20 dynes/cm^2 the flames became increasingly unstable. Sprays with higher thrusts than represented in Figure 1 often caused stabilization of the flame as a relatively flat flame above the vessel after a period of instability. The minimum spray thrust at which this phenomenon occurred was 77 dynes/cm^2. It would be expected that under these conditions the bulk of the spray, even if it were fine and of a peaked pattern at the fire area, would penetrate to the burning fuel; this might also be inferred by extrapolation of the results in Figure 1. This critical thrust, T_c might be related to x, the height of the flames as judged visually prior to the application of spray, by equation (1).

$$T_c = 0.5\, \rho_0\, g\, x \tag{1}$$

ρ_0 = density of air, g = acceleration due to gravity.

It would be expected that since equation (1) represents the thrust in the air current of the spray required to overcome the buoyancy head of the flames, T_c should scale with flame height for larger sizes of fire than the fire tested.

For a given flow rate of spray in the absence of fire, and for a given pressure, the thrust of the spray in these experiments was approximately independent of the drop size. Therefore, as the drop size decreased the penetration decreased. However, as the drop size decreased the efficiency of unit mass of spray in reducing the rate of burning increased since the finer spray cooled the liquid more efficiently. As a result of these two phenomena a drop size occurred at which there was a minimum rate of burning for a given flow rate and pressure. This drop size depended on the spray thrust, and decreased from 0.8 to 0.33 mm as the thrust increased from 6 to 26 dynes/cm^2.

Mechanism of Extinction

There are two main ways of extinguishing a fire with water spray: (1) cooling the burning fuel and (2) cooling the flame. The mechanism of smothering the flame with steam is one aspect of cooling the flame and will be dealt with under that heading.

Cooling the Fuel

To reduce the temperature of the fuel the spray must be capable of abstracting heat from the fuel at a rate greater than the rate at which the fuel will take up sensible heat. Heat will normally reach the fuel by heat transfer from neighbouring hot bodies and from the flame. Information on heat transfer from bodies may be obtained from texts on heat transfer although there are many important cases, for example, on the flow of films of fluid over hot surfaces where information is lacking. There is evidence, which will be given later, that radiation from the flame to the fuel that is being cooled does not normally play a large part in determining critical conditions for extinction, although if only a part of the fire is being extinguished at any one time, radiation from the rest of the flames might become an important factor. In this paper, therefore, particular attention will be paid to estimating critical conditions when the surface receives heat mainly by convective or conductive transfer from the flame. Such estimates may be obtained from known relationships between the rate of burning and the heat transferred from the flame to the surface. The method used may be best illustrated by an example. Equation (2) was found by Spalding to give the rate of burning of liquid fires flowing over surfaces with a vertical dimension (d).[2]

$$\dot{m}'' = \frac{0.45k}{dc} B^{\frac{3}{4}} \sqrt[4]{\frac{gd^3}{\alpha^2}} \qquad (2)$$

where

$\dot{m}''$ is the average rate of vaporization per unit surface area,
d is the linear dimension of the surface,
k, c α^2 are thermal conductivity, specific heat and thermal diffusivity of air at room temperature,
g is the acceleration due to gravity,
B is a transfer number equal to

$$\frac{M_{og} H/r + c\,(T_g - T_s)}{Q}$$

where

Q is the heat transfer to the fuel surface per unit mass of fuel vaporized,
M_{og} is the concentration of oxygen in air (by weight),
H is the heat of combustion of the fuel,
T_g is the ambient gas temperature and T_s the surface temperature,
r is the stoichiometric ratio (weight of oxygen/weight of fuel).

Normally, under steady conditions, the value of Q in the transfer number is equal to λ_f, the heat required to vaporize unit mass of fuel. However, when a spray is acting on the fuel and heat is being removed from the fuel, Q will be greater than λ_f.

For most liquid hydrocarbons equation (2) may be reduced with little error to

$$\dot{m}'' = \frac{0.17}{d^{0.25}\, Q^{0.75}} \qquad (3)$$

($\dot{m}''$ in g cm^{-2}s^{-1}; d in cm; Q in cal/g.)
The rate at which heat reaches unit area of the burning liquid from the flame is Q $\dot{m}''$; the rate at which heat needs to be transferred to vaporize the fuel is λ_f $\dot{m}''$. Therefore, a steady condition as expressed in equation (3) will be maintained if the spray removes from the liquid a quantity of heat γ given by

$$\gamma = (Q - \lambda_f)\, \dot{m}'' \qquad (4)$$

Combining equations 3 and 4 gives either

$$\gamma = \frac{0.17}{d^{0.25}\, Q^{0.75}} (Q - \lambda_f) \qquad (5)$$

or

$$\gamma = \left(\left(\frac{0.17}{d^{0.25}\, \dot{m}''} \right)^{4/3} - \lambda_f \right) \dot{m}'' \qquad (6)$$

If the spray is capable of removing heat at a greater rate than the temperature of the fuel will be reduced. This will result in a smaller value of $\dot{m}''$ and a correspondingly larger value of Q and γ. The reduction in temperature will also bring about a reduction in the rate at which spray can remove heat from the fuel.

In a burning fuel in which the temperature of the fuel has reached steady conditions, $Q = \lambda_f$ and $\gamma = 0$. The application of spray with a lower temperature than the fuel will therefore result in the fuel being cooled. This will continue until either a steady burning condition is established at a particular temperature or one of the two following critical conditions for extinction is reached.

1) The value of Q may reach the maximum value, Q_c, which the flame is capable of imparting to the surface without becoming extinguished.
2) The value of $\dot{m}''$ may reach a minimum value, $\dot{m}_c''$ below which a flame cannot continue to exist above the surface.

The rate γ_c at which the spray must abstract heat from the fuel at the particular fuel temperature at which these critical conditions occur will be given by one of the equations (5) and (6), and if Q_c and $\dot{m}_c''$ are assumed independent of the linear dimension of the burning surface, then γ_c will be expected to decrease slowly as this dimension increases.

By a similar argument to that developed above, it is possible to put forward equations giving γ_c for a wide range of conditions, indeed for all conditions for which there is a known relationship between the Nusselt number for heat transfer from a gas and other relevant dimensionless groups, e.g., the Reynolds, Grashof, and Prandtl numbers. By these means it may be shown that above a certain dimension of the surface γ_c will cease to decrease with increase in d, and if the wind is sufficiently strong γ_c will be proportional to the square root of the wind velocity and inversely proportional to the square root of d.

A certain amount of information is available for the critical value of Q. Thus for flame quenching in channels [3] and in flame arresters [4] it has been found that for stoichiometric hydrocarbon flames the maximum amount of heat a flame can impart to a surface before it is extinguished is 23 per cent of the heat of combustion of the fuel, i.e., about 2500 cal/g. Spalding [2] carried out experiments on the circulation of kerosine burning on the surface of a sphere and here again it was found that the fire was extinguished when the heat transferred to the burning surface by the flame was 2500 cal/g of fuel vaporized. Spalding's experiment is analogous to extinguishing a fire by cooling with water spray, the only difference being that heat was removed by excess fuel rather than by water spray. It would be expected that the conditions under which the maximum fraction of the heat of combustion can reach the surface of the burning fuel would occur when a stoichiometric mixture burns very close to the liquid surface. The temperature of the surface should, therefore, be near to the value corresponding to equilibrium with a stoichiometric mixture. For kerosine this temperature is 15°C higher than the temperature at which the surface is in equilibrium with the lower limit mixture and is approximately equal to the fire point.

Using 2500 cal/g as the value for Q_c the following values for γ_c may be calculated for fires burning under conditions of natural convection.

Pool or spill fires	$\gamma_c = 0.6/d^{0.25}$	(7)
Fires on tubes	$\gamma_c = 1.2/d^{0.25}$	(8)
Fires on vertical surfaces	$\gamma_c = 1.2/l^{0.25}$ for $l < 100$ cm	(9)
	$= 0.4$ for $l > 100$ cm	(10)

γ_c is in cal/cm²/sec; d, l characteristic dimension in cm.

There is little information on the minimum value of $\dot{m}''$ below which a flame will not be sustained. It might be postulated that $\dot{m}_c''$ should be not less than the value required to sustain a lower limit flame at its appropriate burning velocity over the whole surface; this would give $\dot{m}_c''$ equal to about 1.5×10^{-4}

g/cm²/sec for fires in hydrocarbon liquids. On the other hand experiments on the extraction of heat from laminar propane-air flames [5] indicate that a stoichiometric mixture may continue to burn close to a surface to which it is imparting heat at a rate similar to Q_c when the combustion rate is as low as 2.6×10^{-4} g/cm²/sec. The above figures for m_c'' are about one-tenth of the rate of combustion of pool fires under steady conditions; they imply that γ_c may depend on critical rate of vaporization when the dimension of the fire is greater than 30 cm, for fires burning in a natural draught.

The analysis so far has dealt only with burning liquids. There are difficulties in applying a similar analysis to wood. The main difficulty as far as the extinction of flaming combustion is concerned is that the heat required to produce unit mass of volatiles is not known. The slow decomposition of wood is an exothermic process, i.e., λ_f is negative, but Klason [6] showed that as the rate of decomposition increases the process changes from being exothermic to endothermic. There is evidence that for the rates of decomposition required to sustain a flame over a wood surface, the decomposition is indeed highly endothermic. For the extinction of glowing combustion the analysis would have to be modified to take into account the loss of heat from the surface by radiation and the effect of surface temperature on the combustion rate.

The above considerations are concerned with the rate at which heat must be removed from the fuel in order that the fire may be extinguished by cooling the fuel. The ability of the spray to remove this heat will depend on the properties of the spray and the fuel; this aspect of the problem will be referred to when experimental results are discussed.

Extinction of the Flame

The criterion of extinction of a flame by heat abstraction inside the flame is that the combustion products as they leave the reaction zone should not exceed the temperature they would have for lower limit flames; this temperature is about 1580°K for a wide range of flammable vapours and gases. A decrease in temperature approximately to this value is obtained when extinction is obtained by adding nitrogen, water vapour, carbon dioxide, or inert dust to flames in stoichiometric mixtures.[7]

The amount of heat which it is necessary to remove from the flame to accomplish this is the difference in heat of combustion of stoichiometric and lower limit mixtures. For most flammable organic compounds and probably also for the volatiles from some common dry woods this is about 45 per cent of the heat of combustion of the fuel. Since with diffusion flames it would be expected that there would be a zone between the fuel and the atmosphere where the stoichiometric mixture occurs, the heat which has to be removed from the flame as a whole is 45 per cent of the heat of combustion of the fuel. It is important, however, that this heat be removed either from the reactants or the reaction zone. If the heat is removed from the combustion products the heat removal will not substantially affect the temperature of the products leaving the reaction zone. In a turbulent diffusion flame it is very difficult to differentiate between the reactants, the reaction zone and the combustion products. However, it would be expected that if a spray is capable of removing all the heat of combustion from the flame, then the flame will be extinguished.

It is interesting to note that the heat removal required to extinguish the flame by cooling the flame is twice as great as the heat which an extended surface on the reactant side of the flame may abstract from the flame before the flame is extinguished. This might be explained by a different balance of heat release and heat loss rates for a vitiated flammable mixture and a stoichiometric flammable mixture close to an extended surface.[8] Owing to the intractability of defining the position and properties of the reaction zone in a turbulent diffusion flame the approach to estimating critical conditions for extinction of the flame by water spray has been made on the basis of heat transfer taking place within the whole flame. If V is the volume of the flame, Z the mass rate of burning, and H the heat of combustion of the fuel, then I, the mean rate of the heat production per unit volume of flame, assuming complete combustion of the fuel, is $\frac{ZH}{V}$. If the capacity for heat transfer of the spray within the flame is defined as X, the rate of heat transfer per unit volume of flame to the spray, then three critical criteria for X may be put forward.

1) Removal of all the heat in the flame neglecting the production of steam as a result of heat transfer to the spray

$$X_1 = I \tag{11}$$

2) Removal of heat only from the reaction zone and the reactants, but also neglecting steam formation

$$X_2 = 0.45\ I \tag{12}$$

3) Removal of heat only from the reaction zone and the reactants, but assuming that all the heat transfer for the drops result in steam formation. This will only be the case if the drops enter the flame at the wet bulb temperature (about 75°C). It may be assumed that the steam formed will contribute to the cooling of the flame a quantity β per unit mass of steam equal to the whole of the sensible heat of steam from 370–1580°K. The ratio of β to λ, the latent heat of steam, is 1.23. This gives

$$X_3 = \frac{\lambda}{\beta+\lambda}\, 0.45\ I = 0.195\ I \tag{13}$$

A fourth criterion may also be put forward if steam is formed outside the flame either at the burning surface or at surrounding hot bodies. Under these conditions the latent heat of vaporization does not contribute to cooling the flame but the sensible heat of steam up to 1580°K does. If the steam is formed at or sufficiently near to the burning surface to accompany the reactants into the flame then the critical flow rate, W, of water required would be

$$W = 0.45 \frac{ZH}{\beta} \tag{14}$$

If the steam is formed well away from the burning surface and is heated by the combustion products, then W may rise to values equal to $\frac{ZH}{\beta}$.

The quantity I in equations (11) through (13) is an intensity of combustion and depends on the conditions of combustion, particularly the air current in which the flame is burning. For petrol, kerosine, benzole and alcohol fires 30 cm diameter burning under conditions of natural draught, I was found to be independent of the fuel or the rate of burning and equal to 0.45 to 0.50 cal $cm^{-3}sec^{-1}$.[9]

The entrained air current in a spray not only affects the intensity of combustion but also affects the critical heat transfer rate required to extinguish flame. There is very little information to allow the assessment of this factor on a quantitative basis, but an indication of what might be expected may be obtained from work on the blowout of flame at obstacles. For example, if the assumption is made that the fundamental burning velocity of the flame decreases in proportion to the heat transfer capacity of the spray, then on the basis of relationships between the blowout velocity and the fundamental burning velocity [10] it may be expected that

$$V_{BO} = a_3 - bX^{1.5 \text{ to } 2} d^{0.5 \text{ to } 1} \qquad (15)$$

where V_{BO} is the velocity of the entrained air current that will cause a blowout when the spray has a flame heat transfer capacity X, d is a characteristic dimension of the system and a_3 and b are constants.

It is of interest to compare critical heat transfer rates for extinction by cooling the flame and cooling the fuel. It follows from equations (11) to (14) that the critical heat transfer rate for cooling the flame is greater than 20 per cent of the total heat of combustion of the fire. Equation (4) and subsequent remarks indicate that for cooling the fuel the critical heat transfer is less than 25 per cent of the much smaller rate of combustion that would occur under critical conditions. On this basis much lower critical flow rates would be expected for extinguishing the fire by cooling the fuel than by cooling the flame. As opposed to this, however, it is feasible that unit mass of water can, under critical conditions, be the sink of a much greater amount of heat from the flame (about 1300 cal/g) than it can from a solid or liquid fuel (45 cal/g for kerosine and 750 cal/g for wood).

Experimental Investigations on the Extinction of Fire

In order to examine the relevance of the above analyses of extinction mechanism, experimental investigations have been divided into two groups covering investigations in which there is substantial evidence that extinction was by cooling the fuel and the flame, respectively. For investigations on the extinction of fires in rooms, however, there has not usually been sufficient evidence to decide on the mechanism of extinction and these investigations will be dealt with separately.

Cooling the Fuel

Critical flow rate of spray for extinction of pool fires. Evidence has been obtained from experiments with pool fires that the critical heat transfer rate for extinction of the fire by cooling the fuel is controlled mainly by convection from the flame to the liquid rather than by radiation from the flame. This evidence may be summarised briefly as follows:

1) With sprays at less than the critical rate a steady fire condition could be established with a temperature near the liquid surface not greatly in excess of the fire point, with a flame size very much less than the size of the flame if no spray were applied, and with the flame reaching down to the surface of the liquid.[1] In these fires the predominant mechanism of heat transfer to the fuel surface was by convection.
2) The effect of scale on the critical flow rate was what was expected if convection controlled the critical heat transfer rate rather than radiation.

The reason for the above phenomenon is that when radiation is the predominant mechanism of heat transfer from the flame to the surface, the bulk of the heat reaching the surface is taken up as latent and sensible heat of the vapour leaving the surface and does not manifest itself as sensible heat in the remaining fuel. There is thus little resistance to the cooling of the fuel by water spray. The temperature of the surface is also much higher than the fire point and the capacity of the water spray for taking up heat is correspondingly much greater. Figure 2

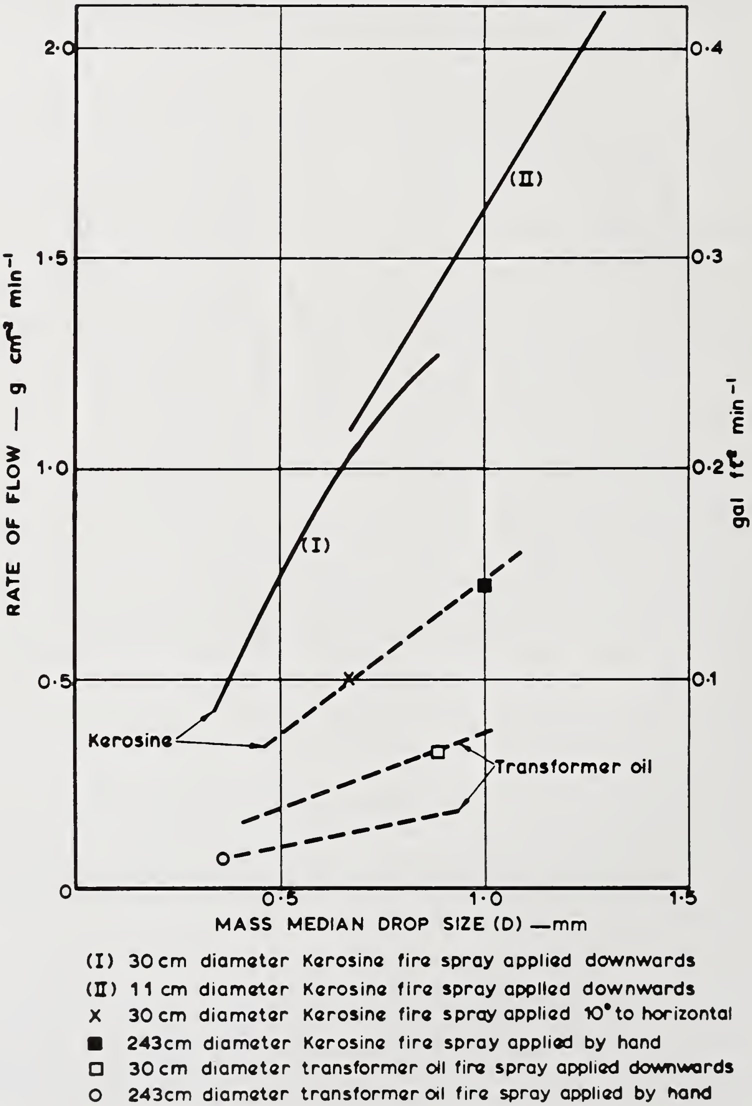

Figure 2. Critical flow rates for extinction of pool fires by cooling the liquid.

shows critical rates to extinguish kerosine and transformer oil fires by cooling the fuel plotted against the mass median drop size for fires burning in vessels 11, 30, and 243 cm diameter. The curves for the 30 and 11 cm diameter kerosine fires were obtained by extrapolating to the fire point relationships between the flow rate of spray reaching the fuel and the resulting steady temperature near the fuel surface for sprays of different drop size; the spray was applied in a downward direction.[11] The curves obtained separate tests in which extinction took place by cooling from tests in which no extinction occurred. Although for both fires the critical rate was approximately proportional to the drop size, for a given drop size the rate was slightly less for the 30 cm diameter fire than for the 11 cm diameter fire. If radiation controlled the critical heat transfer rate, the critical flow rate for extinction would be expected to be 100 per cent greater for the 30 cm diameter fire but, if convection controlled, about 15 per cent smaller. The difference between the points for tests with horizontal application of spray to a kerosine fire 30 cm diameter and for hand application of spray to a fire 243 cm diameter may be accounted for by the different drop sizes of the spray. If radiation controlled the critical heat transfer rate, a ratio of 2.5 would be expected in the critical rate. After taking into account the probable effect of drop size there was in fact no difference in the critical rates. However, the critical rate for horizontal application for the 30 cm diameter fire was about half that for vertically downward application. A possible reason for this difference is that the spray pushed the flame sideways; as a result the drops did not become heated in the flame and had a greater cooling capacity when they reached the liquid.

The effect of radiation is likely to be much greater with pool fires in which the burning surface can "see" all the flame than with other fires. Since radiation from the flame of the fuel being extinguished has a minor effect on the critical rates for extinguishing pool fires by cooling, it is reasonable to neglect it for other fires.

The effect of drop size on the critical rate follows from the fact that the drops are in the liquid for only a limited time and their size is a controlling factor in the rate at which heat is transferred. It would be expected[11] that the heat transfer from the body of the liquid to the drops would be proportional to $D^{-4/3}$. However, the transfer of heat from the surface of the liquid to the interior would be expected to increase as the eddy conductivity caused by the turbulent eddies set up by the motion of the drops on the liquid; this is estimated to increase as $D^{1/3}$. The actual effect of drop size results from a combination of these two factors.

The driving force for heat transfer in the liquid may be represented by ΔT, the difference in temperature between the surface of the liquid under critical conditions (for practical purposes the fire point) and the temperature of the drops (for practical purposes the ambient temperature). It would, therefore, be expected that for a given drop size the critical rate should be inversely proportional to ΔT. Measurements of critical rate indicated in Figure 2 for downward application of spray to a 30 cm diameter transformer oil fire and hand application of spray to a 243 cm diameter fire support this.

Extinction Time for Pool Fires

As long as the flow rate of spray is greater than the critical value, then extinction will take place in a time which depends on the amount of heat present in the burning fuel which must be removed by the spray to reduce the surface temperature to the fire point. With most pool fires this heat content increases as the preburn time increases up to about 10 to 20 minutes but for hot zone forming liquids, e.g., heavy fuel oils, this heat content may increase indefinitely. Experiments [12, 13] on extinction of pool fires using fixed nozzles sited vertically above the burning liquid (see Plate 1) and for hand extinction of an 8 ft diameter fire gave the following relationships:

Fixed nozzle

$$t = 6800 \ (D/M)(Y/\Delta T^{1.75}) \tag{16}$$

Hand application for 8 ft diameter vessel

$$t = 121{,}600 \ D^{0.85} \ F_1^{-0.68} \ Y^{0.39} \Delta T^{-1.67} \ L^{-0.33} \tag{17}$$

where

D is the mass median drop size of the spray in mm
M is the flow rate of spray in gallons $ft^{-2}min^{-1}$ *
Y is the preburn time in minutes
ΔT is the difference between fire point and ambient temperature °C
F_1 is the total flow to the fire in gallon/min
L is the total number of tests carried out by the operator
t is the extinction time, sec

The influence of drop size and of flow rate of spray are as may be expected from considerations of heat transfer between the liquid and the drops. The influence of ΔT, however, is greater than may be expected from a heat transfer basis alone. A reason for this may be that the higher the value of ΔT the greater was the temperature of the surface of the liquid in excess of 100°C, particularly when application of water spray commenced, and the greater was the steam formation in the liquid during the extinction process. This steam probably accelerated the cooling of the liquid surface by stirring the bulk liquid. An increase in the preburn time increased the extinction time, although to a lesser extent for hand application than for fixed application. The experience of the operator as expressed by the factor L in equation 17 was also an important factor in the extinction of fire by hand application.

Both the equations (16) and (17) presume that the bulk of the spray reaches the burning liquid. If the downward thrust of the spray was less than the upward thrust of the flames and if the flames could burn vertically upwards against the spray, then the extinction time was prolonged. In this connection it is noteworthy that the size of the flames in the first few seconds of application were usually considerably greater than the size before application of spray, as indicated in Plate 1. This was due to the sputtering of fuel into the flame. However, for tests on fires 3 ft and 4 ft diameter in a large roofless structure, the ambient wind was usually sufficient to blow the flames away from the upright position and the force of the spray was not a significant factor in extinction of the fire, if the spray was much wider than the fire. With hand application of spray to an 8 ft diameter fire there was no difficulty in enabling even fine sprays of low thrust to reach the burning liquid, since the fire could be approached on the upwind side and the spray applied directly to the base of the flames. A complicating factor in all these tests was the occurrence of splash fires with coarse sprays; burning fuel was splashed into the flame by the spray and a vigorous flame maintained even though the liquid was cooled well below the fire point. If, when a splash fire was established, the spray were taken away the fire often went out.

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* "gallon" refers to imperial gallon in this paper—1 imp. gal.=1.2 U.S. gal.

Fires in Oil Running Over Metal Work

When sprays are applied to a pool fire which has been burning for some time, there is an initial upsurge of flame and the flames then reduce in size gradually within the extinction time. When burning liquids are flowing over a surface the liquid layer is very thin and the sensible heat in the liquid which needs to be removed is very small. Providing the flow rate of water spray is near the critical rate the flames are reduced in size almost immediately after turning on the water spray and thereafter are reduced in size much more slowly. This is illustrated in Plate 2 which shows a fire in transformer oil flowing over a test rig consisting of a bank of tubes 5 cm diameter. The rate of flow required to extinguish the fire in a given time depended on the preburn time in this case, since during the preburn period the tubes themselves were heated and acted as a reservoir of heat during the application of spray. The effect of the temperature of the tubes on the rate

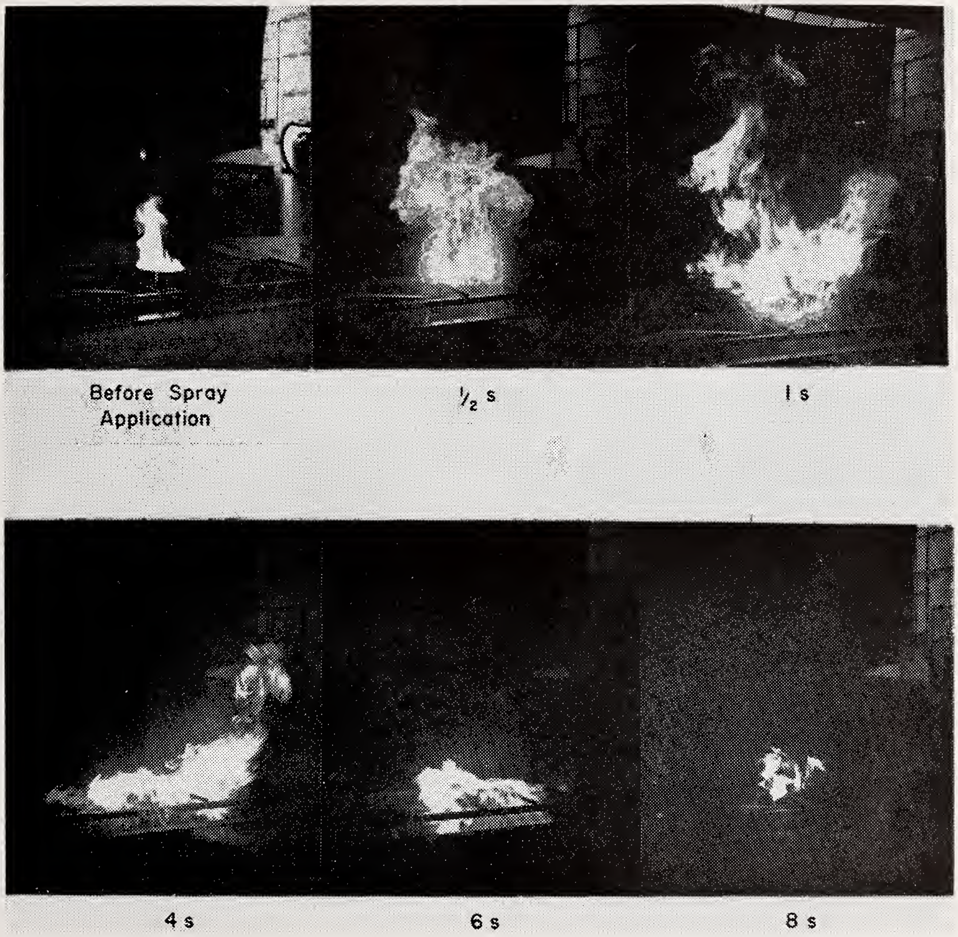
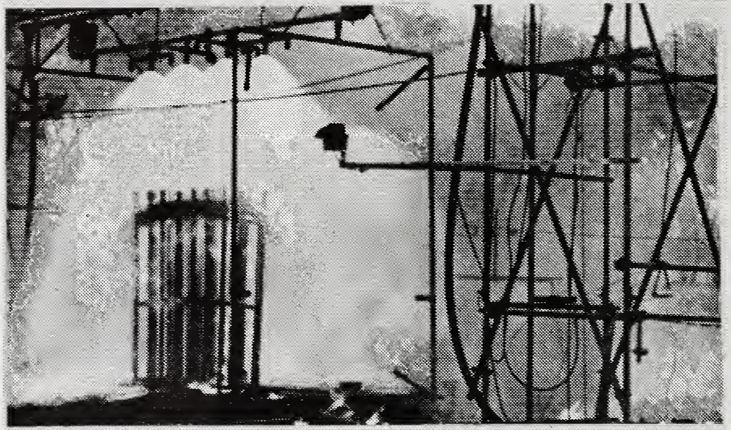


Plate 1. Extinction of fire in transformer oil by downward application of spray from fixed nozzle (extinction time 8.8 sec).

Application



5 s

30 s

Plate 2. Control of fire in transformer oil on a bank of tubes.

of flow required to control and extinguish the fire is given in Figure 3. The relationships in Figure 3 were obtained for sprays projected directly downwards from 5 ft above the point in the tube rig where oil was injected (6 in below the top), but tests in which the sprays were projected from a similar distance from the side of the

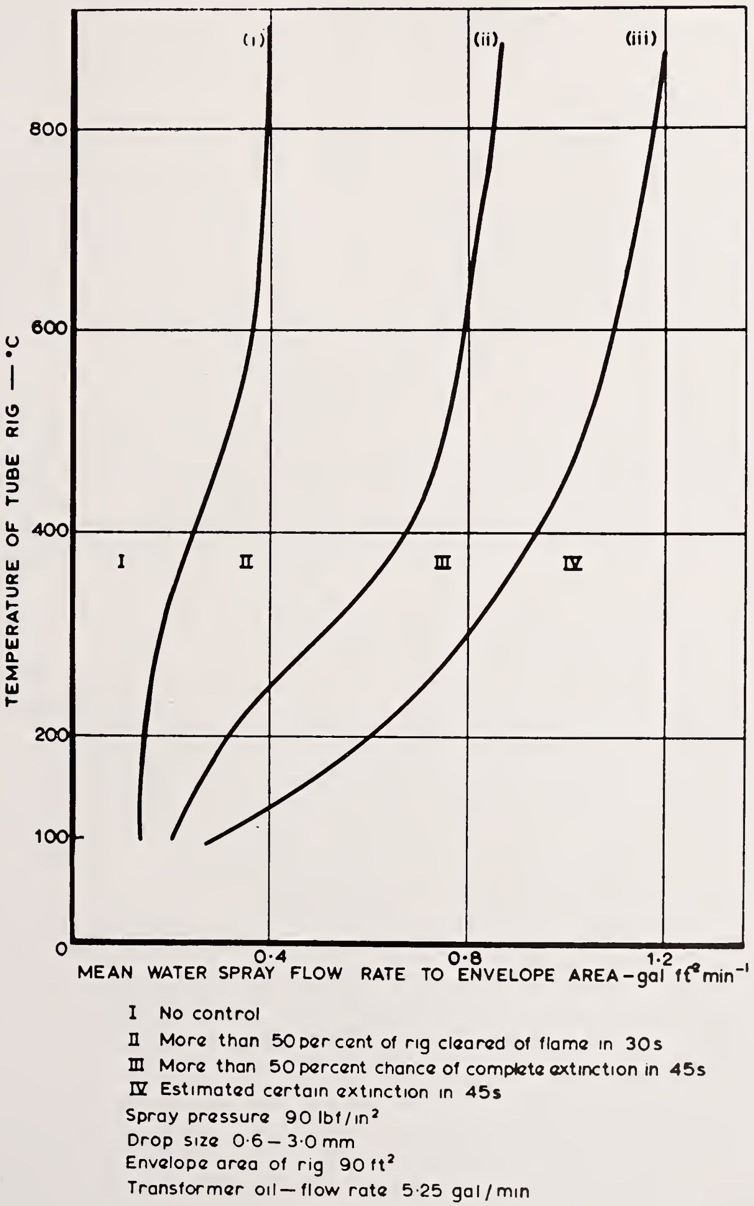


Figure 3. Control and extinction of oil fires on tube rig.

rig did not give significantly different results, nor was there any difference if the tube bank was horizontal rather than vertical. The drop size of the spray was found to have no significant effect in the range tested (mass median 0.6 to 3.0 mm); there was evidence, however, that an increase in drop velocity increased the efficiency of the spray[14] and the effect of the drop size may have been masked by the fact that the ratio of drop size to drop velocity was constant for the sprays referred to in Figure 3. The tests covered a wide range of ambient wind conditions. However, Figure 3 indicates that the critical rate for these varying conditions increased as the temperature of the tubes increased. These critical rates may be taken as lying between curves (1) and (3) in Figure 3.

A large number of tests have been carried out in the United States in which water spray has been applied to oil fires on sheet metal structures simulating transformers.[15, 16] A comparison between the results of these tests and those carried out on the tube rig in England has indicated that to obtain a given extinction performance under given conditions of nozzle pressure, oil fire point and preburn time, a mean flow to unit area of the envelope of the tube rig on the average 2.3 times as great as that to the large sheet metal simulated transformers was required. Equations (8) and (10) indicate that the ratios of critical heat transfer rates to the surface would be about 1.8, the expected ratio of flow rates to the envelopes of the two risks would be between 1.8 and 2.8. If the wind velocity controlled the critical heat transfer rate the expected ratio would be greater. It is unlikely that the condition for heat transfer to the drops in the oil would differ between the oil running down tubes and a vertical surface although it would be expected that the accessibility of spray to the surfaces would be easier for a flat surface than for a nest of tubes. Broadly, however, the comparison does support the theoretical approach.

Critical Rate for Extinction of a Wood Fire

Bryan[17] has measured the critical rate for a wood fire consisting of 2 inch square pieces with a total surface area of 80 ft^2. The minimum rate at which he obtained extinction with water was 0.16 g/min corresponding to a rate of 0.01 g/cm^2/min. Bryan concluded from other observations that extinction was by cooling the wood. Under the conditions he used it may be assumed that the water was entirely vaporized; this would correspond to a heat transfer of 0.1 cal/cm^2/sec at the wood surface. From information on the heat of combustion of wood volatiles and assuming that critical criteria as described above may be applied to burning wood, it may be estimated that 0.8 cal/cm^2/sec would have been transferred from the flame to the wood surface under critical conditions. The difference between the measured and estimated values might be taken to indicate that a substantial heat transfer, of the order of 800 cal/g, was required to cause the evolution of sufficient volatiles for combustion.

Direct Extinction of Flame

To examine the relevance of the theory developed above it is necessary to have an estimate for X, the heat transfer capacity for the sprays. These estimates were obtained using equation (18), a modification of the Ranz and Marshall relationship for heat transfer from gases to drops [18] which was found to hold for water drops evaporating in a bunsen flame.[19]

$$\frac{hD}{k}=\frac{1}{1+0.4\beta/\lambda}\left[2+0.6\left(\frac{c\mu}{k}\right)^{0.33}\left(\frac{V_D D\rho}{\mu}\right)^{0.5}\right] \qquad (18)$$

c, μ, k, ρ	specific heat, viscosity, thermal conductivity, density in boundary layer;
D	drop size, V_D drop velocity relative to gas stream;
h	heat transfer coefficient;
β	enthalpy increase per unit mass of vapour between surface and flame temperature;
λ	heat required to vaporize unit mass of the liquid.

In estimating X it was assumed that the concentration and velocity of the drops in the flame were the same as in the approaching spray, and that the contribution of the individual fractions of the different drop sizes could be added. Since the surface area of drops of size D present per unit volume of space through which the drops are passing is proportional to $M_D/V_D D$ where M_D is the flow rate per unit area, it follows from equation 18 that

$$X \alpha M D_r^{-(1.5\text{ to }2.0)} V_r^{-(0.5\text{ to }1.0)} \qquad (19)$$

where M is the total flow rate per unit area, D_r and V_r are a representative drop size and drop velocity.

The extinction of fire by water spray by extinguishing the flame has been studied with fires in kerosine, petrol, and benzole is a vessel 30 cm diameter.[20, 1] Extinction of the flame differed from extinction by cooling the fuel in that there was a sudden clearance of a comparatively large volume of flame which led to extinction.

When the spray was applied in a downward direction the flames of the petrol and kerosine fires were not extinguished unless the downward thrust of the spray was greater than 60 and 40 dynes/cm², respectively. These forces are comparable with the upward force of the flames before the spray was applied. With sprays of greater downward force the flames were extinguished as long as the heat transfer capacity of the spray was greater than about 0.15 cal/cm²/sec, and as long as the preburn time was not very short. The above value is intermediate between those expected from equations (12) and (13), if I is taken to refer to the upward moving flames before spray application.

For a given type of spray the most important factor in the heat transfer capacity is the drop size of the spray (equation (19)) and in the thrust of the spray the rate of flow per unit area of the fire. If the drop size of the spray is plotted against the critical rate of flow for extinction at that drop size, the above phenomenon of critical thrust manifests itself as a flow rate below which the fire is difficult to extinguish with sprays of any drop size. Critical flow rates for extinction of a flame have been plotted in this way in Figure 4 for the kerosine and petrol fires; points for extinction and nonextinction are shown for the petrol fire. For comparison critical flow rates for the extinction of the kerosine fire by cooling the liquid have been included. Similar relationships obtained by the author for sprays produced by hypodermic needles acting on a kerosine fire 11 cm diameter,[21] and by the National Board of Fire Underwriters for sprays acting on a petrol fire 15 cm diameter [22] have been given elsewhere. The critical flow rate below which extinction was difficult was smaller in both cases than those shown in Figure 4 for the 30 cm diameter fires. This may be mainly attributed to the smaller dimension of the fires and the resulting smaller upward force of the flames, but different conditions of test and different patterns of spray at the fire area also probably played a part. Extinction of the flame has been found to be easier if the peak concentration of the spray is near or even outside the edge of the vessel, since after a clearance of part of the flame, the remnants of flame from which a flash back may occur are at the edge.[20] This phenomenon may account also for comparatively low flow rates for extinction of flame reported by Y. Yazi.[23]

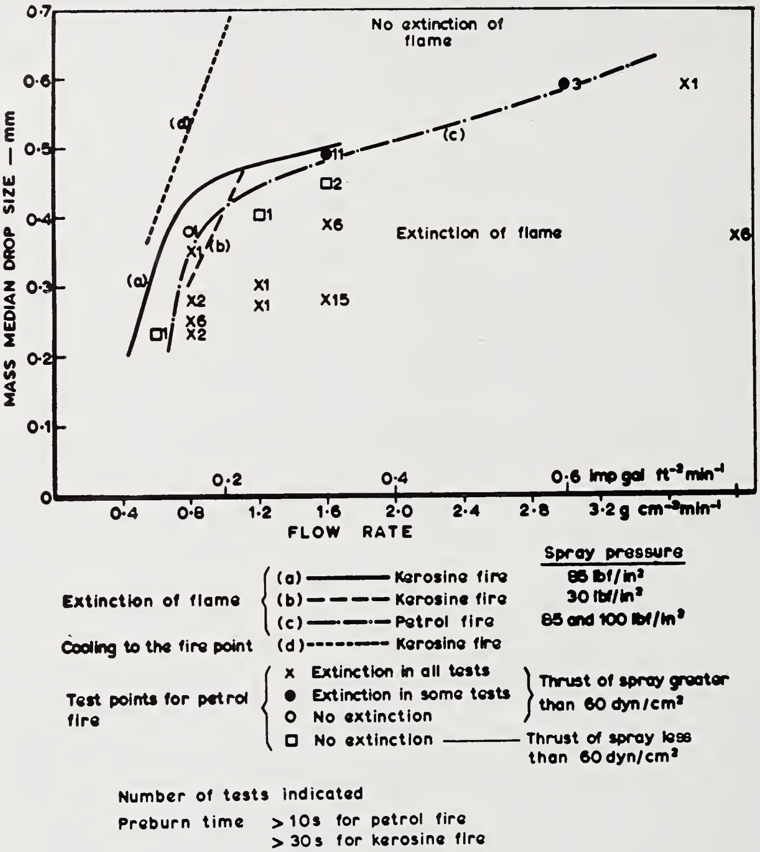


Figure 4. Critical flow rates for extinction of kerosine and petrol fires 30 cm diameter, downward application of spray.

During the tests the flames were usually wild with frequent partial clearance and flash backs. However, with petrol and benzole fires when the preburn time was very short (less than 10 sec) and when sprays with high downward thrust were used, the spray pushed the flame immediately into a flat flame close to the liquid surface which was very difficult to extinguish. The appearance of the flame depended on the drop size and heat transfer capacity of the spray. A spray with a value of X equal to 0.44 cal/cm^3/sec gave thin blue flames near the inside edge of the vessel; with a value of X of 0.14 cal/cm^3/sec, a belt of yellow flame covered the whole vessel. Flames stabilized close to the liquid surface were also obtained if spray were applied to the surface at an angle less than 30° to the horizontal. It was estimated that the value of I for flames stabilized in this way was about 2.5 cal/cm^3/sec. It would, therefore, be expected that value of X equal to about 0.5 to 1 cal/cm^3/sec would have been required to extinguish these flames reliably.

Regression analyses on the extinction time for the kerosine and petrol fires [20] indicated that for sprays with a given value of X the entrained air current had a powerful effect on the extinction time. This effect was much more powerful than might be expected from a relation such as is given in equation (15). This may be attributed to two reasons. Firstly, the entrained air current helped to present the spray to all parts of the flame; associated with this reason it also helped the spray penetrate to the burning liquid, cooling the latter and thus reducing the size of the flame. Secondly, the entrained air current tended to blow away the thick vapour zone which was usually established after burning for about 10 seconds and thus rendered the flames unstable.

Extinction of Fires in Rooms

Tests have been carried out by many authorities on the extinction of solid fuel fires in rooms. It is not yet clear, however, whether these fires are more efficiently controlled by cooling of the fuel or by the formation of steam which cools the flames.

Kawagoe [24] has found that the rate of burning in room fires is, on the average, directly proportional to the ventilation, and the constant of proportionality indicates that the ratio of air to fuel volatiles is the stoichiometric ratio. When fires in rooms are attacked with sprays from an opening in the wall, then additional air would be entrained into the room comparable with the normal ventilation rate through the opening. Under these conditions it may, therefore, be expected that the fire is burning with excess air when extinction is commenced. The critical amount of steam required to smother the flames would then be governed by equation (14). It may be estimated using equation 14 that if steam is obtained by the impact of spray on the burning surface, the critical flow rate of water to form sufficient steam to extinguish the flames is 10 to 15 times greater than that found by Bryan [17] to be necessary to extinguish a wood fire by cooling. However, conditions in practical fire fighting may still frequently be such that steam extinction would require the use of a smaller total quantity of water.

From the intrinsic nature of extinction of the flame by steam and extinction by cooling the fuel, the qualitative effect of various factors on the efficiency of control (i.e., critical flow rate and quantity of water required) may be deduced. These effects are compared in Table 1.

Available test results have been summarised by Hird *et al.*[25] but owing to the lack of a systematic investigation of the above factors, at least on the full scale, it is not possible to give a firm opinion on the extinction mechanism. The amounts of water used to control the fires varied from 2 to 15 gal/1000 ft^3. The above workers also carried out a comprehensive series of tests in which sprays of varying pressures from 80 to 500 lb/in^2 and with flow rates from 5 to 25 gal/

min were used against a standard fully developed fire in a room of volume 1750 ft^3. The quantity of water required to control and extinguish the fire was 7 and 17 gallons, respectively, and within the variance of the results, was independent of the pressure, the flow rate and whether jets or sprays were used.

TABLE 1

EFFECT OF VARIOUS FACTORS ON CONTROL OF ROOM FIRES BY COOLING AND BY STEAM FORMATION

Factor	Cooling the Fuel	Steam Formation
1. Increase in preburn time.	Critical flow rate increased somewhat. Quantity increased approximately in proportion to preburn time.	No effect.
2. Decrease in ease of access of water spray to burning surfaces.	Quantity increased.	No substantial effect if walls are hot.
3. Increase in the fraction of incombustible surface present; total area of combustibles remaining the same.	Critical flow rate increased (due to radiant heat falling onto burning surfaces).	No substantial effect if incombustible surfaces are hot.
4. Increase in ventilation.	No effect.	Critical flow rate and quantity increased.
5. Linear dimension d.	Critical rate proportional to d^2.	Critical rate proportional to $d^{5/2}$.

Use of Water Sprays in Practical Fire Fighting

The following broad principles may be put forward on the basis of the experimental work carried out at the Joint Fire Research Organization and elsewhere.

1) In general the best way of putting a fire out is that spray should be made to reach and cool the burning fuel. The rate at which the spray need absorb heat in doing this is generally far less than the rate of production of heat by the fire. Experimental results are available giving information on critical rates for a few systems. On the basis of equations (7) to (10) or other relationships developed in similar manner, it is possible to extrapolate these results to other systems as long as heat transfer between the spray drops and the fuel behaves in a similar way. Perhaps the most important consequence of equations (7) to (10) is that critical flow rates per unit area for a given type of system should not increase as the scale increases; under some conditions they may in fact decrease.

2) If sprays are applied downwards to a fire with a flame moving steadily upwards, then for the bulk of the water to reach the burning fuel the downward thrust of the spray should be comparable to the upward thrust of the flame. These two thrusts may be calculated as indicated in the paper. If the sprays are applied laterally or by hand from the windward side of a fire, a much smaller thrust is necessary.

3) Water sprays in current use are unreliable in extinguishing a fire that cannot be extinguished by cooling the fuel. However, extinction may frequently be obtained with available fire sprays produced by pressure nozzles (mass median

drop size 0.2–0.4 mm) particularly if there is no change to stable burning in the air current of the spray. When extinction is not obtained, a large reduction in the size of flame may be achieved.

4) For most of the fires for which water sprays are useful, e.g., fires in solids and fires in high boiling liquids flowing over solid surfaces, the drop size of the spray is not usually an important practical factor. However, for fires in deep pools of high boiling liquids the efficiency of the spray increases as the drop size is reduced.

5) The pressure at a nozzle influences a number of factors that affect the extinction of fire. However, where sprays may be reliably used for extinction of fire, an increase in pressure about 100 lb/in^2 with a given flow rate of spray has not been found to confer any extra efficiency on the spray, providing that the water can reach the seat of the fire. The choice of pressure for a pump, therefore, depends rather on operational factors, in particular the length and diameter of hose line and the flow rate which it is desired to give the operator, than on intrinsic efficiency of the spray in fighting the fire. It should be added here that an increase in flow rate, or a decrease in cone angle, has a greater effect on increasing the throw of a spray [26, 27] than an increase in pressure, and that an increase in pressure has a smaller effect on reducing the drop size of a spray when the pressure is above 100 lb/in^2 than when it is below 100 lb/in^2.

Finally, it is instructive to compare quantities of water which have been found necessary to extinguish experimental fires with those actually used in practical fire fighting. For fires in rooms it has been found experimentally that about 10 gallons per 100 ft^2 of floor area is required and, according to the drop size of the spray, from 5 to 15 gallons may be used to extinguish a gas oil pool fire of the same size. According to information provided by Mobius [28] the minimum quantity of water to extinguish fully developed room fires under operational conditions is about 100 gallons. Thomas [29] made an analysis of the amount of water used at large fires based on the number of pumps called to the fire. It may be estimated from this analysis that for large fires approximately 1000 gallons of water are used for 100 ft^2 of the fire. Thus, either wastage or operational difficulties in applying water to fires is by far the most important factor governing the amount of water used, and this would appear to be a direction where a substantial research effort is worthwhile.

APPENDIX

Thrust of Flames and Sprays

Thrust of Flames

A complete analysis of the movement of flame has not yet been made, but as this movement is controlled by the buoyancy of the flame, it would be expected that the upward thrust would be proportional to the flame height. Analysis of buoyant columns rising from small heat sources indicate [30, 31] that the thrust at the centre of the column is given by

$$\rho_z V_z^2 = 1.5 \text{ to } 2.0(\rho_0 - \rho_z)gz \qquad (20)$$

where ρ_z is the density of the column at a point z above the source and ρ_0 is the density of the ambient air.

In Figure 5 some calculated thrusts based on measurements of the upward velocity of flames and the flame temperature [9] are plotted against the buoyancy

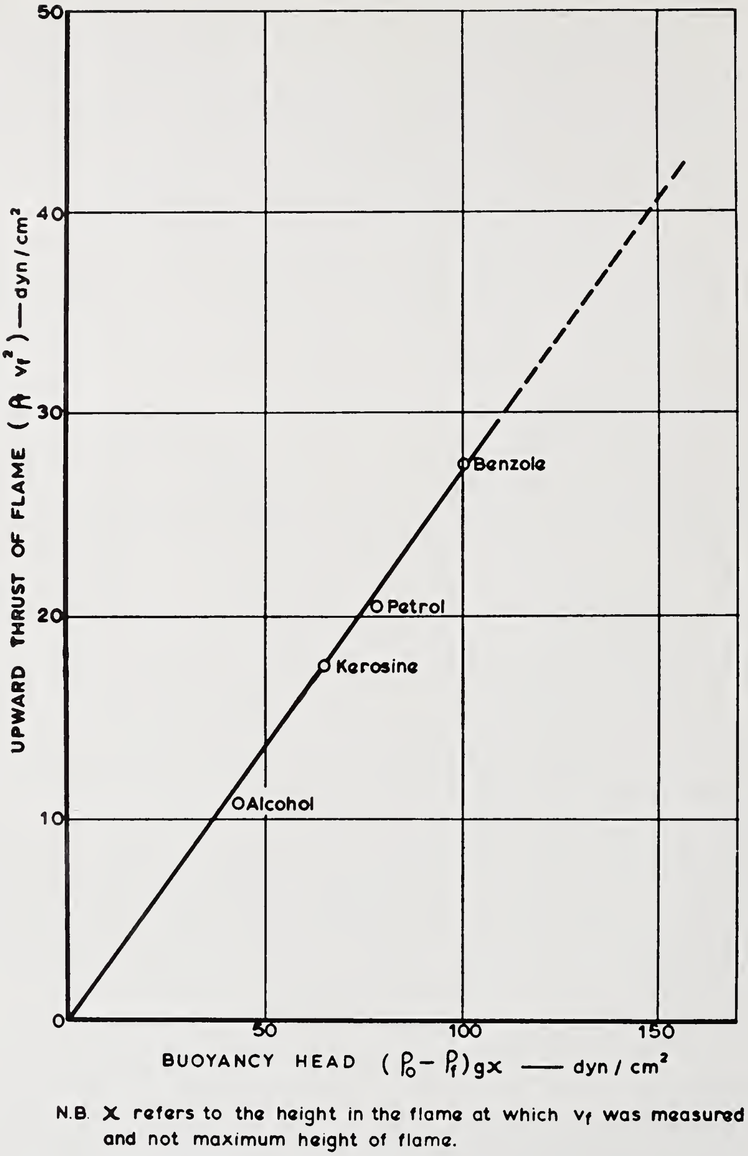


Figure 5. Relation between upward thrust of flames and buoyancy head—freely burning liquid fires 30 cm diameter.

head $(\rho_o - \rho_f)$gx for fires in different liquids burning in a vessel 30 cm diameter; ρ_f is the density of the flame and x the height of the point in the flame for which the thrust was estimated. The velocity measurements were made by observing the upward motion of the top of the flame and eddies at the side of the flame as recorded by a cine camera; the calculation of the thrust was made for the mean time of burning and the mean height of the flame at which measurements were made. The temperature on which ρ_f was based was a mean temperature across the flame as measured by the Schmidt method. The straight line relation (equation 21) obtained

$$\rho_f v_f^2 = 0.27(\rho_o - \rho_f)gx \tag{21}$$

confirms the proportionality expected and indicates that thrust is independent of the nature of the burning fuel. The constant, however, is considerably less than would be expected from equation (20).

On the basis of equation (21) it is possible to calculate the upward thrust of the flame knowing the flame heights. The latter has been related by Thomas to the rate of burning and the main dimension of the fuel layer for solid fuel fires.[32]

Thrust of a Spray

A spray after leaving a nozzle very soon becomes a suspension of drops moving in an air stream. The air stream is generated by the transfer of momentum from the drops and is of importance in determining the velocity of the drops and the motion of the spray as a whole. The total forward thrust of a spray may be measured by the reaction at the nozzle. Measurements of the entrained air current of sprays directed downward from a number of nozzles [33] have shown that for sprays of mass median drop size less than 1.0 mm, the bulk of the thrust is transferred into momentum of the airstream by the time the spray has reached a plane 6 ft below the nozzle; most of the remaining thrust may be accounted for by momentum of the drops moving at the velocity of the air stream. For very coarse sprays (mass median drop size 1.5–3.5 mm) about 50 per cent of the initial thrust is converted into momentum of the air current.

The reaction of a jet is the product of the flow rate and the velocity at the nozzle, both these factors being proportional to the square root of the pressure. The reaction of a spray nozzle, however, is less than the product mentioned above due mainly to the presence of lateral motion in the spray. Figure 6 shows the ratios of the reaction of a number of spray nozzles to that of corresponding perfect jets and indicates the extent to which the reaction is reduced as the cone angle increases and as the spray pattern becomes less peaked in the centre. Knowing the reaction at the nozzle, an approximate estimate of the mean forward thrust in a plane is given by R/A, where A is the cross-sectional area of the spray in the plane, and if the assumption is also made that the thrust has been entirely converted into movement of the entrained air stream then the air velocity v_a may be given by:—

$$\rho_o v_a^2 = \frac{R}{A} = a_1 \rho^{0.5} \frac{F}{A} \tag{22}$$

where

a_1 is a constant depending on the nozzle
P is the nozzle pressure
F is the flow rate

Equation (22) gives, of course, a mean value of v_a. There is evidence, however, that the distribution of entrained air velocity in a plane perpendicular to the spray axis, when both entrained air velocity and distance from the axis are expressed in dimensionless terms, is approximately independent of the distribution of flow rate within the spray. In addition the distribution of the entrained air

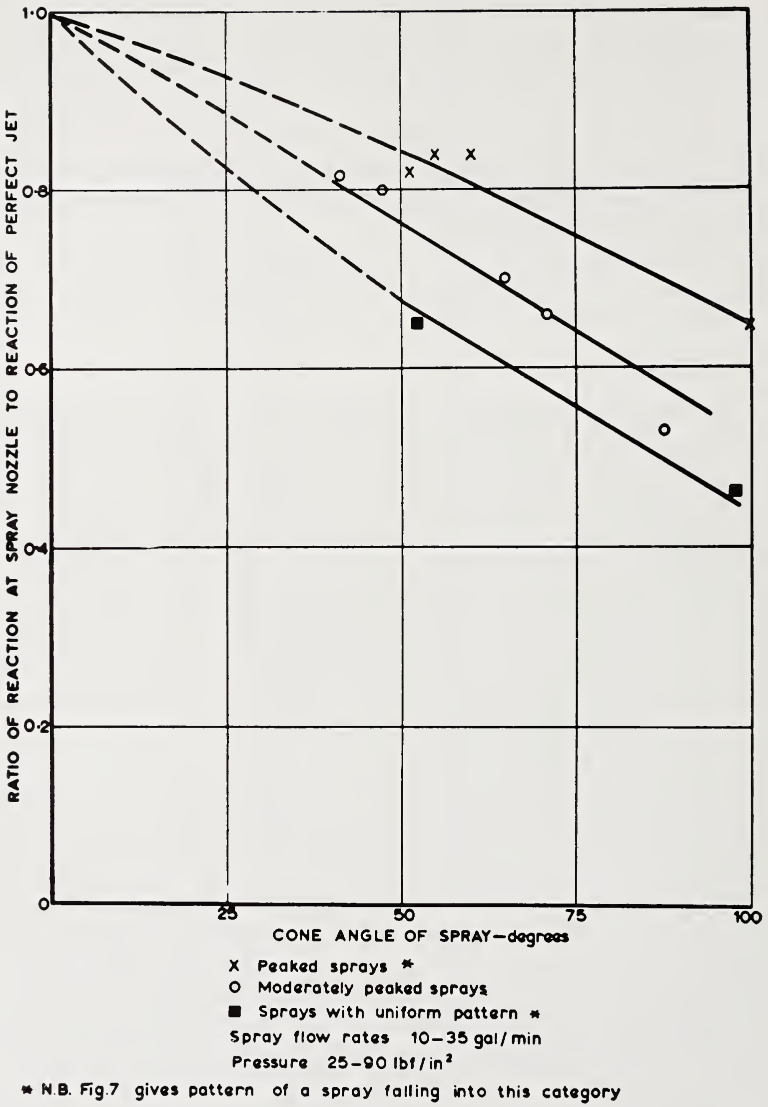


Figure 6. Reaction of spray nozzles.

velocity is similar to the distribution found in a turbulent air jet. These points are illustrated in Figure 7 which shows an almost identical distribution of the entrained air for sprays with widely different spray pattern. The radii of the sprays referred to in this figure are those radii where the entrained air velocity and water flow rate were respectively 1/100 of the values in the centre of the spray.

For sprays with a similar pattern over a given area it follows from equation 22 that for a given part of the spray

$$v_a \ \alpha \ P^{0.25}M^{0.5} \qquad (23)$$

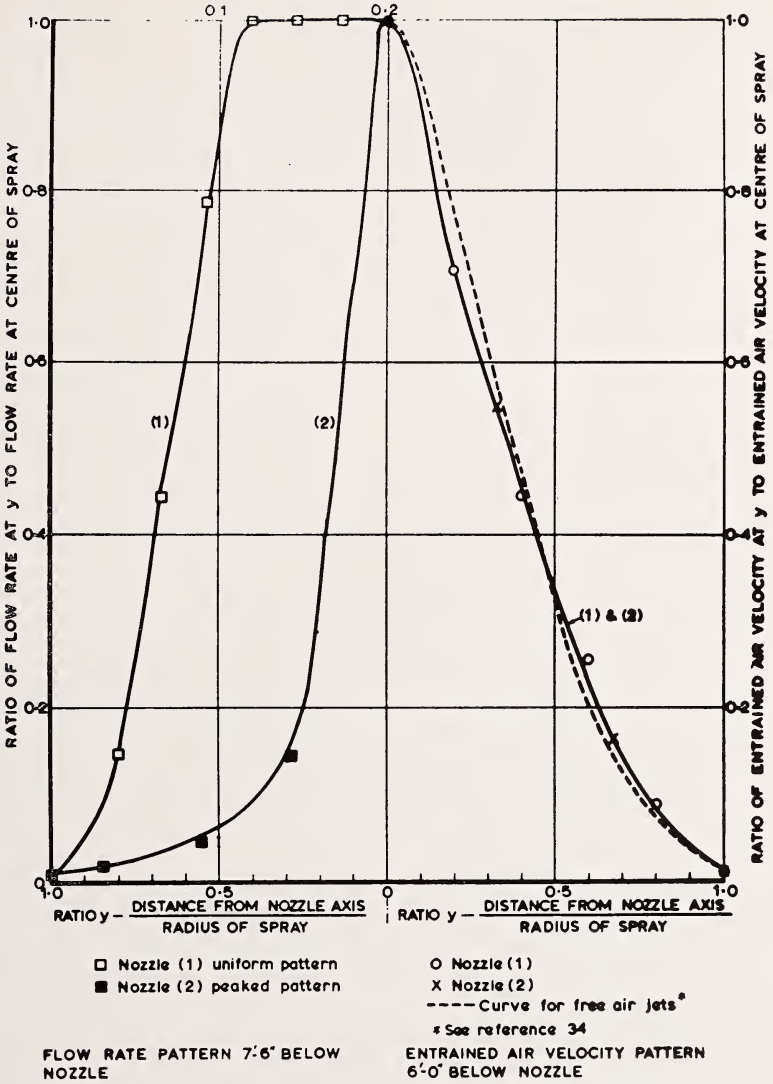


Figure 7. Comparison of distribution of entrained air current and water flow in sprays from given nozzles.

where M is the local flow rate per unit area. A relation similar to this has been found to hold for a wide range of values of P and M for sprays projected downward from a battery of impinging jet nozzles.[26]

Symbols

a_1 a_2 a_3 b	Constants
c	Specific heat in gas boundary layer
d	Linear dimension
g	Acceleration due to gravity
h	Heat transfer coefficient
k	Thermal conductivity
l	Linear dimension
M_{og}	Concentration of oxygen in the air
$\dot{m}''$	Rate of burning per unit area per unit time
r	Stoichiometric ratio (weight of air/weight of fuel)
t	Time
v_a, v_D, v_{BO}	Velocity of entrained air, of spray drops, and velocity to blow out flame
v_f, v_z	Upward velocity in flame, in buoyant hot column
x	Height of flame
z	Height of buoyant column
A	Cross sectional area of spray
B	Transfer number (after Spalding)
D	Drop size
F	Total flow rate of spray
H	Heat of combustion
I	Intensity of combustion in flame
M, M_D	Total flow rate of spray per unit area, flow rate of drop size D
L	Number of tests carried out by operator
P	Pressure to produce spray with pressure nozzles
Q, Q_c	Heat transfer to fuel surface per unit mass of fuel vaporized, critical value of Q
R	Reaction of nozzle
T_g, T_s	Gas temperature, surface temperature
ΔT	Difference in temperature between fire point and ambient
V	Volume of flame
W	Critical flow rate of water to extinguish flame by steam formation
X_1, X_2, X_3	Critical values of X
X	Heat transfer to spray within unit volume of flame in unit time
Y	Preburn time
Z	Rate of fuel consumption in fire
α	Thermal diffusivity
β	Sensible heat of steam or vapour
γ	Heat taken up as sensible heat in fuel per unit area of surface per unit time
λ, λ_f	Heat required to vaporize unit mass of liquid, of fuel
μ	Viscosity in boundary layer
ρ, ρ_f, ρ_o, ρ_2	Density in boundary layer, in flame, ambient air, in buoyant column
T_c	Thrust of spray
γ_c	Critical value of γ

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Improving the Effectiveness of Water for Fire Fighting

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Introduction

Fire is of great benefit to mankind. It furnishes heat for cooking and warmth for shelters. Until the relatively recent advent of nuclear power, some form of combustion process (that is, fire) provided the major source of energy for power.

But fire has also proved to be a terrible enemy of mankind. Few people need to be convinced of the heavy annual waste in destroyed businesses, disruption of production, and loss of life which result from uncontrolled fires in the civilized world, as well as in less developed areas.

This paper discusses a new method to help mitigate the terrible toll of fire waste. The best way to combat the problem of fires is to prevent them, an approach which unfortunately appears to be one of the most difficult to implement. Another way is to increase the rapidity with which fire-extinguishing agents function. Research scientists in fire fighting are constantly working toward this goal. If an improved extinguishing agent can be developed, fire loss can be decreased. Scientists at Syracuse University have been working toward such a goal for the past 14 years. From 1947 to 1957, the primary concern was with methods to increase the effectiveness of fire-fighting foams. During the past four years, these researches have been concentrated on methods to improve the fire-fighting characteristics of water.

The studies on foam had led to the belief that some of their outstanding qualities, such as blanketing ability and high viscosity, might be obtainable in water through the use of certain additives. The present study was thus initiated to determine whether additives improve the fire-fighting characteristics of water, and if so, which additive is effective and in what degree.

Water in its natural state has been used to extinguish fires for many centuries. It has great advantages because of its cooling properties, heat absorption through its high sensible and latent heat capacity, low cost, and almost universal availability. Before the trend toward urbanization, these qualities were sufficient to offset some of the limitations of water as a fire-fighting agent. Today, however, when a city fire is feared, not only because of the damage inflicted to one building but also because of the possibility of damage spreading to a great area, these limitations cannot be completely neglected. There is also a further danger—with the current population explosion the supply of water has become extremely limited in some areas. The limitations of water as a fire-fighting agent are essentially three. First, because of its low viscosity, water rapidly runs off the burning structure. Second, water's continued blanketing ability is limited. Third, water has relatively poor reflective powers. Additives can change these limitations and reduce them.

Experimental Procedure

The approach to this problem has been to prepare solutions of various additives in water and to test these new solutions for fire-fighting effectiveness.

Basically, the experimentation has been with two major groups of additives: viscosity additives and opacifier additives. Detergents have been used in limited amounts to improve the initial dispersion of opacifiers in the viscous water. Viscosity additives are utilized to improve the blanketing and runoff properties of water. The opacifier additives are employed to reflect radiant energy away from the burning and/or adjoining structures. Work to date has been directed primarily toward the evaluation of viscosity additives, and these additives generally have been the most effective. However, experience with opacifiers also has been accumulated.

Essentially, the basic approach has been to screen these additives in the laboratory and then test the more promising ones on small- and large-scale fires in a controlled environment.

Such variables as rain, snow, and wind velocity do not affect the test conditions.[1] Both small- and large-scale fire tests are conducted in an enclosed fire room. This room consists of a Butler building approximately 13′ x 12′ x 12′ constructed of galvanized sheet metal. A window has been inserted on one side of the enclosure so that performance of the solution as it is sprayed on the burning surface can be observed. Exhaust facilities have been provided to permit adequate control of ventilation or draft.

The fuel generally used for both large- and small-scale fires is California clear pine which has been presoaked in kerosene for approximately 30 seconds. For the small-scale tests, eight pieces of wood, 1″ x 3″ x 10″, are arranged in two tiers. A single nozzle (Fulljet ⅛ GGS, manufactured by Spraying Systems Company) is located at a height of six feet above the fire. The wood is ignited and the fire is allowed to burn four minutes before extinguishment is started. Through use of thermocouples and a radiometer, it has been found that almost all of the test fires reach their maximum intensity at this time interval. In studying the effect of viscosity on extinguishment, a uniform preburn time of four minutes was used. On the small-scale fire tests, the sample solution was sprayed on the burning structure at a rate of 1 GPM.

After the various solutions of additives are tested on the small-scale fires, the surviving promising ones are further tested on larger-scale fires. In this test the wood, which is 2″ x 4″, is arranged in three tiers. The first tier is comprised of 13 pieces each 36″ long, spaced one inch apart. The second tier is comprised of 12 pieces each 35″ long, and the top tier consists of 12 pieces each 34″ long. This is shown in Figure 1. Thus, a type of truncated pyramid structure is obtained. Only the wood in the first tier is presoaked in kerosene. In this test, four nozzles (Fulljet ¼ GGS nozzles, manufactured by Spraying Systems Company) are used for extinguishing the fire. The nozzles are equally spaced at a distance of 1.4 feet from the center line of the fire crib, and approximately 12 feet above the wood arrangement. In the larger-scale fire tests, varied preburn times are used but the sample solution is sprayed on the burning structure at a rate of 3.6 GPM, approximately 19 psi.

After ignition, the intensity of the large-scale fire increases to a maximum in about three minutes (Figures 2 and 3). The preburn time for the large-scale fire tests are varied in order to permit thorough analysis of the effects of various additives on extinguishment. Each formulation is tested on the large-scale fire and the results are compared with corresponding data obtained using water alone.

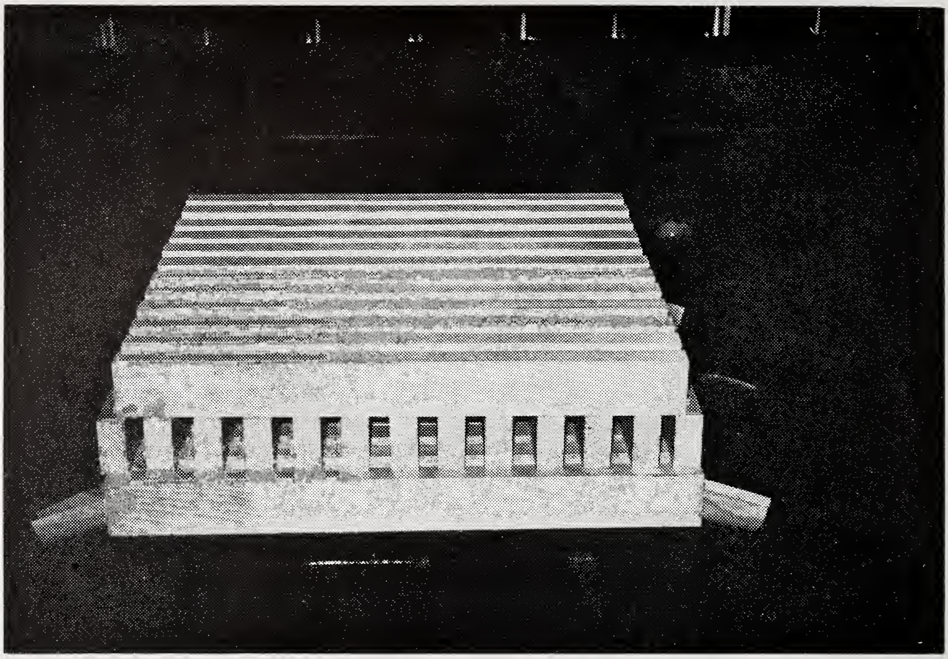

Figure 1. Crib arrangement before ignition.

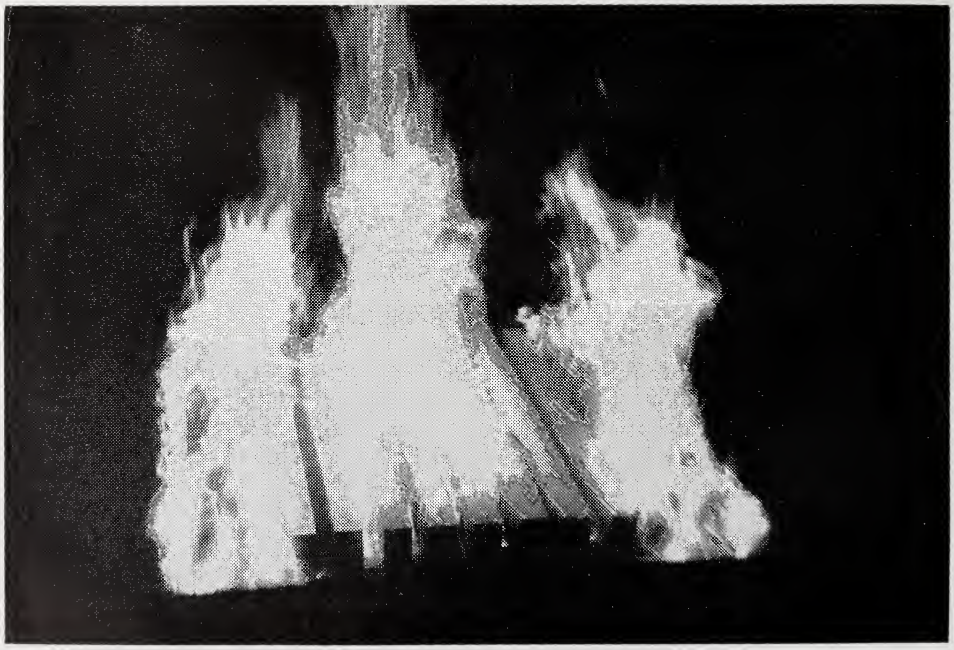

Figure 2. Early stages of fire.

Recent work has been concentrated on transferring the optimum formulation results from the laboratory to field fire tests. In these efforts, local county fire departments have cooperated. Several series of field fire tests have been run in cooperation with the Navy Fire School at Norfolk, Virginia on cribs of seasoned 2″ x 4″ pine wood, measuring approximately 8 feet on a side and 4 feet in height.

In addition to these relatively controlled tests, close liaison and collaboration have been maintained with the U.S. Department of Agriculture, Forest Service, Division of Forest Fire Research, Berkeley, California. Mr. Carl C. Wilson, chief of the Division, and associates ran operational studies in cooperation with forest-fire control agencies in California and Nevada during the summer of 1960. Additional operational studies were continued in 1961, utilizing viscous water on a large number of tank fire trucks for fighting forest fires in more massive tests.

Figure 3. Fire at peak of burning.

Results and Discussion

Studies to date have yielded significant results. A number of viscosity-increasing additives have been found which improve the effectiveness of water as a fire-fighting agent. Some additives are more effective than others. Opacifiers have been shown to decrease the radiant energy transfer. Further study on opacifiers has been delayed since over 75 per cent of the total improvement was attributable to increased viscosity. Viscous water without opacifiers offers fewer storage problems.

From tests to date, the optimum viscosity appears to be from 10 to 15 cp for laboratory test fires. The solution could not be tested at much higher velocities due to the occurrence of improper spray patterns. As the fires get larger and hotter (relatively controlled field test fires or operational fires), an increase in viscosity to a range of 50 to 300 cp, seems to give more effective control. One important point should be mentioned. As the viscosity is increased the spray distribution pattern from the nozzle is changed. For example, a nozzle which gives a full spray with plain water will very likely give a hollow cone spray pattern as viscosity is increased. Some modification of nozzle is indicated to obtain fully effective use of viscous water.

Figure 4. Fire during extinguishment.

Initial Control

One of the important factors in fighting Class A fires is the "knockdown" or initial control. This is a very difficult parameter to measure quantitatively due to differences in fire-fighting personnel and procedures. However, experience in the laboratory fire tests (Figure 4) and in the field fire tests has shown that viscous water "knocks down" the fire much more rapidly than plain water. Fire fighters can advance up to or into the burning structure for rapid control and later for final cleanup or mopup. As a further advantage, more rapid initial control means less fire damage and in some cases preserves life.

A vivid illustration of this phenomenon was reported[2] from some tests run jointly by the Los Angeles City and County Fire Departments at the Van Nuys, California Airport. A previously exposed building was ignited and one room was allowed to become completely involved. The fire was then "knocked down" in 15 to 20 seconds with viscous water at an application rate of 30–40 GPM. The demonstration was repeated several times. Finally, the building was allowed to burn until it was completely involved and about one-half of the roof had caved in. One of the Los Angeles City Mountain Battalion Crews attempted to extinguish it, using a small pumper with plain water at a rate of about 35 GPM. Little if any progress was made so the crew gave up after one of the firemen received minor burns. The crew with viscous water, using about the same application rate, took over and brought the fire under control in about four minutes. This type of operational test experience has been noted in various other reports. The Oregon Department of Forestry[3] in a series of tests found that viscous water appeared to be superior to plain water in speed of "knockdown" and cooling of the fire under various burning conditions with a variety of fuels.

Extinguishment Time

Small fire tests were conducted on cribs consisting of eight pieces of California clear pine as described previously. The viscous water was applied at a rate of one GPM after a preburn time of four minutes. The extinguishment time decreases as the viscosity is increased. Figure 5 illustrates this effect for two different viscosity additives, Monsanto DX–840–91 and bentonite clay, Volclay.[4] Volclay reaches its peak of effectiveness at a viscosity of five centipoises, while Monsanto DX–840–91 reaches its peak at ten centipoises. The reason for this difference is not fully explainable.

Larger-scale fire tests were run as previously described. The results[5] of a series of tests comparing extinguishment time for water and for viscous water, obtained from the addition of Dow ET–460–4 are shown in Figure 6. Certain uncontrollable variables, such as the chemical and physical properties of the wood and the difficulty of obtaining a perfectly reproducible test fire, cause a scattering of the data. However, it can be seen clearly that the use of viscous water gives a marked reduction in extinguishment time when plotted as a function of minutes of preburn time. For example, at a preburn time of four minutes, water took about eight minutes for complete extinguishment, while viscous water (5.5 cp) averaged about 1¾ minutes. With water, the wooden crib collapsed during extinguishment for preburn times of more than five to six minutes. On the other hand with viscous water, extinguishment was so rapid that it was possible to use preburn times of as much as nine minutes, with no structure collapse. Other additives for increasing viscosity, e.g., sodium alginates, have been tested in the laboratory with results of the same order of magnitude.

The results on extinguishment time for Dow ET–460–4, carboxymethyl cellulose (CMC), and water are shown in Figure 7, with preburn time as a parameter. Each viscosity additive reduces extinguishment time, although at the same viscosity Dow ET–460–4 appears to be more effective than CMC. As shown earlier, there appear to be differences between inspissators as regards extinguishment time, even when applied at the same viscosities. This difference in effectiveness has not been fully investigated or explained.

It was noted that high molecular weight thickening agents appeared to be more effective in controlled laboratory fire tests than lower molecular weight materials. Table 1 shows the results of a series of laboratory fire tests with two different molecular weights of the same chemical monomer. The range of 5 to 10 million molecular weight at a viscosity of about 5.5 to 6 with a preburn time of four minutes, was much more effective than 400,000 molecular weight.

It was surmised that there might be a difference in effectiveness between different salts of the same inspissator at the same viscosity. Both the ammonium and potassium salts of Dow ET–460–4 were used in laboratory fire tests at 5.5 cp for various preburn times. These results are shown in Table 2. It can be seen that there are no significantly measurable differences in the extinguishment times for the various preburn times.

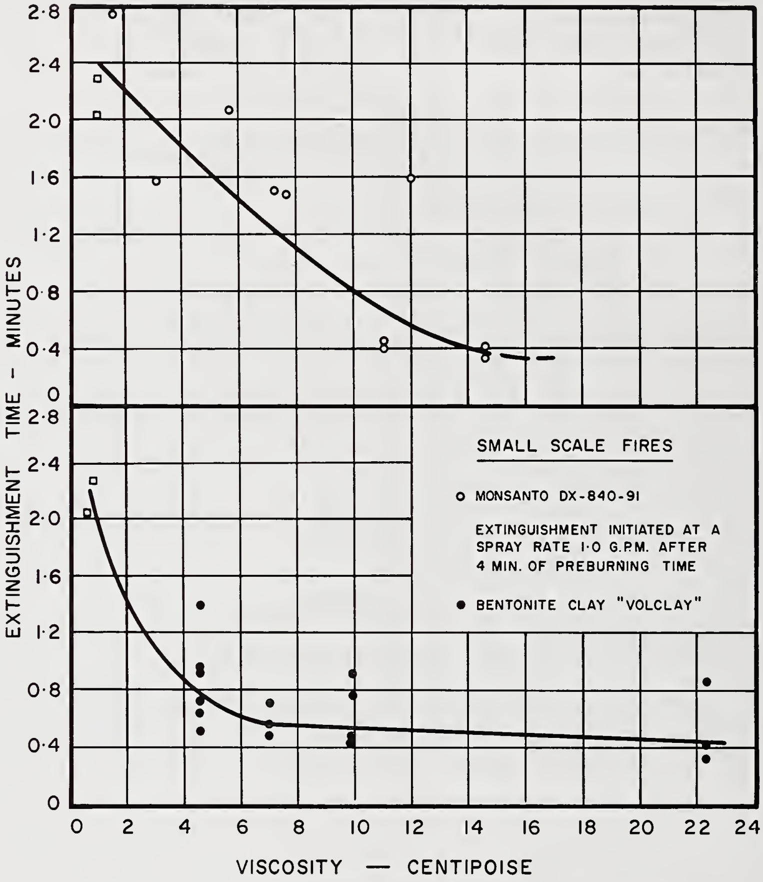

Figure 5. Extinguishment time vs preburn time.

Measurement of viscosity on various thickened solutions over a period of mixing or recycling showed that many thickeners are shear sensitive, with a consequent loss of viscosity as a function of time. This is a problem which users of thickening agents for fire fighting must face unless manufacturers can overcome it. A recently developed Dow viscosity additive, ET–570, has shown good results in laboratory fire tests and is less shear sensitive.

Field fire tests at the Navy Fire School in Norfolk, Virginia have confirmed the fact that there is a reduction in extinguishment time when viscous water

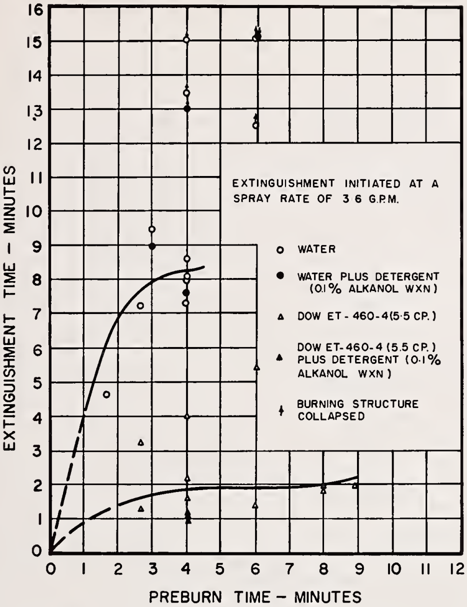

Figure 6. Extinguishment time vs preburn time.

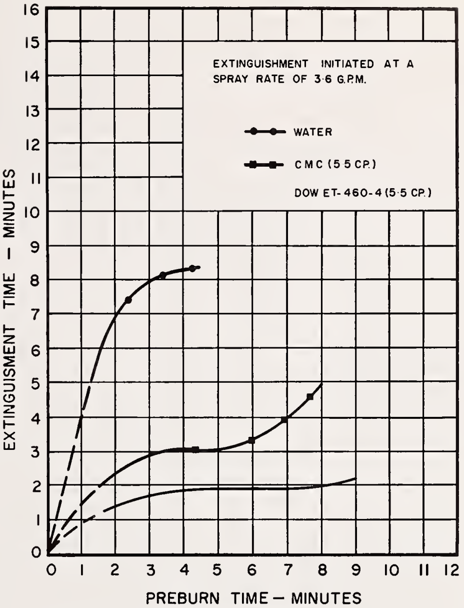

Figure 7. Extinguishment time vs preburn time.

is used. The percentage reduction is not as spectacular as in the laboratory. Control and reproducibility of open field fires are much more difficult and scatter of data is much wider. The most recent series of tests at Norfolk on new cribs constructed of 2″ x 4″ lumber gave about 40 per cent reduction in "knockdown" time, and about 52 per cent reduction in flame-out time for viscous water (52 cp)

TABLE 1

LABORATORY FIRE TESTS—EFFECTS OF MOLECULAR WEIGHT

Molecular Weight	Viscosity cp.	Preburn Time—Minutes	Initial Extinguishment Time—Minutes	Remarks
5,000,000	5.5	4	1.45	No reignition
to		4	1.89	No reignition
10,000,000				
		6	3.3	Reignited three times
		6	1.45	No reignition
		8	1.86	Reignited three times
		8	1.80	" " "
		9	2.06	Reignited twice
400,000	4.7	4	7.00	Reignited once
	6.1	4	4.75	" "
	10	6	2.90	No reignition
	8	6	4.70	Reignited twice
	8	8	6.75	Reignited once
	8	8	4.55	Reignited twice

TABLE 2

LABORATORY FIRE TESTS—EFFECTS OF SALTS

Solution	Viscosity cp.	Preburn Time Minutes	Initial Extinguishment Time—Minutes	Remarks
Dow ET–460–4	5.5	4	1.45	No reignition
(Amonium Salt)	5.5	4	1.17	Reignited once
	5.5	4	1.89	No reignition
	5.5	6	3.3	Reignited three times
	5.5	6	1.45	No reignition
	5.5	8	1.86	Reignited three times
	5.5	8	1.80	Reignited three times
	5.5	8	2.06	Reignited twice
Dow ET–460–4	5.5	4	1.65	No reignition
(Potassium Salt)	5.5	4	1.60	" "
	5.5	6	1.70	" "
	5.5	6	2.05	" "
	5.5	8	1.85	Reignited once
	5.5	8	2.85	" "

over plain water. The results are shown in Table 3 and Figure 8. Even though there was only 28 per cent reduction in total extinguishment at 52 cp viscous water over plain water, there was no rekindling or reignition. In fighting these crib fires, it was necessary for the nozzleman to place his nozzle in almost every opening for final mopup. It is believed that some of the effectiveness of viscous water is obscured by this necessary technique of fighting these crib fires. In the laboratory fire tests with spray heads the possibility of utilizing viscous water in sprinkler systems has also been demonstrated.

The most recent series of field fire tests was run with the help of the volunteer fire departments in Onondaga County, New York. Five rooms were constructed of lumber. Each room was 8′ x 8′ x 8′ with an opening about the size of a door on one side. Two rooms were made of old well-dried lumber and three of new rough hemlock, which was not kiln-dried. Representative results were obtained on the two rooms made of old lumber, and are shown in Table 4.

The tests on these two buildings indicated almost 50 per cent reduction in "knockdown" time and flame extinguishment for 15.5 cp viscous water over plain water.

Based upon laboratory results, fire-fighting agencies in California and Nevada pooled their efforts in 1960 to conduct a series of suppression and retardant tests to determine whether chemical additives could be used to help control forest fires

TABLE 3

FIELD FIRE TESTS (NORFOLK, VIRGINIA)

Solution	Viscosity	"Knockdown" Time—Minutes	Flame Extinguishment Time—Minutes	Total Extinguishment Time—Minutes
Water	1	1.75	2.20	3.88
Water	1	0.75	3.05	3.85
ET–570	19.5	0.70	1.55	2.55
ET–570	52	0.75	1.25	2.95

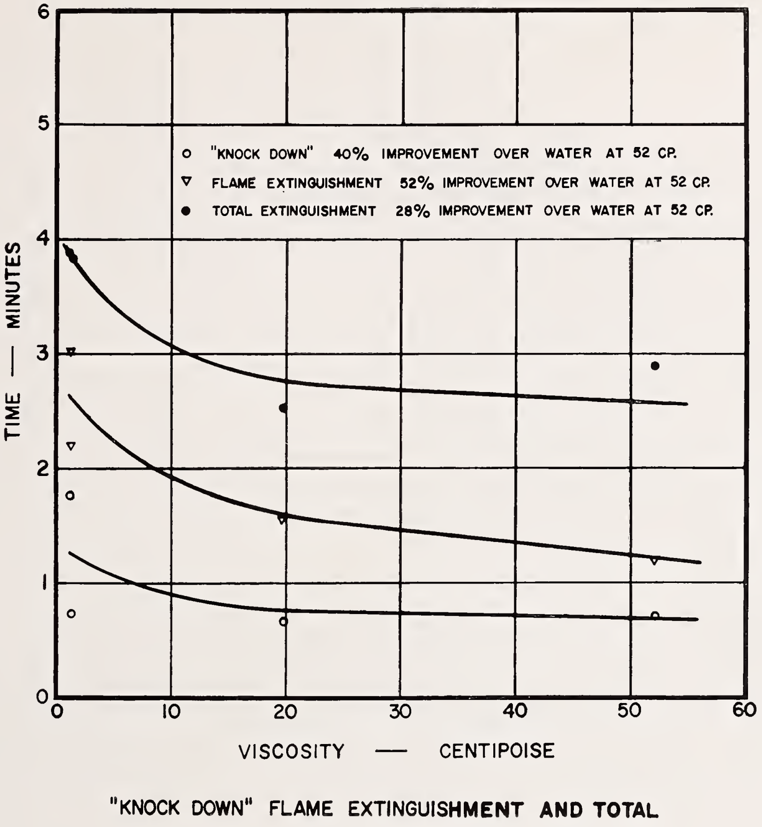

Figure 8. "Knockdown" flame extinguishment and total extinguishment time of field fire tests (Norfolk, Va.).

with ground equipment. A report[6] on this effort from the U. S. Department of Agriculture, Forest Service, Division of Forest Fire Research states: "Viscous water reduced suppression time under many conditions and was outstanding in keeping fires from rekindling. The residual film of algin-thickened water seemed to be particularly effective in extinguishing usually difficult-to-extinguish fires

TABLE 4

FIELD FIRE TESTS (ONONDAGA COUNTY, NEW YORK)

	Water	Viscous Water, Dow ET-570, 15.5 cp.
Preburn time, Minutes	3	3
Nozzle Flow, GPM	20	20
Knockdown Time, Minutes		
Outside of Building	1.75	0.9
Inside of Building	2.75	1.4
Flame Extinguishment, Minutes	5.5	3.0

in fuels such as baled hay and sawdust. Although there were operational difficulties such as spoilage and slight corrosion of metal parts, most problems can be solved. The dry powder that makes the water thick can be mixed on the fireline in one to five minutes using the jet-type mixer which is easily installed on the truck."

A very pertinent comment[7] on the use of CMC-thickened water as a fire retardant was made by the State Forest Ranger in charge of tests on forest fires during the summer of 1960. He stated: "CMC retards the rekindling of a fire and it is possible to prelay a wet lane with much less chance of losing the fire than if plain water is used."

Operational tests with 50 to 60 fire trucks were continued on forest-fire control in California, Nevada, and Oregon during the summer of 1961. Carl C. Wilson[8–10] reports the following results to date: "Recently three fire trucks, one of which contained viscous water, were dispatched to a burning dump. The two trucks using plain water made little headway because of continual rekindles deep within the dump. The viscous water crew (obviously well trained in mopup) used an applicator nozzle which they stuck down into the burning refuse and made excellent progress. The other two crews backed off, and the fire became a mopup demonstration with the use of viscous water. Eventually, one of the two water trucks was filled with viscous water and the control job completed . . . Our viscous water reports are coming in regularly now that our fire season is in full swing. So far, they are continuing to be almost 90 per cent favorable. . . . The hotter the fire the greater the advantage of viscous water appears to be. So far, about the hottest fire we have had involved a truckload of creosoted poles and pilings. Two fire trucks with plain water arrived first and had little if any effect on the fire. A short time later the viscous water truck arrived and had the fire under control within two or three minutes. In this case viscous water was many times more effective than plain water."

Reignition

A common problem in Class A fire fighting is reignition of the fire due to the residual heat after it has been extinguished. Many such experiences have been presented in fire-fighting annals. One of the outstanding characteristics of viscous water extinguishment is the almost universal lack of reignition after the fire is "out." This has been evident in controlled laboratory test fires. A large number of detailed tests have been reported[5, 11] which show that fires extinguished with water reignited after initial extinguishment from one to four times, while most of the comparable fires extinguished with viscous water did not reignite. It was also evident that water-extinguished fires retained much more residual heat, necessary for reignition, than viscous-water-extinguished fires.

Comparable results on reignition have been observed in various field fire tests at Norfolk and at Mariposa Airport, California. Reignition occurs at times even with extinguishment with viscous water; however, it is much delayed and is more easily controlled. Davis[12] stated in regard to the Mariposa Airport tests: "The chemicals also had a noticeable effect on rekindling of the charred cribs that remained after the initial suppression. Although cribs sprayed with viscous chemicals did reignite, rekindling was slower in starting and cribs that rekindled burned at a lower rate than those sprayed with water." The Oregon

Department of Forestry[3] also observed that viscous water appears to slow the rekindling processes that might otherwise take place if plain water were used.

Reduced Water Consumption

In many laboratory tests it has been shown that the rate of extinguishment with viscous water is many times greater than with plain water. This means that a given fire can be fought with reduced water consumption since the water actually used is much more effective. While in many parts of the world water is available in unlimited quantities for fighting fires, there are many places on the globe where water is very scarce. A good example is Southern California.

Where fires need to be fought in isolated places and all fire-fighting water must be brought in by trucks, it becomes gravely important to utilize fully every gallon of water. If one assumes a fivefold increase in rate of extinguishment for viscous water, it is easy to see that one tank truck of viscous water can control as much fire as five tank trucks of plain water. It should be emphasized here that on the average a fivefold increase has been reproducibly achieved in laboratory fire tests but not in field fire tests under less controlled conditions. A 30 to 50 per cent reduction in water use is more common in field fire tests to date.

Reduced "Runoff"

An obvious disadvantage of poor utilization of water is the rapid "runoff" so that only a portion of the water is effective. A large number of laboratory fire tests have shown that viscous water is more effectively used for extinguishment. A group[5] of comparative tests were run to check this point under controlled conditions. Plain water, applied at a rate of 3.6 GPM, averaged three pounds per minute of "runoff"; for CMC at a viscosity of 5.5 cp, the "runoff" was only 1.5 pounds per minute; and for Dow ET–460–4 the rate was less than 1 pound per minute of 5.5 centipoise viscous water.

A corollary to the more effective use of viscous water is the reduced water damage to structures, contents, and adjoining facilities. One recalls the large fire several years ago in lower New York, in which the old Wanamaker store building was destroyed, but, does one recall that the adjacent subways were flooded out of service for many hours? Frequently, firemen complain that water damage to the contents of a structure is as great as the fire damage and that salvage of contents from such water damage is often very difficult.

Logistics of Chemical Additives

The amount of chemical additives required to achieve an optimum viscosity of water for fire fighting varies with the characteristics of the chemical. Satisfactory viscosity usually can be achieved with less than 0.2 per cent of a chemical additive. This percentage would require about 16 pounds for treatment of 1,000 gallons of water.

Some of the chemical additives are only in pilot production, so that costs per pound are not firm. Others, such as CMC and Keltex FF, are in full production. At a price of $0.50 to $1.00 per pound for chemical additives, it would cost between one and two cents per gallon to raise the viscosity of the water to a satisfactory point. This would not be considered prohibitive under many conditions of fire fighting and control. Davis and Phillips [6] state that for fighting forest fires even a higher cost per gallon for chemical additives is not prohibitive. "The price per gallon is reasonable for all of these chemicals, only 3 to 14 cents per gallon."

Conclusions

1) Viscous water produces much more rapid initial control of Class A fires.
2) The rate of extinguishment of Class A fires is more rapid with viscous water.
3) The danger of reignition is markedly reduced when Class A fires are extinguished with viscous water.
4) A smaller amount of viscous water is required for extinguishment of Class A fires.
5. Reduced "runoff" of viscous water gives better utilization for fire control and minimizes water damage.
6) The logistics of chemical additives for fire fighting is economical.

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Flammability of Methane-Air Mixtures in Water-Base Foams

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Abstract

A method of preparing a water-base foam, of controlled wetness and bubble size, containing flammable methane-air mixtures as the gas phase, is described. Effects of the two foam properties on the limits of flammability of the gas mixture in the foam have been measured, using a horizontal flammability tube. These effects appear to be explicable in terms of two controlling processes: (1) in dry foams, the formation of water droplets from the bubble walls and their vaporization by heat transfer ahead of the advancing flame; (2) in wet foams, the ability of the flame to break through the bubble walls, in consequence of heat transfer from the flame to the walls and the lowering of surface tension of the latter.

This investigation forms one of a series of studies of flame-propagation phenomena in two-phase systems, in which the gas phase is accompanied by a physically distributed liquid phase—for example, as spray, foam, or film—which participates, either as fuel or suppressant in the process of flame propagation. In the present instance, the object was to examine the extent to which the range of flammability of methane-air mixtures is influenced when the mixture is included in water-base foams of defined properties. The foam properties considered were bubble size and wetness. The method of foam preparation aimed at uniformity of bubble size in each foam, but the widest possible variation in different cases. Wetness was defined by an inverse function, expansion ratio, which was taken to be the ratio of the volume of a certain quantity of foam to the volume of its liquid content.

So far as we are aware, the only previous study of a similar nature consisted of a limited number of experiments (as yet unpublished) carried out at the Safety in Mines Research Establishment, Buxton, England, where the matter first came to our attention. The influence of water *vapour* upon the flammability range of methane in air has been studied by Coward and Gleadall[1] and by Yeaw and Shnidman.[2] Billett[3] has examined the effect of water spray on the inflammability of butane in air.

Apparatus and Methods

A continuous-flow system was employed to prepare methane-air mixtures and to incorporate them in water-base foams of controlled bubble size and expansion ratio. Figure 1 shows a diagram of the arrangements.

Air and methane from compressed gas cylinders were passed through drying towers, flow control valves, and orifice flow meters before mixing. The mixture passed through a water saturator, followed by a capillary to smooth bubbling pulsations before entering the foam generator (Figure 2). In this, the mixture bubbled through a copper gauze, submerged at a controlled depth in a solution of a foaming agent. The uniform-sized apertures in the gauze gave rise to bubbles of uniform size which, at the surface of the solution formed foam, also of reasonably uniform bubble size. The foam ascended a polystyrene drainage column of controllable height, before turning into the horizontal flammability testing tube. This consisted of a perspex tube, 2¾ in. internal diameter and some 4 ft long, which was continuously rotated about its axis, so as to minimize drainage from the foam while travelling along it. Foam emerging from the open end of the tube fell into an open waste receiver.

Inflammability of the foam in the tube could be tested at any time by applying a one-inch coal gas flame to the open end to see whether or not flame would propagate throughout the contents of the tube. The products of propagation, if any, were swept out by the oncoming foam in readiness for another test. The rate of flow of foam along the tube did not exceed 1 cm/sec whereas the minimum rate of flame propagation was 12 cm/sec. The flow of foam did not, therefore, interfere with flammability testing.

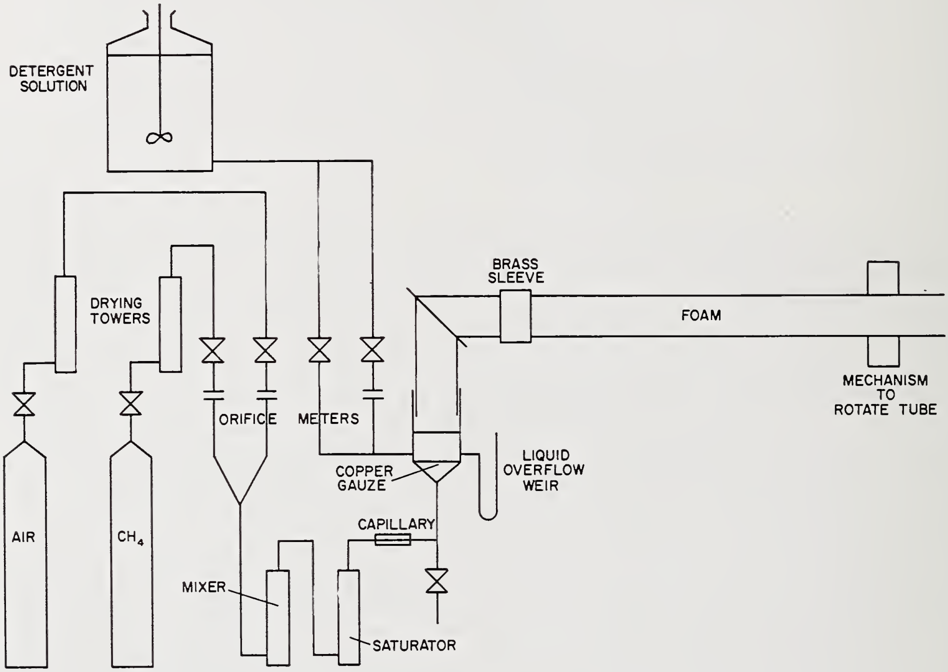

Figure 1. Diagram of apparatus.

The foam properties were measured on samples emerging from the end of the tube. Expansion ratio was measured by allowing a known volume of foam to fall into a measuring vessel containing a layer of hexanol as separable foam-breaker, and by measuring the volume of the aqueous liquid formed. Bubble size was measured by allowing the foam to fall into a flat-bottomed polystyrene receiver containing a thin layer of the detergent solution. The foam was photographed through the bottom of this receiver, which was inscribed with a cm scale, and after suitable enlargement of the plate, the mean diameter of some 250 bubbles was found by measurement. Figure 3 shows a typical histogram of a foam.

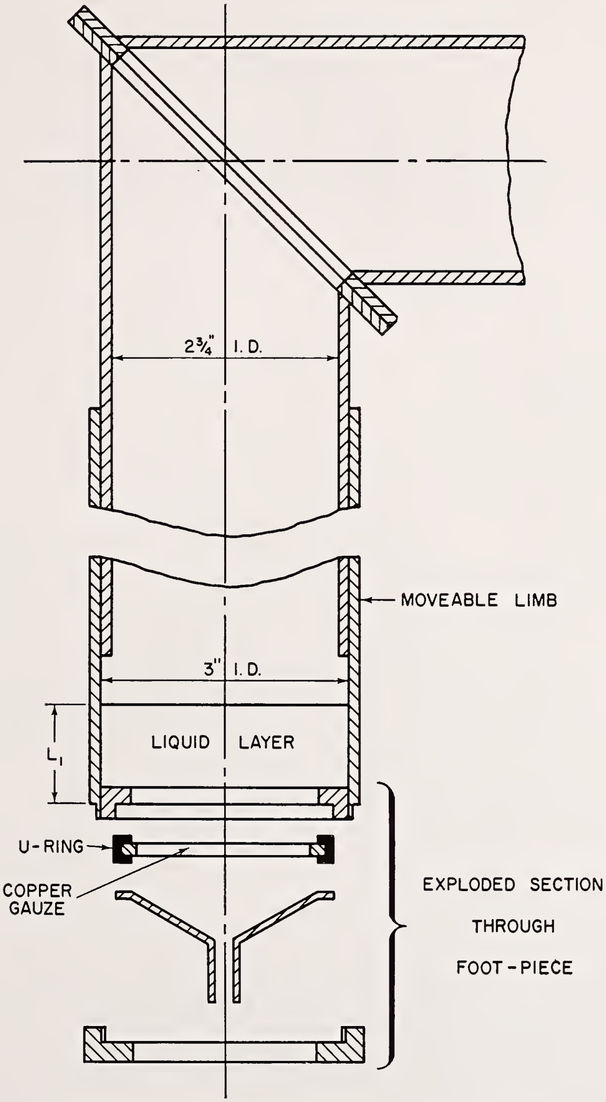

Figure 2. Section of foam generator.

The detergent solution consisted of a 1% solution, in distilled water, of "Perlankrol" (Lankro Chemicals Ltd., Eccles, Manchester, England) and had a surface tension of 26.3 dynes/cm at 20°C, as measured by the capillary-rise method.

The expansion ratio of the foam could be controlled by the gas flow (bubbling) rate and also by varying the height of the foam drainage column. Bubble size was primarily controlled by the mesh of the copper gauze through which bubbling took place, but was also influenced by the gas flow rate. Approximate ranges of variation available for satisfactory use were: expansion ratio 20 to 1500; bubble diameter 1 to 4.5 mm.

The method of conducting an experiment was as follows. With a gauze appropriate to the bubble size required, the air flow was adjusted to give approximately the desired expansion ratio. Methane was then added to the gas stream and its flow rate adjusted to give a limit mixture in the foam, as judged by repeated flammability tests. Samples of foam were then taken for measurement of properties and these were recorded against the limit gas mixture composition as determined from the flow meter readings.

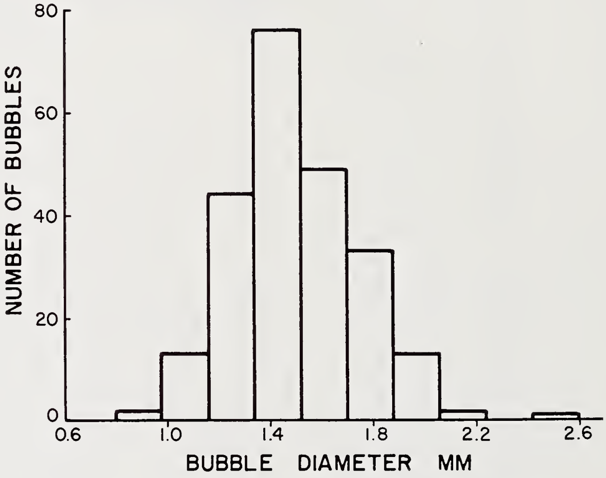

Figure 3. Typical size histogram of foam.

Results

Control of foam properties

Bubble size of the foam was primarily controlled by the sizes of apertures in the gauzes used for dispersing the gas flow beneath the surface of the foaming agent solution. Information on the relation between mesh of gauze and bubble size will be given with the results of flammability measurements.

In addition, effects upon foam properties of the following factors were studied systematically:

1) gas-mixture flow rate (Q ml/min),
2) depth of submergence of gauze in solution (L_1 cm),
3) drainage volume, i.e., height of vertical limb above solution surface.

Gas flow rate influences both expansion ratio R and bubble size d. Figure 4 shows the effect upon expansion ratio, using a 100 mesh gauze and two solution depths, 3 and 9 cm. Over a considerable range,

$$R = KQ^{-1.60}$$

where K is a constant dependent upon depth.

Increasing gas flow rate had a small lowering effect upon bubble size. Thus with a 100-mesh gauze, the mean bubble diameter fell from 1.46 mm at 500 ml/min to 1.30 mm at 2000 ml/min.

Solution depth (L_1) had only a small effect on foam properties. Both expansion ratio and mean bubble size decreased slowly with increasing depth.

Drainage height (L_2) influenced the foam after production and was therefore without effect on bubble size. The expansion ratio, however, increased with increasing drainage height at a slightly accelerating rate. The results were correlated with those on the effect of gas flow rate on R, by calculating residence times (t_0) of the foam in the drainage volume in each series. The relations between t_0 and log R are plotted in Figure 5 and are seen to be coincident for each solution depth (3 and 9 cm). It appears, therefore, that the effect of gas flow rate upon the expansion ratio is almost entirely explicable in terms of its effect upon the time allowed for drainage following foam production.

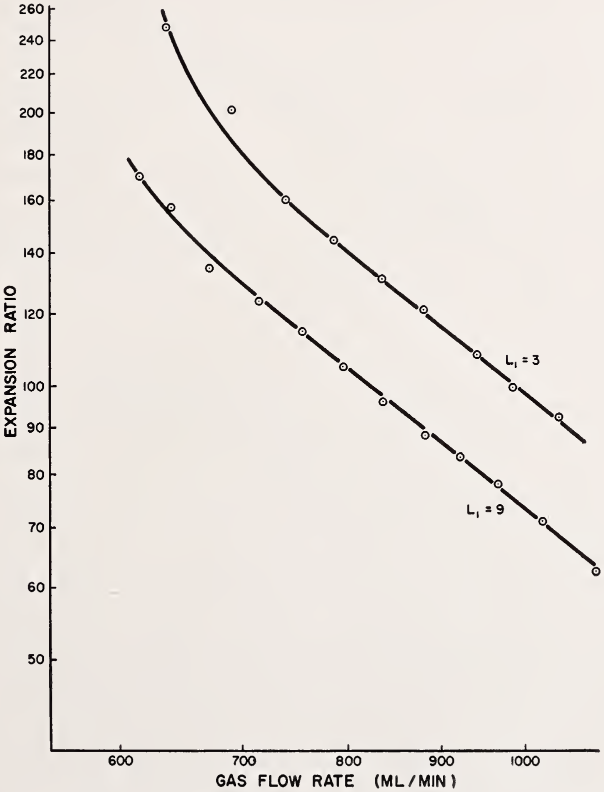

Figure 4. Effect of gas flow rate on expansion ratio of foam.

Flammability Limits

In the absence of any foam, the flammability limits of methane in air in the dry, horizontal tube were 5.41 and 13.94 vol%. In the presence of foam,

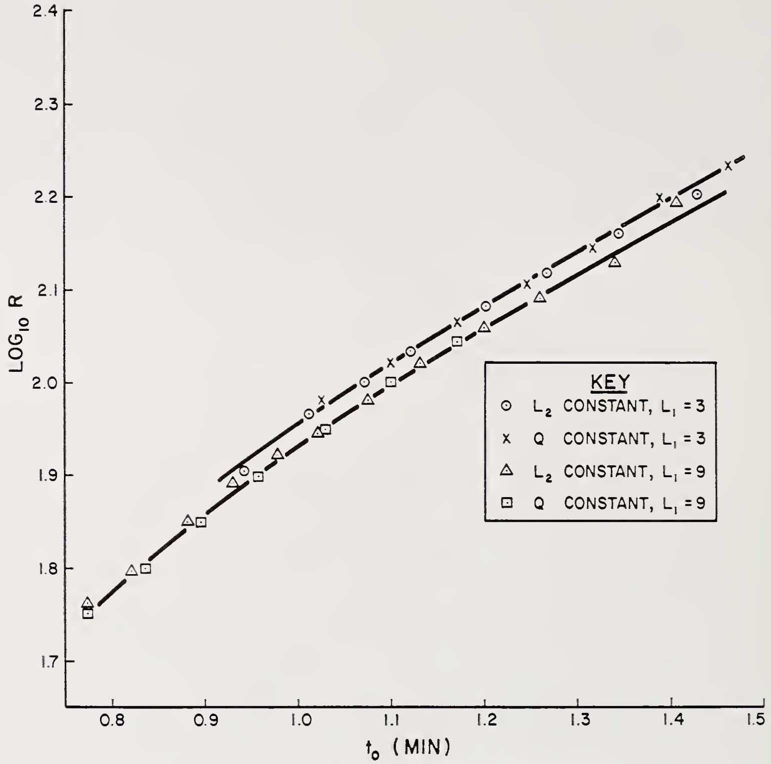

Figure 5. Effect of drainage time on expansion ratio of foam.

the range of flammability was narrowed to varying degrees depending upon foam properties. The results as a whole are shown in Figure 6, in which limit values are plotted against logarithm of expansion ratio, for several series of experiments in which gauzes having different mesh apertures were employed in the foam generator. For each series, the expansion ratio was varied chiefly by varying the total gas flow rate through the generator. Increasing flow rates led to decreasing expansion ratios accompanied by a small decrease in bubble size. The following table provides a key to Figure 6 and shows the range of bubble diameters, as well as mean values, for each series.

Type of Point	Mesh Size Used	Bubble Diameter (mm) At Highest Expansion Ratios *	Bubble Diameter (mm) At Lowest Expansion Ratios *	Mean Bubble Diameter
△	150	1.20 (180)	1.05 (20)	1.1
⊡	100	1.50 (250)	1.28 (22)	1.4
⊙	72	1.82 (878)	1.51 (37.8)	1.7
X	60	2.14 (1490)	1.94 (44.7)	2.0
▽	52	2.52 (1337)	2.40 (73.7)	2.5
+	44	2.77 (1249)	2.66 (78.8)	2.7
◊	36	3.00 (1478)	2.88 (87.8)	2.9
⌖	perforated plate	4.60 (1500)	4.45 (219)	4.5

* Corresponding expansion ratios given in brackets.

The effects of varying expansion ratio R upon the two limits of flammability were generally symmetrical, but otherwise rather complex. They may be summarized as follows:

(1) For value of R between 1500 (the highest used) and about 300, the flammable region narrowed progressively with decreasing R (i.e., increasing wetness), and at 300–250 reached a minimum. With the driest foams, bubble size had little effect on the limits, but the effect increased progressively with decreasing R, the flammable region being narrowest for smaller bubble sizes. With mean bubble diameters below 1.7 mm flammability was completely suppressed in the region R = 200–250.

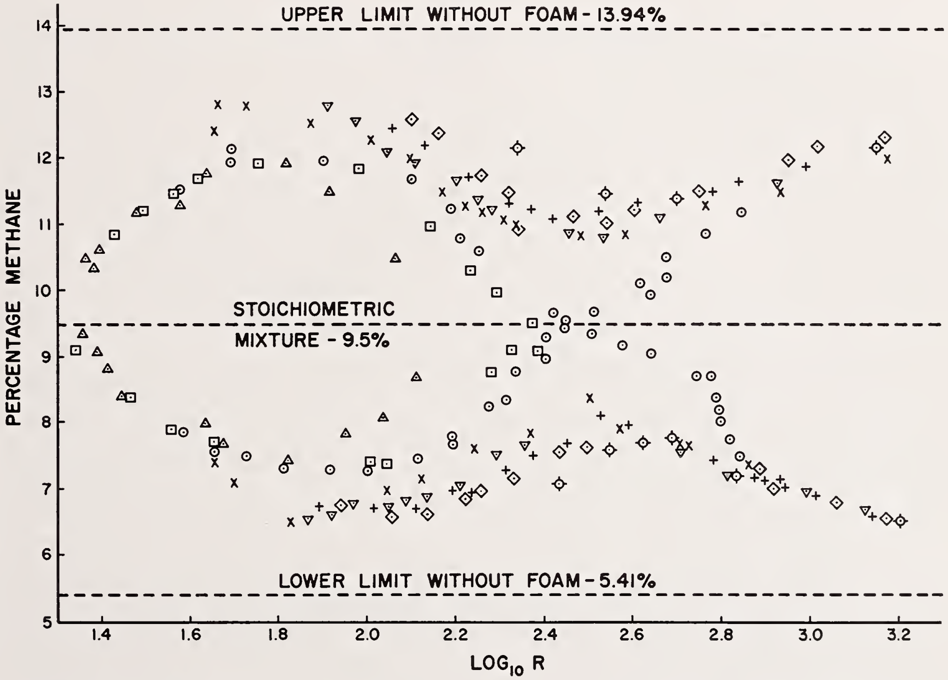

Figure 6. Effect of expansion ratio (and bubble size) of foam on limits of flammability of methane in air.

(2) For values of R between 300 and 70, the flammable region widened again, being still narrowed however by decreasing bubble size.

(3) For values of R below 70, the flammable region was narrowed with increasing wetness of the foam and the bubble size effect diminished. At about R = 20, flame propagation ceased, apparently irrespective of bubble size.

In regions (1) and (2) the flame front was almost flat and vertical. With the driest foams in region (1), a definite gap appeared between the flame front and the collapsing foam ahead. In both regions spray arising from the collapsing foam could be seen in and near the flame front.

In region (3), the passage of the flame did not result in complete destruction of the foam. Kernels of flame travelled independently of one another, leaving behind considerable amounts of unconsumed foam.

A convincing demonstration of the existence of regions (1) and (2) could be provided by allowing an initially nonflammable foam of expansion ratio about 300, mean bubble size 1.50 mm containing a 9% methane-air mixture, to drain for about 20 sec by stopping the rotation of the tube, prior to ignition. The upper and lower halves of the foam could then be ignited separately and would propagate flame independently leaving unconsumed a central layer some 2 cm thick. Due to drainage, the upper and lower layers had moved respectively into Regions (1) (dry) and (2) (wet), leaving the central layer nonflammable between the two regions.

Discussion

The bubble sizes employed were mostly such that the diameters were below the minimum quenching diameter for methane/air mixtures (*ca.* 2.8 mm). Ignition of the foam would therefore presumably involve ignition of the contents of several bubbles at once. In dry foams, a nearly flat flame front spread along the tube, breaking foam ahead and forming water droplets in the path of the flame. It seems likely then, that in Region (1), flame was suppressed at the limits by premixed water vapour derived from the evaporation of droplets released ahead of the flame. However, the proportion of water present was in all cases well in excess of that required for suppression of premixed methane-air flames, and evidently vaporization and mixing of water ahead of the flame was never complete. With decreasing R however, the total proportion of water available increased and so limits were progressively narrowed.

Simultaneously, however, thickening films, due to increasing wetness, would lead to drop sizes becoming larger and the proportion of available water vaporized ahead of the flame becoming less. Ultimately this effect prevailed and the flammable range widened again—Region (2). At this point, since diminishing bubble size at constant wetness would result in thinner films and hence smaller drops, smaller bubbles were associated with greater suppression.

In Region (2), drop formation ahead of the flame finally ceased; the flame evidently experienced increasing difficulty in breaking through the thickening bubble walls. This would lead again to suppression of flammability—Region (3). The flame tended to pursue a tortuous path through the now very wet foam, presumably preferring those regions where the bubble walls were slightly less thick than elsewhere.

In Regions (2) and (3), it may be suggested that the controlling process in flame propagation is the transfer of heat from the flame to the bubble wall, whereby the surface temperature of the latter is reduced to a certain value. The requisite heat flux would be proportional to the wetness, i.e., to liquid volume/foam volume, or 1/R, irrespective of bubble size. Hence the lack of bubble size effect.

In Regions (1) and (2) on the other hand, the controlling factor should be the rate of heat transfer to (and hence vaporization of) the droplets ahead of the flame. This would be proportional to total droplet surface area and hence to total film area, which is proportional to R/d. That this is confirmed by the results is shown in Figure 7 where limits in Region (2) and the transition from Region (1) are plotted on a base of R/d instead of R, giving a common curve for the various bubble diameters.

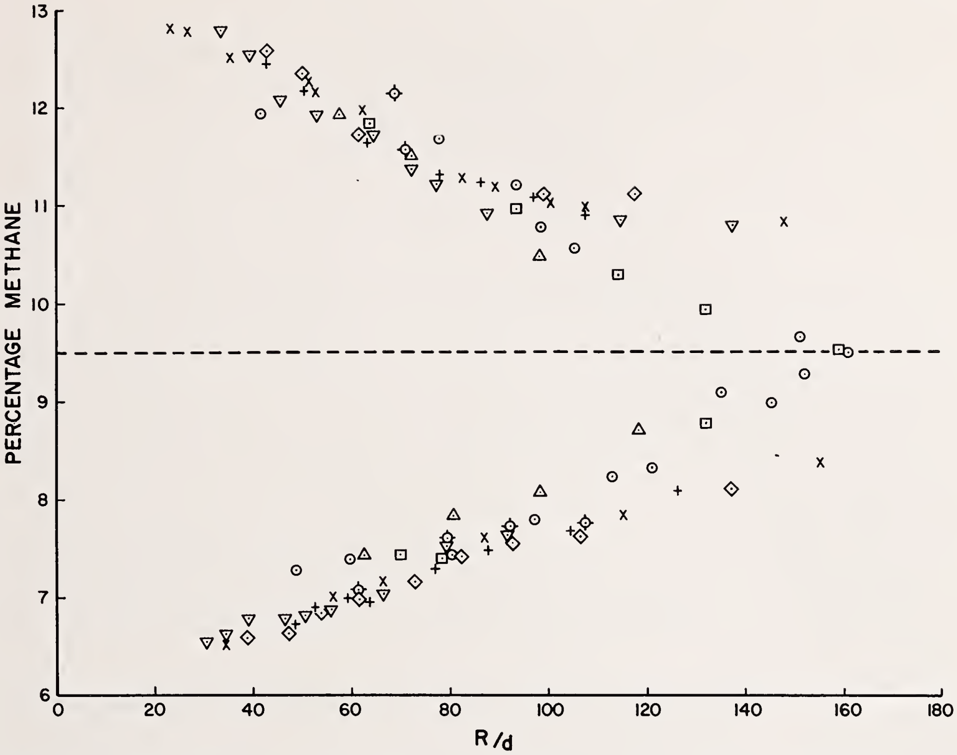

Figure 7. Variation of limits with R/d in Region (2). (Point symbols as in Figure 6.)

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Thermogravimetric and Differential Thermal Analysis of Wood and of Wood Treated with Inorganic Salts During Pyrolysis

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Burning of wood is preceded by pyrolysis to form gases and vapors and a solid residue of charcoal; some of the gases and vapors can burn in flames when mixed with air, and the charcoal can burn in air by glowing without flame. Empirically it has long been known that flaming combustion can be retarded by impregnating wood with suitable materials, such as certain inorganic salts. Although a number of theories of flame-retardant action have been proposed,[6] the mechanism of wood's combustion and the effect of chemical treatment on it remain uncertain. It appears most likely that the best flame retardants act by altering favorably the preliminary step of wood pyrolysis.

The present research was undertaken to study the mechanism of wood pyrolysis and the effect of chemicals on it by the methods of thermogravimetric and of differential thermal analysis. Results so far indicate that the methods are promising but that much further work will be needed before their significance can be fully established.

In dynamic thermogravimetric analysis, wood samples were weighed and the weight recorded continuously and automatically as a function of the temperature attained by the sample while it was being heated in a stream of nitrogen with the temperature rising steadily at a linear rate. Such graphs disclosed the threshold temperature for active pyrolysis, the range of temperature within which most of the pyrolysis occurred, and the yield of char (or extent of volatilization) when pyrolysis was practically completed.

In static thermogravimetric analysis, the sample weight was recorded as a function of time at constant temperature at each of a series of temperatures from about the threshold for active pyrolysis to a temperature at which pyrolysis became inconveniently rapid. Such graphs served as a basis for calculating reaction-rate constants and activation energies for an early stage of pyrolysis. In differential thermal analysis, the difference in temperature between wood or treated wood and a reference material was recorded continuously as a function of the sample temperature while both sample and reference material were being heated with the furnace temperature rising steadily at a linear rate. Such graphs revealed the occurrence of endothermic or exothermic reactions at the various levels of temperature and a rough estimate of the relative extent of evolution or absorption of heat.

Apparatus

A thermogravimetric balance made by the American Instrument Company was used.[2] The sample to be pyrolyzed was suspended from a calibrated spring, within a glass enclosure that could either be evacuated or supplied with a gas flowing at a controlled rate. The lower portion of the glass enclosure, the reaction chamber, could be quickly encompassed by an electric furnace that was either preheated to a desired constant temperature or programmed to rise in temperature at a predetermined linear rate. Movement of the balance spring was picked up by a transducer and demodulator and the impulse transmitted to the y-axis of an x-y recorder. The x-axis could be set to record the temperature attained by the sample as measured by a thermocouple located about 5 millimeters below the sample in the reaction chamber; or, by the flick of a switch, the x-axis could be set to record time instead of temperature. When the x-axis was set to record temperature, there was provision also for a discontinuous record of time in the form of pips scribed in the curve at intervals of 1, 5, or 20 minutes.

By a simple modification, the thermogravimetric balance was adapted for differential thermal analysis. A switch was provided to disconnect the impulse from the transducer and demodulator of the weighing system and to substitute for it the input from a differential thermocouple, with one junction in the sample and the other junction in a reference material. Sample and reference material were contained each in its own glass tube with stopper carrying a thermocouple well and inlet and outlet tubes through which either vacuum or a stream of nitrogen could be applied. The nitrogen entered the tube through a glass sleeve at a point slightly above the level of the sample or reference material and was discharged, together with any volatile products, from the top of the tube. Sample tube and reference tube slipped into wells drilled in a metal cylinder, which in turn fitted into the cylindrical chamber of the electric furnace of the thermogravimetric balance, now having become a differential thermal balance.

Preparation of Samples

The size and shape of wood samples may affect the rate of pyrolysis and the yield of products because the diffusion of heat into the interior of the sample and the escape of volatile products from the interior enter into the over-all process. Within thick samples, the temperature at any instant varies more than in thin samples; the yield of char is greater for thick than for thin samples because volatile products formed at first undergo secondary pyrolysis, yielding tar coke to add to the wood charcoal if the volatile products cannot escape fast enough. When delayed escape of volatile products is significant, pyrolysis in vacuum proceeds faster and yields less char than pyrolysis at atmospheric pressure.

Since the present purpose was to study as nearly as possible the initial stage in pyrolysis, it was necessary to minimize the effects of diffusion of heat and volatile products. Use of veneer (shavings) 0.16 millimeter thick, cut from green or resoaked wood with a tool designed especially for the purpose, accomplished the objective remarkably well. This is demonstrated in Figure 1, in which the curve for dynamic thermogravimetric analysis in nitrogen at atmospheric pressure nearly coincides with a curve for pyrolysis in vacuum. Similar experiments with samples in the form of dowls about 1 centimeter in diameter showed that in nitrogen the pyrolysis proceeded much less rapidly, and the yield of char at the end of active pyrolysis was much greater than in vacuum.

Ponderosa pine sapwood samples, 0.16 by 46 by 77 millimeters, were used for most of the tests so far. Samples were conditioned at 27°C and 30 per cent relative humidity. Those to be impregnated with a salt were immersed in aqueous solution of suitable concentration to provide the desired degree of treatment, evacuated for 30 minutes, left immersed at atmospheric pressure for approximately 2 hours, removed, wiped to remove excess solution, dried, and conditioned at 27°C and 30 per cent relative humidity. The quantity of salt retained by the wood was calculated as the difference between the equilibrium weights before and after treatment, corrected for a loss of approximately 1.5 per cent of water-soluble components of the wood to the treating solution, as determined by similarly impregnating matched wood specimens with distilled water and reconditioning them.

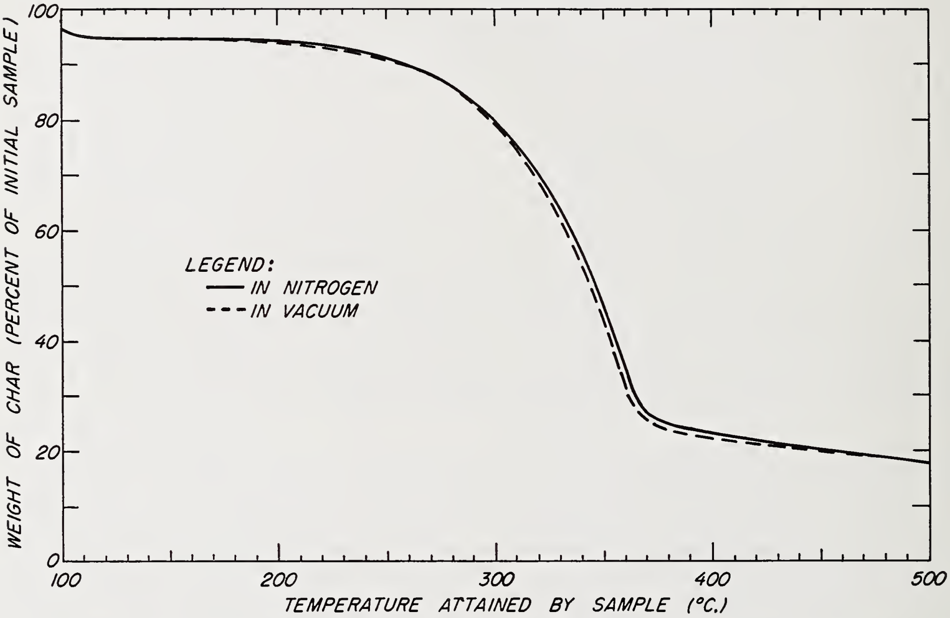

Figure 1. Close agreement between curves for dynamic thermogravimetric analysis of thin veneer (0.16 mm thick) in nitrogen flowing at 2 liters/minute at atmospheric pressure and in vacuum of 10 mm Hg absolute.

For differential thermal analysis, ponderosa pine sapwood was ground to particles less than 0.25 millimeter in diameter. Samples to be treated were placed on a glass filter, repeatedly washed with aqueous solution with the aid of suction, drained with suction for about 30 minutes, dried, and conditioned at 27°C and 30 per cent relative humidity.

Inorganic Salts Tested

Tests so far have been made with the inorganic salts listed in Table 1, together with the residual weight left at 200, 250, and 400°C, respectively, when a sample of the salt was subjected to dynamic thermogravimetric analysis under the conditions described farther on for examination of wood treated with the salt.

Data in handbooks state that those of the salts that contain water of crystallization lose it before the temperature reaches 200°C. The ammonium phosphates and ammonium chloride begin to decompose before they reach a melting point. Ammonium sulfamate melts at 132.9°C and begins to decompose to ammonia and sulfamic acid at 160°C. Ammonium sulfamate and ammonium chloride are distinctly volatile and sublime completely at temperatures well below 400°C. The four remaining salts do not melt, decompose, or sublime before reaching temperatures at which active pyrolysis of wood has been completed.

Hunt, Truax, and Harrison,[8] on the basis of laboratory tests by the fire-tube method, described the salts marked I in the last column of Table 1 as "chemicals that have a considerable effect in retarding flame in light absorptions and a marked effect in heavy absorptions." They did not test ammonium sulfamate, but subsequent tests at the Forest Products Laboratory place it in group I. Salts of group II were described as "chemicals that have a very minor effect in retarding flame in light absorptions but a marked effect in heavier absorptions," salts of group III as "chemicals that have a moderate effect in retarding flame when present in wood in large quantities," and salts of group IV as "chemicals that have a noticeable but not important effect in retarding flame even when present in wood in large amounts."

TABLE 1

SALTS USED TO TREAT WOOD SAMPLES

Salt	Residual Weight on Dynamic Thermogravimetric Analysis			Classification for Relative Flame Retardance
	At 200° C	At 250° C	At 400° C	
	Per cent	*Per cent*	*Per cent*	
Dibasic ammonium phosphate, $(NH_4)_2HPO_4$	97	88	71	I
Monobasic ammonium phosphate, $NH_4H_2PO_4$				I
Ammonium sulfamate, $NH_4SO_3NH_2$	94	91.5	0	I
Ammonium chloride, NH_4Cl	99	95	0	I
Sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$	52.8	52.8	52.8	I
Tribasic sodium phosphate, $Na_3PO_4 \cdot 12H_2O$	43.1	43.1	43.1	III
Potassium carbonate, $K_2CO_3 \cdot 1.5H_2O$	83.6	83.6	83.6	III
Sodium chloride, NaCl	100	100	100	IV

Experimental Procedure

For thermogravimetric analysis, a sample of 0.16 millimeter veneer weighing between 0.25 and 0.5 gram was suspended from the balance spring in a central position in the pyrolysis chamber. The y-axis of the recorder was so calibrated that the full weight of the sample just spanned 100 divisions of the graph paper, and the x-axis was set to span the range in sample temperature to be studied. The system was evacuated and then flushed with nitrogen three times to remove air with its oxygen from the sample and the pyrolysis chamber.

For dynamic thermogravimetry, the furnace, still unheated, was raised into position enclosing the pyrolysis chamber, heating was started at the programmed linear rate (usually 6°C a minute), flow of nitrogen through the system was established at the desired rate (usually 2 liters a minute), and the recording mechanism was set in motion. The recorder scribed the decrease in sample weight in per cent of its initial weight against the temperature attained by the sample and also indicated the lapse of time by pips scribed at 5-minute intervals.

For static thermogravimetry, the furnace was brought to a constant temperature selected in advance and was then raised to enclose the pyrolysis chamber. The recorder was set in motion when the furnace reached its position with the x-axis of the recorder charting sample temperature, together with 1-minute pips, until the constant furnace temperature was nearly reached (usually in 13 to 15 minutes), after which the x-axis was switched to record time instead of temperature.

For differential thermal analysis, the sample tube was packed with about 5 grams of groundwood and the reference tube was packed to an equal depth with aluminum oxide. Alternatively, for certain tests the sample tube contained chemically treated wood and the reference tube untreated but otherwise similar wood. With tubes in position, the furnace was set to rise in temperature at the rate of 12°C a minute until it reached 600°C. The recorder charted the difference in temperature between sample and reference material against the temperature attained by the sample.

Results by Dynamic Thermogravimetry

Figure 2 records the portion of the dynamic thermogravimetric curves between 130 and 400°C obtained for wood, lignin, and alpha-cellulose. The wood was ponderosa pine sapwood veneer 0.16 millimeter thick. The lignin was sulfuric acid lignin from aspen in the form of fine powder. The alpha-cellulose was from southern yellow pine in the form of a thin felted mass. The differences in origin and form of the samples do not impair qualitative comparison of the three materials in view of the great differences in the course of their pyrolyses.

The loss in weight of 5 per cent for cellulose and of 6 per cent for wood and lignin recorded at 200°C in Figure 2 had actually been attained already at 100°C and represented moisture in the samples initially. Further loss in weight attributable to pyrolysis began near 220°C for both wood and lignin, but not until 275°C for cellulose. On the other hand, pyrolysis of cellulose proceeded very rapidly as temperature rose still further, whereas the pyrolysis of lignin accelerated very slowly. Cellulose pyrolysis was essentially complete at 400°C with a yield of char of only 15 per cent, which decreased to 9 per cent at 800°C. Lignin at 400°C still was 70 per cent unvaporized and, at 800°C, was 45 per cent unvaporized.

The relatively sudden collapse of cellulose within a narrow range of temperature and the slower disintegration of lignin over a broad band of temperature perhaps are explicable from the nature of their macromolecules. Cellulose, as a repeating polymer of a single monomer of moderate size, may well follow a shorter and less involved path to complete pyrolysis than the more intricate macromolecule of lignin with its more varied constitution of aromatic nuclei connected by straight-chain links. The indication that the threshold temperature of pyrolysis is lower for lignin than for cellulose seems at first to conflict with much of the literature,[6] which holds that the hemicellulose in wood pyrolyzes most readily, the cellulose less so, and the lignin least readily; but the apparent conflict is easily reconciled, because only a small fraction of the lignin has been lost at temperatures at which the cellulose is already completely pyrolyzed.

Figures 3 and 4 present similar thermogravimetric curves for ponderosa pine treated with each of the salts listed in Table 1, except monobasic ammonium phosphate, which is omitted because its performance was almost identical with that of dibasic ammonium phosphate. It may be assumed reasonably that the loss in weight while the temperature rose to the neighborhood of 130°C came chiefly from loss of moisture. For untreated wood and for wood treated with anhydrous salts (the three ammonium salts and sodium chloride), the loss at 130°C was always 5 to 6 per cent. For wood treated with salts that may contain water of crystallization (sodium tetraborate, sodium phosphate, and potassium carbonate), the loss at 130°C exceeded 6 per cent, presumably by the amount of salt hydration. The moisture that, from such thin samples, was driven off completely at a temperature at which the wood had scarcely begun to pyrolyze could hardly have had any effect on the subsequent pyrolysis. Therefore, the curves for wood treated with the hydrous salts should be moved upward along the ordinates until the weight at 130°C coincides with that for untreated wood if the true effect of the hydrous salts on the thermographic curve for wood is to be revealed.

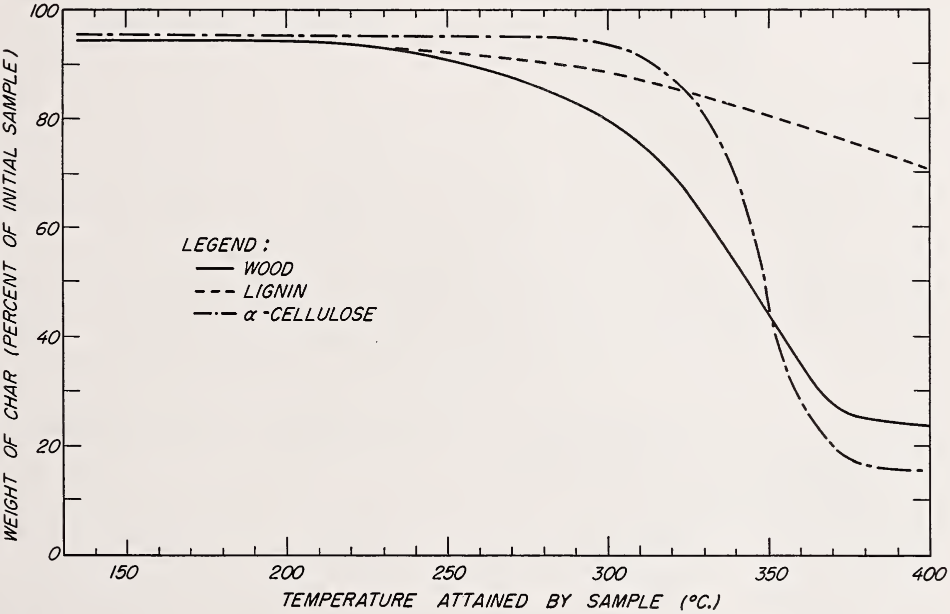

Figure 2. Portion of dynamic thermogravimetric curves between 130° and 400°C, with temperature rising 6°/minute, for wood, lignin, and α-cellulose.

When such adjustment is made, the curves for wood treated with either sodium chloride or sodium tetraborate coincide almost exactly with the curve for untreated wood until the temperature reached about 340°C, and pyrolysis in the

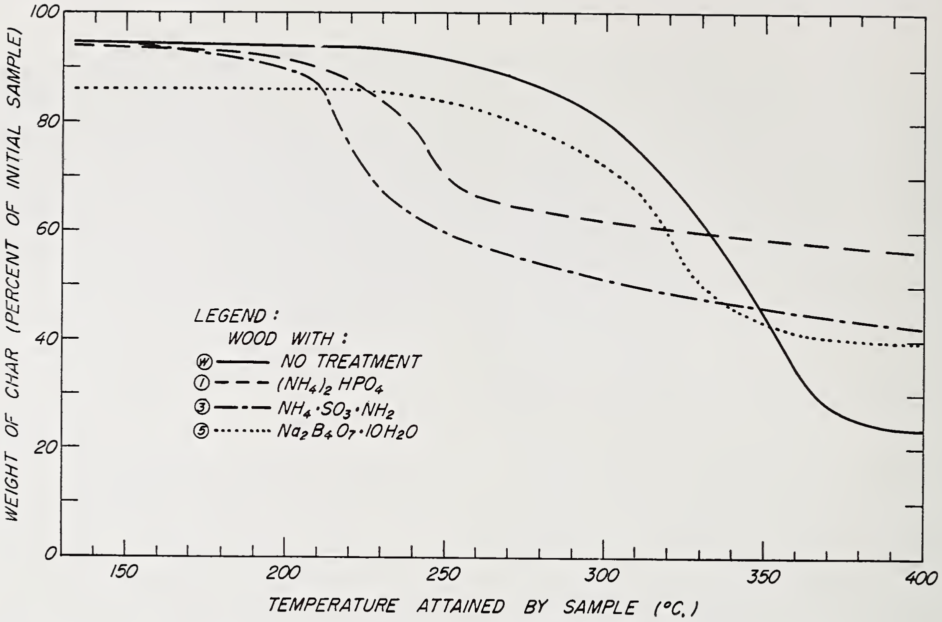

Figure 3. Portion of dynamic thermogravimetric curves between 130° and 400°C, with temperature rising 6°/minute, for untreated wood and for wood treated with dibasic ammonium phosphate, ammonium sulfamate, or sodium tetraborate, respectively, at the maximum retention of salt indicated in Table 2.

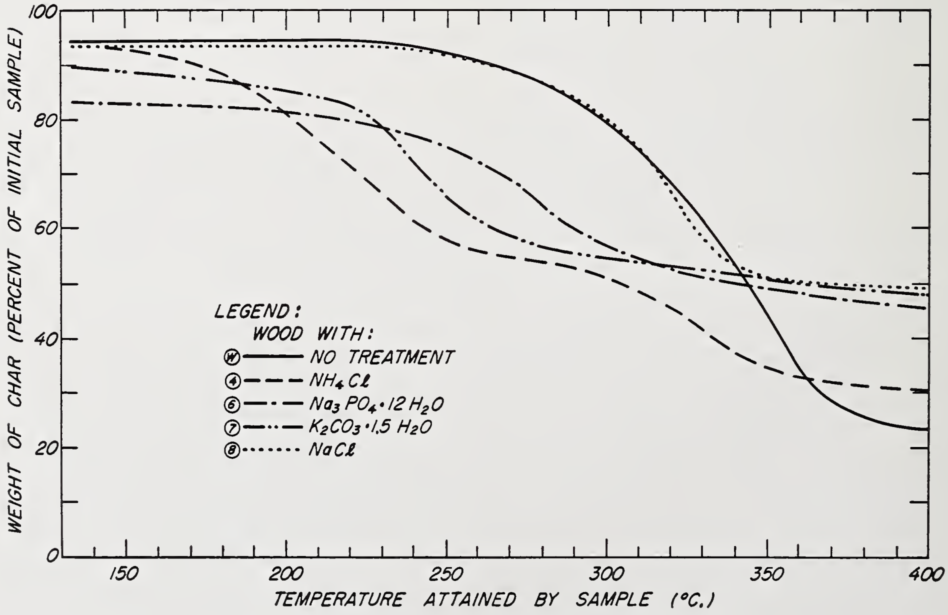

Figure 4. Portion of dynamic thermogravimetric curves between 130° and 400°C, with temperature rising 6°/minute, for untreated wood and for wood treated with ammonium chloride, tribasic sodium phosphate dodecahydrate, potassium carbonate sesquihydrate, or sodium chloride, respectively, at the maximum retention of salt indicated in Table 2.

salt-treated samples was almost complete. All other salts decreased the temperature at which weight loss began to accelerate and increased the weight loss in a wide region of temperature below 340°C. The departure from the curve for untreated wood was greatest for ammonium chloride, diminished in the order of ammonium sulfamate, ammonium phosphate, potassium carbonate, and was least for sodium phosphate.

Thus, except for sodium tetraborate, the more effective the salt was as a flame retardant, the lower the temperature at which it caused active pyrolysis of the wood to begin and the greater the loss in weight attained by the time the temperature reached about 250°C. With the highly effective sodium tetraborate, however, as with the ineffective sodium chloride, the thermogravimetric curve for treated wood was essentially the same as that for untreated wood up to about 340°C.

Beyond about 340°C, the weight of residue from wood treated with any one of the salts exceeded the weight of char from untreated wood. The residue from some but not all of the treated samples still contained the injected salt or products of its decomposition. The inorganic component of the residue at any temperature was calculated from the weight of salt present initially and the fractional weight left at the required temperature when a sample of the salt alone was analyzed thermogravimetrically. It was then possible to estimate the weight of wood charcoal left and the weight of wood substance volatilized at 200, 250, and 400°C as reported in Table 2. Table 2 shows also the content of salt in the sample

TABLE 2

DYNAMIC THERMOGRAVIMETRIC ANALYSIS OF UNTREATED WOOD AND OF WOOD TREATED WITH INORGANIC SALTS

Salt Present in Wood	Content of Salt in Sample	Temperature of Onset of Active Pyrolysis	Extent of Volatilization of Wood in Sample		
			At 200° C	At 250° C	At 400° C
	Per cent	° *C*	*Per cent*	*Per cent*	*Per cent*
None (untreated wood)	0	220	0.5	3.7	76
VERY EFFECTIVE FLAME RETARDANTS (GROUP I)					
Dibasic ammonium phosphate	40.5	180	4.3	38	50
	11.1	180	3.2	21	51
	2.4	180	2.6	11	57
Ammonium sulfamate	23.4	180	4.4	45	41
	16.6	180	3.2	37	43
Ammonium chloride	29.8	150	19	54	54
	18.6	150	14	35	57
	9.0	150	11	23	61
Sodium tetraborate	11.0	220	0	4.4	50
	1.0	220	0	2.2	57
MODERATELY EFFECTIVE RETARDANTS (GROUP III)					
Potassium carbonate	29.2	210	2.5	32	59
	18.6	210	1.9	27	57
	6.7	210	1.6	17	58
Trisodium phosphate	37.6	200	2.6	15	67
	3.2	200	1.1	9.3	63
INEFFECTIVE RETARDANT (GROUP IV)					
Sodium chloride	31.1	220	2.4	7.9	73
	13.5	220	1.9	6.2	70

initially and the temperature at which active pyrolysis of the wood began. Although the assumptions on which the estimates are based may have to be modified in the light of further study, the general trend of the results is believed to be reliable.

Untreated wood began to pyrolyze actively at 220°C, was volatilized at 250°C to the extent of 3.7 per cent only, but at 400°C volatilization attained 76 per cent. Wood treated with one of the ammonium salts began to pyrolyze at much lower temperatures, 150 to 180°C, was much more extensively volatilized than untreated wood at 250°C, but was much less extensively volatilized than untreated wood when active pyrolysis was essentially completed at 400°C. Treatment with potassium carbonate advanced the onset of wood pyrolysis slightly (to 210°C), increased volatilization of wood at 250°C significantly but somewhat less than the ammonium salts, but permitted somewhat greater volatilization of wood at 400°C than the ammonium salts did. The three sodium salts altered very little the temperature at which wood pyrolysis began and increased little, if at all, the volatilization of wood at 250°C. At 400°C, however, sodium tetraborate restricted volatilization of wood about as much as the ammonium salts did, whereas sodium phosphate restricted volatilization much less than the better retardants did and sodium chloride permitted nearly as much volatilization of wood as occurred in untreated wood.

Apparently the extent to which a salt might lower the temperature at which pyrolysis began, depended on the nature of the salt but not, within wide limits, on the quantity of salt in the wood. On the other hand, at 250°C volatilization of wood was greater the greater the concentration of salt. The salts that are highly effective flame retardants seemed to decrease the volatilization of wood at 400°C to a greater extent the higher the concentration in the wood before heating, even though some of them, such as ammonium sulfamate and ammonium chloride, had been driven off completely before the temperature reached 400°C.

Results of Static Thermogravimetry

The effort to study the kinetics of wood pyrolysis by static thermogravimetry presented problems that have not yet been solved satisfactorily.

The pyrolysis of wood usually has been considered amenable to treatment as a pseudo first-order reaction.[1, 3, 5, 11, 17] The rate of loss in weight was therefore recorded at each of a succession of temperatures not too far above the threshold temperature for active pyrolysis, and the logarithm of the as yet unvolatilized fraction of the wood ultimately volatilized at the given temperature was plotted against the time since heating began. The weight loss of as much as 35 per cent during the period of some 15 minutes required for the sample to attain the constant furnace temperature had to be ignored. Beyond this point, the charts took the form of straight lines, from the slopes of which the velocity constant for each temperature was calculated. The slope of plots of the logarithm of the velocity constants against the reciprocal of the absolute temperature, which proved linear, yielded the activation energies given in Table 3.

The activation energy for untreated wood, 35.8 kilocalories per mole, was somewhat higher than that found by Stamm [17] for slower pyrolysis at a lower range in temperature, 29.5 kilocalories per mole. For wood treated with one of the four ammonium salts the activation energy, 31.9 to 34.8 kilocalories per mole, was only slightly lower than that for untreated wood, if for ammonium chloride only the second of the two steps in pyrolysis (Figure 4) is considered. These salts are decomposed and wholly or at least substantially volatilized before pyrolysis of the wood has been completed. (The reason for the two-step pyrolysis, observed only in the presence of ammonium chloride, is not clear.) The three alkali salts that caused lowest activation energies, 24.7 to 29.3 kilocalories per mole, are all hydrous, but loss of hydrate water is an unlikely source of low activation energy, since it occurs before pyrolysis becomes active. The anhydrous portions of the three alkali salts, except for partial loss of carbon dioxide from the carbonate, do not volatilize during pyrolysis of the treated wood, but it may be noted that they are all salts of a strong base with a weak acid. Sodium chloride, a salt of a strong base with a strong acid, left the activation energy, 33 kilocalories per mole, in the same range as was found in the presence of the ammonium salts.

TABLE 3

ACTIVATION ENERGIES COMPUTED FROM STATIC THERMOGRAVIMETRIC ANALYSIS OF UNTREATED AND TREATED WOOD

Salt Present in Wood	Content of Salt in Sample	Activation Energy
	Per cent	*Kilocalories per mole*
None (untreated wood)	0	35.8
Ammonium choride[1]	17.7	8.1 (1st step)
		34.8 (2d step)
Ammonium sulfamate	15.7	34.0
Monobasic ammonium phosphate	15.1	33.1
Dibasic ammonium phosphate	10.8	31.9
Sodium tetraborate	17.4	24.7
Potassium carbonate	20.0	25.4
Tribasic sodium phosphate	18.0	29.3
Sodium chloride	12.0	33.0

[1] Figure 4 shows that pyrolysis in the presence of ammonium chloride occurs in two steps, for each of which the activation of energy was computed.

Results by Differential Thermal Analysis

Curves for differential thermal analysis of wood, alpha-cellulose, and lignin, made with aluminum oxide for reference, are given in Figure 5. All three substances presented endothermic nadirs at 130°C that came chiefly from dehydration. By the time the samples had again caught up with the temperature of the reference material, the temperature had reached 225°C. Lignin then showed a marked exothermic peak at 415°C. Cellulose, on the other hand, after keeping nearly in step with the reference material up to 310°C, fell rapidly to a sharp endothermic nadir at 350°C succeeded by a strong exothermic peak at 470°C. Schwenker[16] observed a weak exothermic peak at 328°C and a strong endothermic nadir at 372°C for cotton fabric (alkali-scoured) but no appreciable temperature differential between 400 and 500°C. Both Schwenker[16] and Keylwerth and Christoph[9] found a weak exothermic peak near 310°C that became strongly exothermic when the pyrolysis took place in air.

The curve for wood revealed the influence of both lignin and cellulose in that the sharp nadir in cellulose at 350°C, which was completely lacking in lignin, in wood became a valley between exothermic peaks at 340 and 440°C. Kollmann[10] and Tang[18] observed this valley in experiments in which the rate of rise in temperature at the center of a "thick" piece of wood was observed while the piece was being heated in a furnace at constant temperature. Keylwerth and Christoph gave the designations β_1 and β_2 to the peaks at 340 and 440°C, respectively.

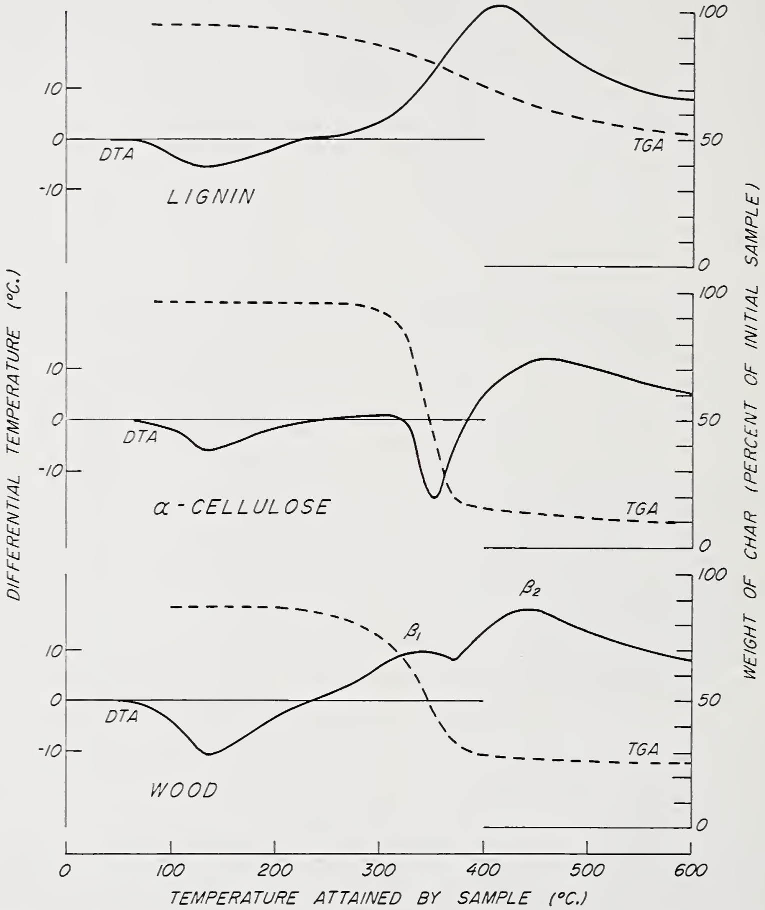

Figure 5. Curves for differential thermal analysis (DTA) of lignin, α-cellulose, and for wood (solid lines, scales at left, reference material aluminum oxide) with the curves for dynamic thermogravimetric analysis (broken lines, scales at right) superimposed.

Comparison of the thermogravimetric with the differential thermal data shows that with lignin loss in weight due to active pyrolysis began when the reaction became exothermic and proceeded fastest in the most strongly exothermic region. Weight loss of cellulose began in the neutral or feebly exothermic region near 310°C, was at first endothermic enough to produce the nadir at 350°C, but became distinctly exothermic before rapid loss in weight ceased. In the DTA curve for cellulose, the exothermic peak at 470°C undoubtedly comes from the heat effect associated with the last portion of the rapid weight loss in the TGA curve, before the weight levels off because of an instrumental lag in registering the full effect of an evolution of heat following so closely after a substantial absorption of heat. With wood, nearly all of the loss in weight took place in the exothermic region spanning the valley between the β_1 and β_2 peaks, recognizing again that the β_2 really occurs at a slightly lower temperature because of instrumental lag.

Figure 6 presents differential thermal analyses of wood treated with salts against untreated wood as the reference material, in order to reveal the effect of the salts on the absorption or evolution of heat in the various regions of temperature. Figures 7 and 8 present the differential thermal analyses for untreated wood

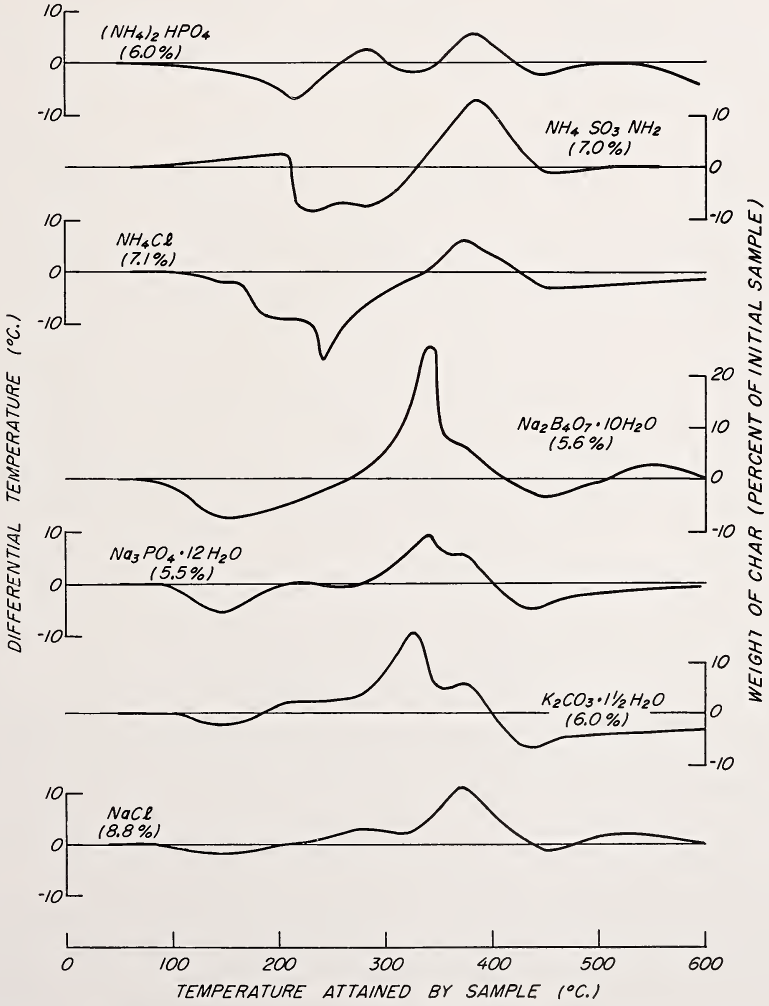

Figure 6. Differential thermal analyses of wood containing salts (at the concentration indicated within parentheses) with untreated wood used as the reference material.

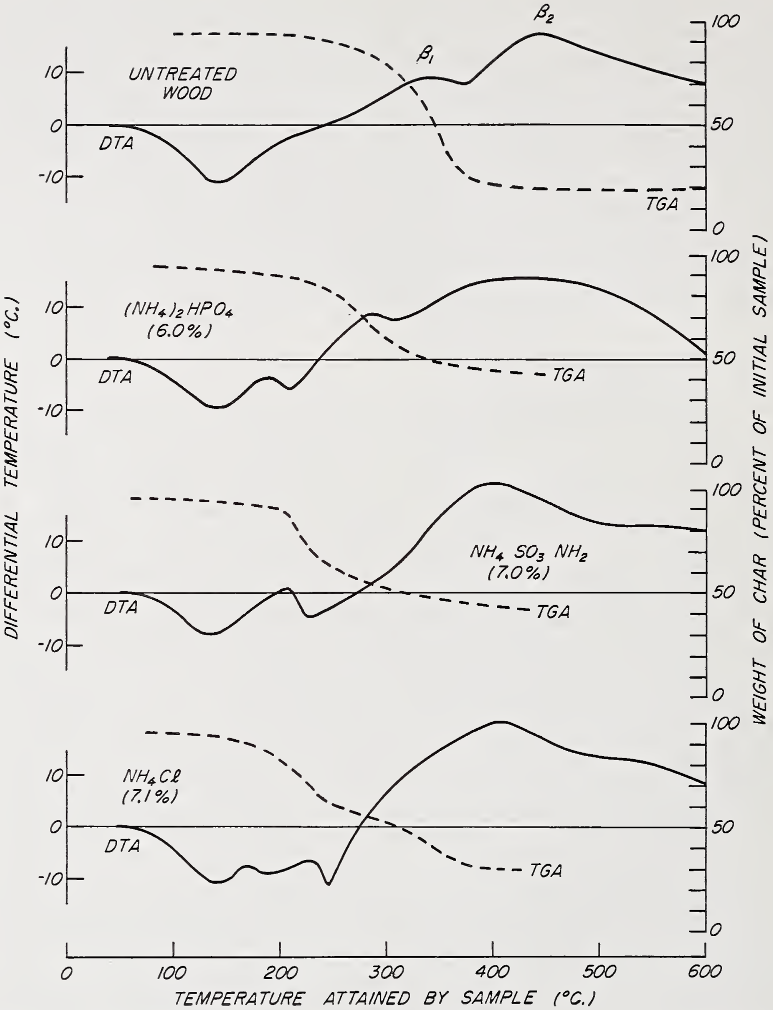

Figure 7. Curves for differential thermal analysis (DTA) of untreated wood and of wood treated with salts that decompose thermally below 400°C (solid lines, scales at left, reference material aluminum oxide) with curves for dynamic thermogravimetric analysis (TGA) superimposed (broken lines, scales at right).

and for wood treated with the salts when the reference material is inert aluminum oxide, together with the corresponding thermogravimetric analyses.

Salts that contained water of crystallization caused an endothermic effect beginning near 100°C and reaching a nadir near 150°C. (Figure 6). (The less striking dips in the same region in the curves for sodium chloride and for ammonium chloride may be due to slightly increased moisture content of the treated wood as suggested also in Figures 3 and 4.) The endothermic effect due to loss of moisture occurs in all the curves of Figures 5, 7, and 8.

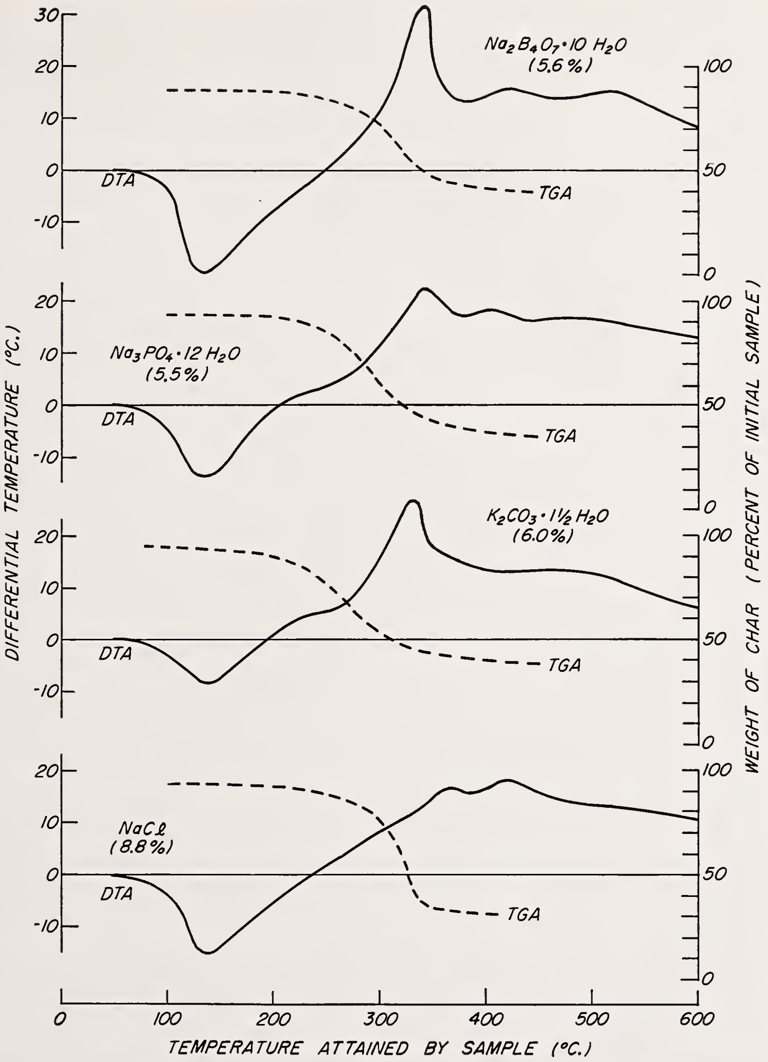

Figure 8. Curves for differential thermal analysis (DTA) of wood treated with salts that, except for loss of water of crystallization, do not decompose below 400°C (solid lines, scales at left, reference material aluminum oxide) with curves for dynamic thermogravimetric analysis (TGA) superimposed (broken lines, scales at right.

In Figures 6 and 7, the three ammonium salts show a common nadir near 220°C due to decomposition of the salts and recognizable also in differential thermal analyses of the salts by themselves. The alkali salts in Figures 6 and 8 present no marked thermal effects attributable to the salts after that due to the evaporation of moisture.

Figures 6 to 8 suggest that all of the salts, even the ineffective sodium chloride, tend to shift the β_1 and β_2 peaks of untreated wood (Figure 5) to lower temperatures. The three ammonium salts overbalance the β_1 peak largely or entirely by the endothermic effects of decomposition of the salts. The alkali salts, on the other hand, tend to accentuate the β_1 peak and make it dominate the β_2 peak.

Conclusions

The methods of dynamic thermogravimetric analysis and differential thermal analysis offer promise of contributing significantly to study of the mechanism of wood pyrolysis and the action of chemical treatments on it. The possible use of static thermogravimetric analysis to study the kinetics of the reactions seems to present greater difficulty.

The threshold temperature for active pyrolysis of lignin and of wood was found near 220°C, whereas that of alpha-cellulose was near 275°C. Once started, the collapse of cellulose was rapid, was essentially complete before 400°C, left relatively little char, and was associated with a marked endothermic nadir. Lignin, on the other hand, lost weight slowly, losing only one-fourth of its weight by the time 400°C was reached and only half at 800°C, and the pyrolysis appeared to be steadily exothermic. Wood exhibited the effects of its two chief constituents; the pyrolysis showed exothermic peaks at 340 and 440°C, with a valley between them that was due to the endothermic region of the cellulose.

The inorganic salts tested so far fall into four classes according to the effects they exhibited:

1) Presence in the wood of sodium chloride, an ineffective flame retardant, had no appreciable effect on the threshold temperature for active pyrolysis, or on the extent of volatilization of wood at either the lower or the higher temperatures of active pyrolysis. It also had very little effect on the apparent activation energy of pyrolysis or the course of the curve for differential thermal analysis.

2) Sodium tetraborate, a very effective flame retardant, likewise left the threshold temperature and the volatilization of wood up to 340°C essentially unaltered but greatly decreased the volatilization at 400°C, where pyrolysis was practically ended. The sodium tetraborate also decreased the apparent activation energy greatly, and it made the β_1 predominate greatly over the β_2 exothermic peak and shifted both peaks to lower temperatures.

3) The moderately effective flame retardants, potassium carbonate and sodium phosphate, slightly lowered the threshold temperature for active pyrolysis, increased the volatilization at 250°C slightly to moderately, and decreased the volatilization at 400°C less than sodium tetraborate did. They also decreased the apparent activation energy and altered the β_1 and β_2 peaks similarly but less markedly than sodium tetraborate did.

4) The ammonium salts lowered the threshold temperature for active pyrolysis substantially, markedly increased the volatilization of wood between the threshold temperatures and 250°C, but markedly decreased the volatilization at 400°C. The ammonium salts did not decrease the apparent activation energy very much but, in contrast to the alkali salts, they suppressed the β_1 exothermic peak. With the ammonium sulfamate and ammonium chloride, at least active pyrolysis was well under way while an endothermic nadir was being attained.

A more extensive study of chemical treatments is needed before decisions can be reached, but it may be mentioned that class (1) is represented by a salt of a strong base and a strong acid that remains unchanged through the range of temperatures of active pyrolysis of wood, class (2) by a salt of a strong base and a very weak acid, class (3) by salts of a strong base and weak acids, and class (4) by salts of a weak base and strong acids. (The first hydrogen of phosphoric acid is strong, the third hydrogen weak.) It has been suggested repeatedly[4, 12, 13] that good flame retardants are likely to be substances that readily decompose to form a strong acid or to form a strong base. No doubt the mechanism of action may differ, depending on whether the effective reagent is an acid or a base.[7, 14, 15]

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Detonation and Suppression of Detonation in Fuel-Air Mixtures at Elevated Pressures

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Introduction

Gaseous detonations have been studied extensively and our basic knowledge of pressures in the detonation wave, its velocity, and detailed structure is extensive. However, there is no way of predicting under what conditions a detonation rather than a deflagration will be established. This is of no particular concern in fuel-oxygen mixtures as a detonation usually forms from a deflagration after a very short time-period and distance from the ignition source. Fuel-air mixtures in contrast have seldom been observed to detonate, although one would expect that given large and long enough vessels, eventually detonation will occur. This has, in fact, been observed in natural gas and air mixtures, where a detonation developed even at 0.4 atm initial pressure in tubes of 61 cm in diameter and 93 m in length.[1]

Detonations and the resulting high-pressure peaks are a danger in many industrial applications. This experimental investigation was undertaken to assess the dangers of detonations or very high-pressure peaks in large volumes containing fuel-air mixtures. Of special interest was the possibility of arresting detonations or deflagrations by spraying into the tube large amounts of water. It was the original intention to conduct all experiments in a tube of 54.6 cm in diameter and 9.85 m in length that was designed to withstand high pressure. However, after initial experiments that led to extremely high-pressure peaks, it was decided to use this large tube for experiments at one atmosphere initial pressure only and to conduct detonation experiments at initial pressures higher than one atmosphere in a tube of smaller diameter but the same length as the large tube.

The experiments fall roughly into four categories.

A. The measurement of the pressure dependence of fuel-air detonations.
B. Comparison of the onset of detonation in the large- and small-diameter tubes.
C. The occurrence of very large pressure peaks in the large tube.
D. The influence of water curtains on explosions and detonations.

The instrumentation was restricted to high-speed pressure measurements. This allowed a full analysis of the pressure history in the tube but gave only indirect evidence of the position of the flame front. Surface thermocouples were tried to get this additional information but were not too successful, no doubt due to the fact that the flame front during the deflagration stage was highly turbulent and clear signals were not received, except when a detonation had been established.

Experimental Apparatus

Two closed tubes of approximately the same length were employed in this investigation. The large tube, 54.6 cm in diameter, was used for the bulk of the tests at initial pressures of one atmosphere and for all tests in which water was injected into the path of a deflagration or detonation. The small tube, 38 mm in diameter, was used principally for tests at elevated initial pressures. Both tubes were equipped to accept piezoelectric pressure gages at various positions along the walls of the tube. The locations of these stations are given in Table 1 and diagrammatically in Figure 1. Free-stream pressures were measured with as many as eight Kistler SLM PZ6 miniature pickups whose signals were displayed on oscilloscopes and recorded photographically by high-speed streak cameras. With appropriate calibrator units, the response of four of the pickups was 150,000 cps; the response of the other four was about 40,000 cps. For the tests in the smaller tube, adapters were necessary to extend the range of the gages to the much higher pressures produced by detonations at elevated initial pressures. These adapters reduce the response of the more sensitive gages to approximately 50,000 cps but have little effect on the response of the others.

TABLE 1

LOCATIONS OF STATIONS AND WATER INJECTION PORTS

	Distance from Spark (in meters)	
Station	54.6 cm Tube	38 mm Tube
1	1.00	0.80
1a		1.53
2	1.48	3.30
3	2.49	5.31
4	3.50	6.30
5	4.00	7.30
6	5.01	7.80
7	6.01	8.30
8	7.01	8.80
9	8.01	
10	8.51	
11	9.01	
12	9.51	
End-Flange	9.85	9.15
Water Injection Port		
1	1.79	
2	1.97	
3	2.15	

Considerable difficulty was encountered in attempting to load to one atmosphere the 2130 liter volume of the large tube with a known, uniform mixture of explosive gases. The most satisfactory method was based on filling the vessel with the component gases premixed externally in the flow system. Ignition of the mixture at one end of the closed tube was ensured by the use of three surface-gap spark plugs, each with an independent capacitor circuit.

Water injection into the 54.6 cm tube was through three poppets located 120° apart on a spiral on the tube circumference. The positions of the three spring-loaded water injectors are given in Table 1 and Figure 1. For runs with water injection, a 100 gallon tank was filled prior to the run. High-pressure nitrogen was admitted into the water tank, forcing the water through the three poppets into the tube just prior to the spark. The time-interval between water-flow initiation and capacitor discharge could be varied as desired.

Loading of the 38 mm tube for elevated initial pressures was achieved in the following manner. A large auxiliary tank was loaded to one atmosphere with the desired gas mixture in the same manner as the filling of the 54.6 cm tube. The mixture in the large tank was then forced by water into the 38 mm tube. By this method, the tube was prepared for tests at initial pressures of from one to 40 atmospheres. Ignition of the mixture was by a single surface-gap spark plug.

Results

High Pressure Data

In the closed steel tube 38 mm in diameter a number of tests were made with fuel-air mixtures at initial pressures of 1 to 40 atmospheres. For these tests, only mixtures of approximately stoichiometric proportions were used.

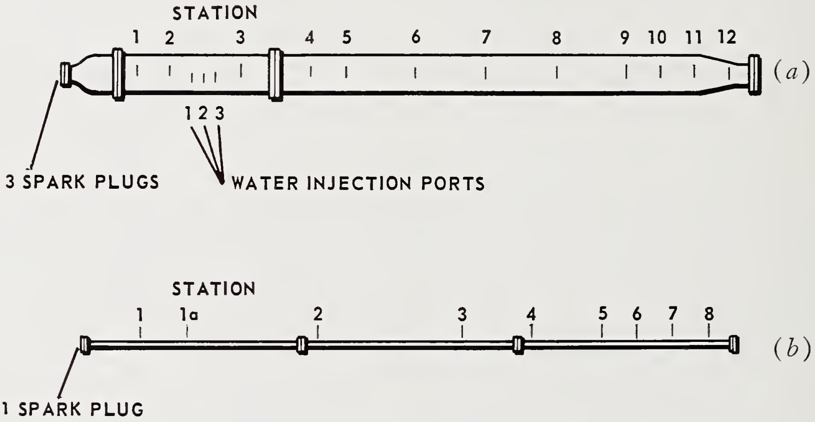

Figure 1. Diagram of detonation tubes.
(a) 54.6 cm diameter (b) 38 mm diameter

In no case was a detonation observed in any methane-air run. Even at the highest initial pressure tested, 40 atm, the wavelike pressure fluctuations within the tube were rounded. The maximum pressures recorded at any station for these methane-air runs were only two to three times the initial pressure.

Quite different results were obtained with the hydrogen-air and ethylene-air mixtures. For these mixtures, pressure ratios of about 15 for the former and more than 20 for the latter mixtures were recorded in some runs. These pressure-ratios are indicative of detonations. Pressure, however, could not be the sole criterion on which to base the description of the type of combustion. Average velocities of the pressure pulses between various stations along the tube-axis provide a better basis. The average velocities for the hydrogen-air mixtures are plotted in Figure 2. The velocities were computed from the measured time-interval for passage of the pressure pulse between two successive stations at which the piezoelectric gages were located. The average velocities so computed are plotted against the distance from the spark to the mid-point between the two appropriate stations. The numbers on the curves refer to the initial pressure, in atmospheres.

Two distinct regimes are evident; the lower corresponding to deflagrations, the upper to detonations. Clearly, detonations form in hydrogen-air mixtures at 6 atm initial pressure or above. Figure 3 is a similar plot for the ethylene-air runs. For these mixtures, 20 atm appears to be the marginal initial pressure at which a detonation generally forms. Below 20 atm, detonations were not observed within the tube length.

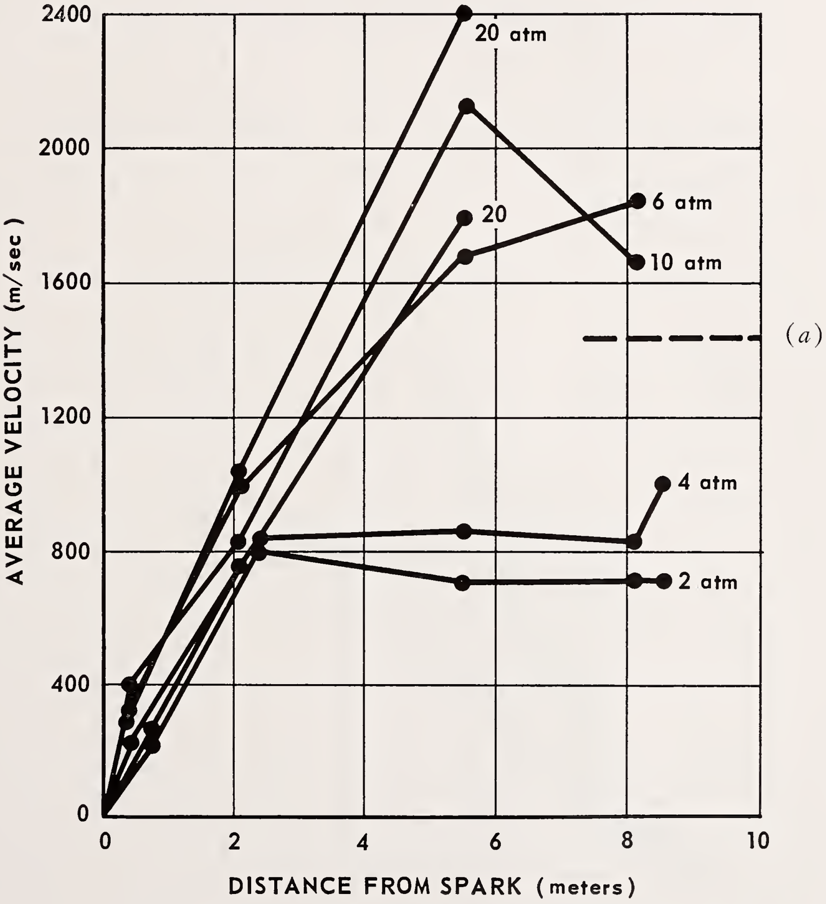

Figure 2. Effect of pressure on propagation velocity of hydrogen/air mixtures (38 mm tube). (a) 1 atm value 40 m x 5 mm tube (ref. 4).

The occurrence of a detonation is readily evident from the average velocity plots. However, they are misleading with regard to the location of the onset of detonation. The pressure-time records show that in those runs in which a detonation occurred, it was formed between stations 1 and 2 in every case. In addition, no precompression of the unburned gas in the hydrogen-air tests was observed at station 2 or at succeeding stations prior to the arrival of the detonation wave. For the ethylene-air detonation mixtures, slight precompression at station 2 was recorded (from 20 atm initial pressure to 28 atm).

Comparison of Detonation Runs in the Two Tubes

A series of tests were made at one atmosphere initial pressure in each of the two closed tubes. The tests used fuel-air mixtures enriched with oxygen in approximately stoichiometric proportions. To describe the degree of oxygen enrichment, the parameter oxygen-index is employed. Oxygen-index is the ratio of moles of oxygen to moles of oxygen plus nitrogen. For air, O.I.=0.21.

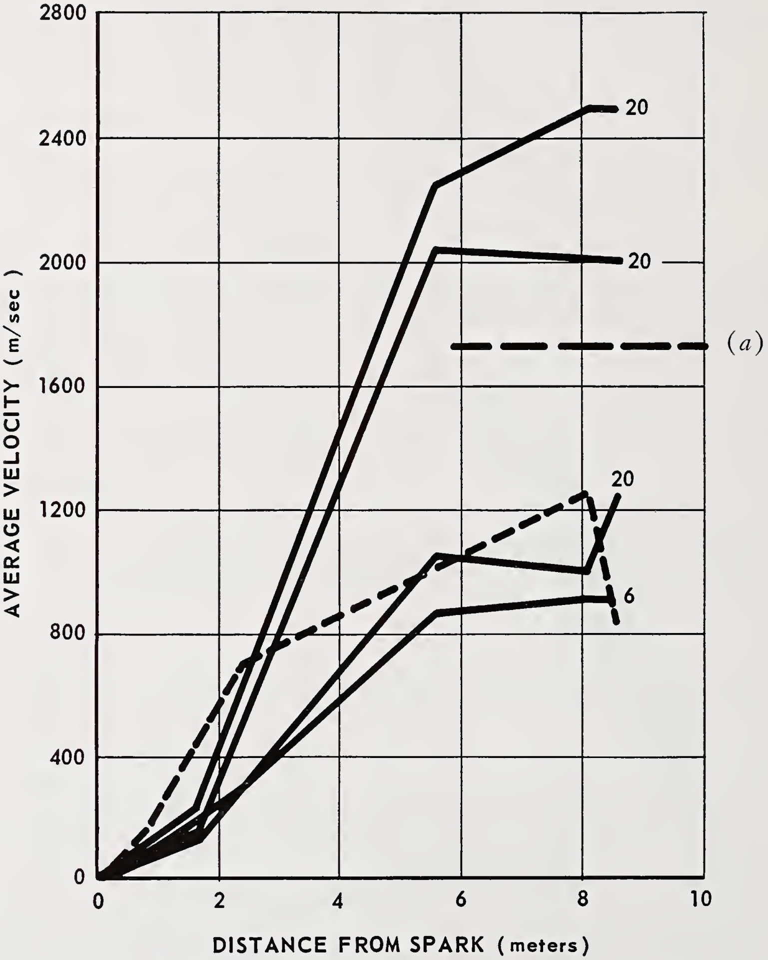

Figure 3. Effect of pressure on propagation velocity of ethylene/air mixtures (38 mm tube). (a) 1 atm value; O/F=2.0, O.I=0.2 (ref. 4).

The results of the runs show that detonations are formed at lower oxygen indexes in the smaller tube. The following table gives the minimum oxygen indexes of approximately stoichiometric mixtures at one atmosphere supporting detonations in each tube.

Fuel	*54.6 cm Tube*	*38 mm Tube*
Hydrogen	0.30	0.23
Ethylene	0.37	0.30
Methane	0.52	0.32

The pressure data of these fuel-"enriched" air detonation runs at one atmosphere reveal with practically no exceptions that the pressures due to the incident waves are higher in the larger tube regardless of which stations in each tube are compared. In general, the oxygen indexes tested were greater for runs in the larger tube in order to cause a detonation. However, ethylene runs with O.I.=0.37 were made in each tube. In this case, the pressures in the larger tube were roughly 50 per cent greater than in the smaller tube.

A comparison of the average velocity values for the one atmosphere detonation runs in each tube leads to some interesting observations. The average velocities of the detonation waves in hydrogen, ethylene, and methane mixtures are plotted in Figures 4, 5 and 6, respectively. In each plot, the abscissa is the distance

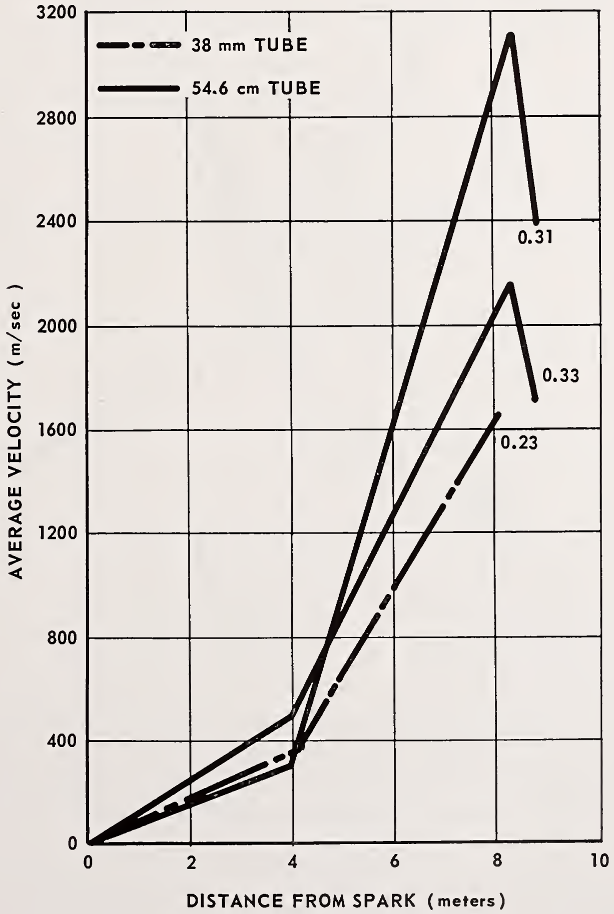

Figure 4. Effect of oxygen index on propagation velocity of hydrogen/"enriched" air mixtures. Numbers on curves give oxygen index. O/F ratio varies between .49 and .58.

from the spark to the midpoint between the two appropriate stations. The numbers on the curves give the oxygen index.

These figures show that the average velocity of the flame front as it traverses the first 80 per cent of the tube length is greater in the smaller tube *for runs with the same oxygen index.* For example, the average flame velocity in the ethylene runs (Figure 5) with an oxygen index of 0.37 was 722 meters/sec between the spark and station 6 in the smaller tube, and just 380 meters/sec in the comparable distance in the larger tube. This trend is to be expected, however, as it leads to the previously stated finding that detonations are formed more readily in the smaller tube.

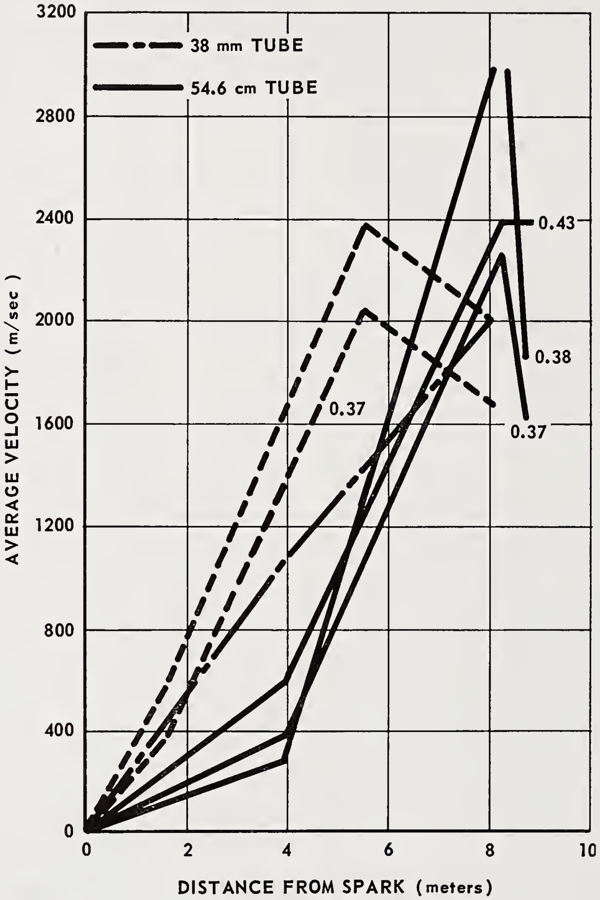

Figure 5. Effect of oxygen index on propagation velocity of ethylene/"enriched" air mixtures. Numbers on curves give oxygen index. O/F ratio varies between 3.4 and 3.6.

Further examination of the figures reveals that the average velocity of the detonation wave in the subsequent 0.5 meter is greater in the larger tube than in the smaller tube. Referring again to the ethylene runs with an oxygen index of 0.37, the average velocity between stations 6 and 7 in the small tube was

1670 meters/sec as opposed to 2270 meters/sec in the comparable region in the larger tube.

The data indicate, then, that for similar mixtures supporting detonations in each tube, the average velocity of the flame front is greater in the smaller tube over the first 8 meters and then lower in the subsequent 0.5 meter. This is also to be expected since the induction distance was found qualitatively to be shorter in the smaller tube than in the larger tube for the same test mixture. Consequently a stable detonation velocity would be approached earlier in the smaller tube; whereas, in the same region of the larger tube, the detonation velocity would still be significantly in the overdriven mode.

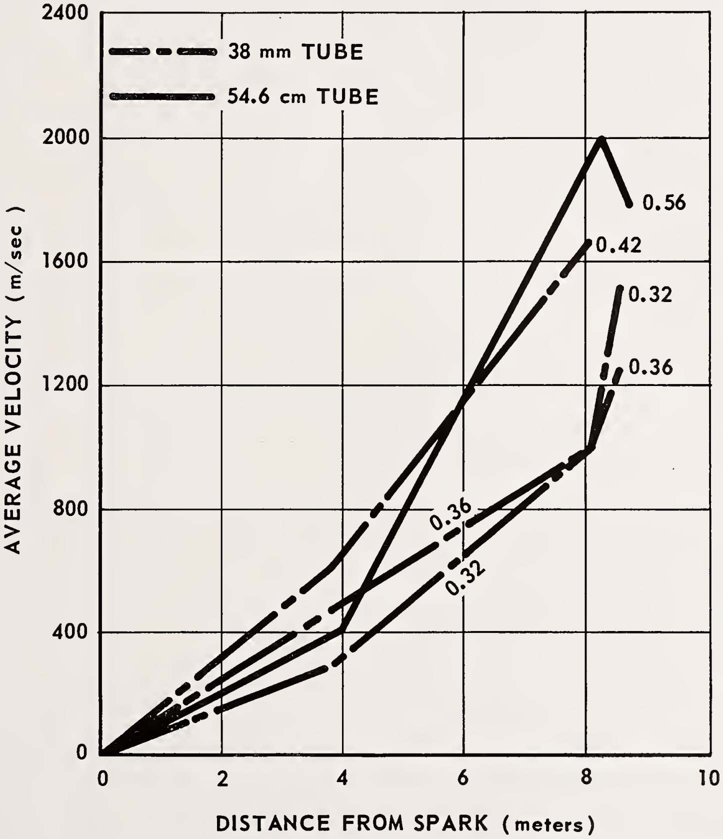

Figure 6. Effect of oxygen index on propagation velocity of methane/"enriched" air mixtures. Numbers on curves give oxygen index. O/F ratio varies between 1.8 and 2.5.

Occurrence of Autoignitions under Marginal Conditions

In addition to the deflagration and detonation processes on which the present work was based, a third phenomenon, termed autoignition, was observed in some runs in the 54.6 cm tube only. Invariably, the process occurred in the downstream end of the closed tube in the region of the conical frustum (Figure 1). In general, the phenomenon was observed in runs in which the oxygen index was between those supporting deflagrations and those forming detonations.

The events leading to the autoignitions in all twelve such runs with the three different fuels can be classed as one of three types:

1. Double shocks of low strength pass down the tube, are reflected, pass up the tube, are again reflected, merge into one shock, and pass down the tube for the second time. A second reflection at the downstream end of the tube, i.e., the region of the conical frustum, may or may not occur just prior to the large pressure "kick" of the autoignition. This mechanism was observed clearly in two ethylene runs and one methane run. All three runs had the lowest oxygen indexes for the particular fuels of any runs in which autoignition occurred. Furthermore, all runs at lower oxygen indexes lead to deflagrations only.
2. Double shocks whose strengths are somewhat greater than those discussed above (i.e., pressure ratios of ~2.5 vs. ~1.8). In this case, the first shock of the pair is reflected at the downstream end of the tube and is then met near station 12 by the second shock traveling downstream. This mechanism was observed in four runs.
3. A single shock of greater strength (pressure ratio ~3.5). Here, no reflected wave was recorded at station 12 prior to the sudden large pressure kick of the autoignition. Five runs exhibited this behavior.

The last two mechanisms occurred indiscriminately at oxygen indexes above those of the first type.

The most striking effect of the autoignitions is the very high pressures generated from initial pressures of one atmosphere. These pressure peaks are greater by a factor of 2 or 3 than the pressures recorded in detonation runs due to the incident detonation wave traveling downstream. Pressure peaks of approximately 80 atmospheres were recorded in two methane runs due to autoignitions.

Water Injection Tests

Several tests were made in the 54.6 cm tube with water injected into the path of a deflagration or detonation. Three poppets were used as injectors, producing a fine spray. The distances between the spark and the three water injection ports are given in Table 1. The thickness of the atomized water curtain was more than 36 cm. Generally, the total water flow rate in each run was 51 kg/sec.

The presence of the water curtain had two principal effects. It either prevented ignition of the combustible mixture by the spark, or it slowed progagation of the flame front.

In nearly half of the runs made with water injection, no pressure rises were recorded and no audible evidence of an explosion was heard. Nevertheless, the capacitor discharge signal was recorded indicating that a spark did occur. In a few of these runs a surface thermocouple, whose response is equal to that of the pressure gages, was located at station 1. The thermocouple, too, gave no indication of combustion in the tube between the spark and the water curtain. It must be inferred, then, that the injected water in no case extinguished a flame already established; rather the water prevented ignition of the gases in such runs.

The second principal effect of the water curtain was to delay the propagation of a deflagration or detonation. Figures 7 and 8 illustrate this fact graphically.

High-frequency oscillations which were generally recorded at each station after passage of a detonation wave have been omitted from the curves for purposes of clarity. These oscillations were usually of relatively low amplitude though occasionally they obscured, to some degree at least, subsequent pressure pulses.

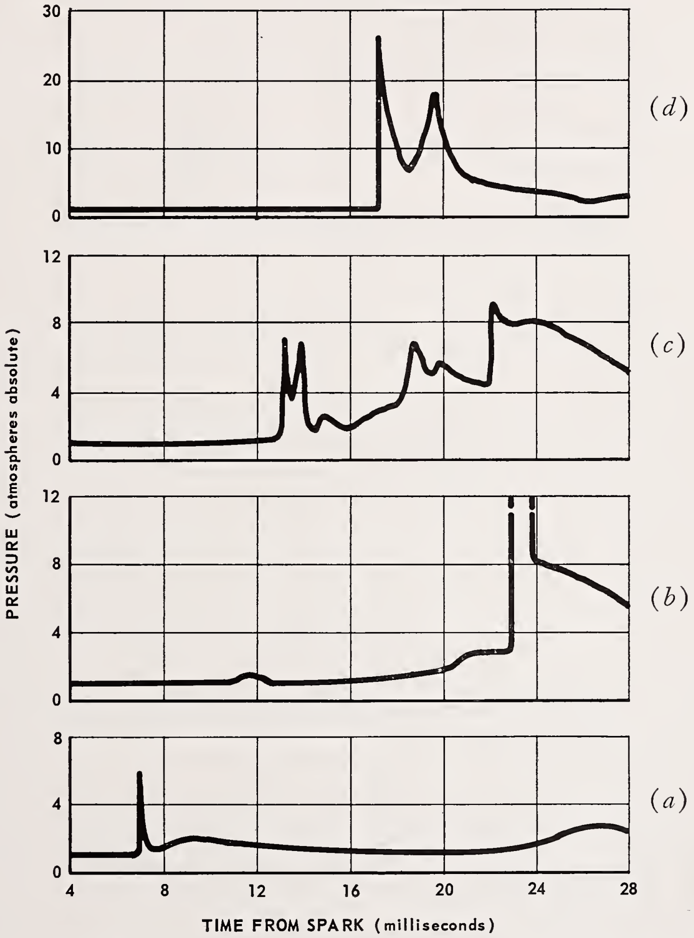

Figure 7. Pressure-time trace of hydrogen/oxygen/nitrogen mixture with water injection. (a) station 2; (b) station 3; (c) station 4; (d) station 9.

The reflected wave of the upper two traces was so effected and consequently their representations are less precise.

The three water-injection ports are located between stations 2 and 3 (Figure 1). It is evident from Figure 7 that the water curtain attenuated the shock recorded at station 2. If it is assumed that the first pressure disturbance recorded at station 3 is due to the shock at station 2, then the average velocity of the wave between the two stations is about 200 m/sec. Clearly, the water curtain not only attenuated the shock but also caused the wave to travel at an apparently subsonic velocity. The pressure traces at stations 4 and 9 give evidence that a flame emerged from the water curtain and subsequently accelerated to form a detonation between the two stations. The second peak at station 9 is due to the wave traveling upstream after being reflected off the closed downstream end of the tube. The reflected wave is seen at a later time at station 4, then at 3 and finally at 2.

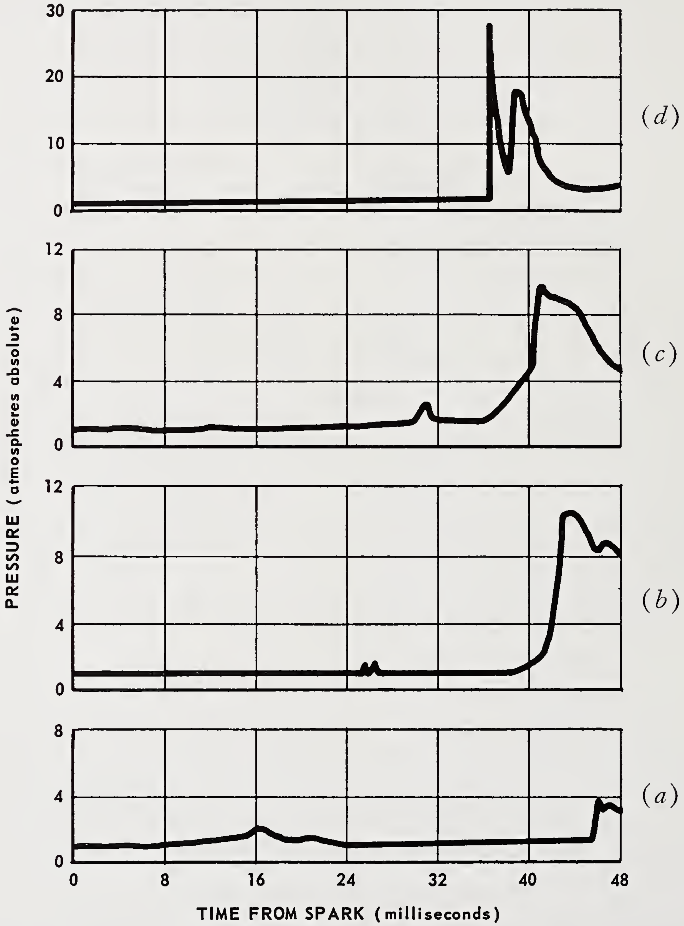

Figure 8. Pressure-time trace of methane/oxygen/nitrogen mixture with water injection. (*a*) *station 2;* (*b*) *station 3;* (*c*) *station 4;* (*d*) *station 9.*

Between stations 3 and 2, the reflected wave was again attenuated as it passed through the water curtain.

Because a detonation was formed between stations 4 and 9 in this run, the double peaks, recorded on the station 4 trace between the incident and reflected waves, are believed to be due to a retonation wave. This wave has been partially overtaken by the reflected wave at station 3 and hence the latter was strengthened to the point of going off the film (indicated by the dotted lines). It is believed that the double peaks recorded on the station 4 trace are due to the three-dimensional characteristics of the combustion in such a large volume. Inside a tube of 54.6 cm diameter, a deflagration wave traveling through a combustible mixture is not a plane surface but rather it advances as tongues of flame leap forward at various acute angles with the tube axis. Consequently, the pressure disturbances which result from these tongues of flame and which are propagated in all directions reach various points on a given circumference of the tube at different times. The waves are then reflected from the tube walls, interact, etc. In consequence of this behavior, a pressure transducer, which occupies but a small point on the large circumference of the tube, can be expected to receive multiple pressure disturbances as it is passed by deflagration or retonation waves. A detonation wave, because of its velocity, is more likely to be a plane and therefore less apt to cause multiple pressure peaks as it passes a transducer.

Discussion

Systematic studies of detonations in fuel-air flames have so far not been reported in the literature. However Bollinger, Fong and Edse [2] found that hydrogen-oxygen flames, slightly diluted with nitrogen have a shorter induction distance from the spark to the onset of detonation at 5 atm initial pressure than at ambient conditions. Thus detonations seem to be induced more easily at high pressures than at 1 atm. It has now been established that hydrogen and ethylene-air mixtures will detonate, given high enough initial pressure in tubes as short as approximately 10 meters. The reason for this fact is not entirely clear. A trivial explanation would be that at lower pressures the tube diameter (38 mm) is below the critical diameter necessary for detonation. This, however, overlooks the fact, as discussed below, that a small diameter tube may induce detonations more readily than a tube of large diameter. More significant is the fact that even at low pressure, deflagration or pressure pulses reach very high velocities, that are normally the precursor of detonation. It is felt that the greater ease with which detonations are established at higher pressure is due to the slower dissipation of heat due to the higher density of the burnt gas. The way a deflagration forms a detonation can be described in general terms as follows: A laminar flame close to the spark is driven forward by the expansion of the burnt gases and gradually becomes highly turbulent. Very high velocities up to 1000 meters/sec are recorded during this stage. Shock waves are formed and partially overtake the flame front. These shock waves form a detonation rather suddenly, creating strong pressure pulses that are also transmitted through the walls of the steel tube and record on the pressure transducers. These pressure pulses in some instances make possible the accurate location of the onset of detonation. The burnt gases also will suffer heat losses due to conduction to the wall. It seems that a critical condition is reached at an early stage before the turbulent flame reaches high velocities. If the burnt gases cool fast enough at low pressure then the forward thrust of the flame front will not reach the value necessary to create the turbulent flame that, in turn, reaches the very high velocities. The creation of the fast turbulent flame will therefore depend on pressure that controls the dissipation of heat of the burnt gases, and on the fundamental burning velocity which controls (together with the forward movement of the gas) the flame speed. This explains the greater ease with which hydrogen-air forms the fast turbulent flames than ethylene-air. In methane-air the very fast flames were never observed.

A second critical condition not yet fully understood is the ease with which a detonation forms from shock waves. This condition may be related to spontaneous ignition with short induction period. In general terms the formation of a detonation thus would depend on two conditions; one relates to the formation of very fast turbulent flames that will create shock waves, the second concerns ignition from shock waves.

Methane-air flames have a smaller burning velocity than ethylene-air flames, but the reduction is rather minor when one considers the difference between hydrogen and ethylene. It is therefore a surprise that methane-air flames do not give rise to detonations at 40 atm; in fact the deflagration is so mild that pressure ratios are very small and much less than theoretical. At one atmosphere the rate of heat dissipation is comparable to the formation of heat in the flame front, thus a fast flame never materializes in a tube of small diameter. At high pressure it has been found that the fundamental burning velocity of methane-air is greatly reduced,[3] and is only about 6 cm/sec at 40 atm. Thus again no fast turbulent flame will form. Methane-air flames seem to be unique in that increased pressure does not promote detonation. In general, it is felt that increased pressure has an influence on the first conditions (fast turbulent flame) for detonation rather than on the second (formation of detonation from shock waves) as shock waves of a given pressure ratio will lead to nearly identical temperature increases independent of initial pressure.

It is also interesting to note that detonations always occurred between stages 1 and 2; thus either detonation sets in relatively early or not at all. It is, therefore, questionable whether hydrogen-air would detonate in a tube of 100 meters length and 38 mm diameter at a lower pressure than in the 10 meter long tube.

In making a comparison between the data on the large and small tube it has to be realized that practically all data were taken in a region where detonation is marginal. Thus no stable detonation velocities are established as yet, detonations may be overdriven and overpressures may be present. This region is of little interest theoretically but of great interest practically as all fuel-air detonations are marginal.

Originally the comparison between small and large tube was made to ascertain that the high pressure data discussed above are meaningful, i.e., may be applicable to the large tube. The oxygen index was thus chosen for a comparison. It was quite unexpected to find that detonations need a higher oxygen index in the large tube than in the small one.

The course of events from spark to detonation as sketched before helps to understand the phenomenon. The early slow flame and its burnt gases will expand into three dimensions rather than only into one direction as in the small tube. Thus accelerations are smaller and a fast turbulent flame will form later or not at all within the given geometry. This qualitatively explains the slower original velocities and the higher oxygen indices necessary for detonation in the large tube. Shock waves formed in the turbulent flame will not only move forward but undergo multiple reflections on the walls and be more subject to attenuation before they can cause a detonation.

Overpressures and overdriven detonations have been observed before but have not been extensively studied. They are of great importance if one considers the safety of containers where explosions or detonations may occur. The present data allows a closer analysis of these phenomena. Little evidence of overpressures is found in the small tube, whereas very large pressure-ratios are found in the large tube. It seems that two phenomena contribute to the large pressures observed and both can only occur in marginal detonations. In the first case a detonation develops so late in the tube that the unburnt gas was already precompressed before the detonation reached the end of the tube. Evidence of this precompression has been found; it has, however, to be pointed out that events under conditions of marginal detonation are not very reproducible. Also the pressure transducers had to be calibrated to read up to 100 atm, thus a precompression of one or two atmospheres is difficult to detect on the records. As detonations developed in the small tube always very early, the detonation could overtake the precompression wave and no overpressures are possible.

A second cause of overpressures is due to the reflection of shock waves at the end of the tube with possible contributions from the adiabatic compression in the tapered-end section of the large tube. Ignitions have been observed due to incident, reflected and double shock waves. In each case the ignition occurs in precompressed gas, thus leading to overpressures, the largest pressure ratio observed being 80. The very high pressure peaks could be fully substantiated by strain gage measurements on the outside wall of the large vessel.

It was hoped that powerful water curtains would cause deflagrations or detonations to die out or at least to moderate appreciably the pressure-peaks in the vessel. This was not found to be the case.

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The authors wish to thank Messrs. A. H. Clark and R. H. Tromans for conducting the experiments and Mr. J. Macatician for many valuable discussions. This work was supported by the U. S. Navy under Contract NOas 60–6047c.

ABSTRACTS

I. Ignition Phenomena

Salooja, K. C. ("Shell" Research Ltd., Thornton Research Center, Chester, England) "Studies of Combustion Processes Leading to Ignition in Hydrocarbons," *Combustion and Flame* 4, 117–136 (1960)

Many independent studies of pre-flame reactions and of the spontaneous ignition temperatures of hydrocarbon fuels have been made but the experimental apparatus used in the two cases have been quite different. In an attempt to evaluate the relation between the pre-flame reactions and the ignition temperature (along with the ignition delay), the author obtained measurements of both within the same apparatus and under similar conditions.

The apparatus consisted of a flow system in which a fuel-air mixture of desired composition is passed through a silica reaction chamber held at a uniform and controlled temperature. With a steady mixture flow, the reaction chamber and mixture temperatures are gradually increased. The exhaust gas is analyzed for the fraction of carbon monoxide and carbon dioxide which are taken as a measure of the degree of pre-flame reaction at the corresponding gas temperature within the reactor. The reactor temperature is increased until ignition occurs which is observed either as an emission of light or, when the flame luminosity is below the visual threshold, by a sudden increase in the gas temperature in the reactor. The gas-residence time is varied by varying the mixture flow rate and this residence time is also considered to be the ignition-delay time when spontaneous ignition occurs. The residence time determined in this manner is not an absolute value since it does not take into account the transient warm-up time of the mixture entering the reaction vessel.

Measurements of degree of pre-flame reaction, spontaneous ignition temperature, and ignition delay were made as a function of fuel-air mixture ratio and reaction chamber temperature for the following hydrocarbons:

1. n-Heptane
2. Methylcyclohexane
3. iso-Octane
4. Di-isobutylene
5. Benzene
6. Toluene
7. m-Xylene
8. Ethylbenzene

The experimental results are presented in a concise form in four graphs for each fuel. These are: (1) per cent of carbon monoxide in exhaust *vs.* temperature for several fuel-air ratios; (2) ignition lag *vs.* temperature for several fuel-air ratios; (3) concentrations of carbon monoxide and carbon dioxide *vs.* temperature for one fuel-air ratio, twice stoichiometric; and (4) a cross-plot showing ignition temperature *vs.* fuel-air ratio for several constant ignition lag times.

In addition to the graphical presentation of data for each hydrocarbon, a qualitative description of the observations are given. For example, it was found that with n-heptane, cool flames were visible from the commencement of pre-flame reactions (at about 280°C) up to about 420°C. Then, none was observed until ignition occurred at about 500°C. The start of pre-flame reactions was accompanied by a 5 to 10°C temperature *drop* indicating an endothermic reaction prior to any energy release.

The variation of fuel-air mixture has a great influence on the ignition temperature and the ignition-delay time and these relationships are a distinct characteristic of each fuel. For benzene, ethylbenzene, di-isobutylene, methylcyclohexane and n-heptane, increasing fuel concentration lowers the ignition temperature although the rate of the effect is quite different in each case. However, with toluene and m-xylene, the ignition temperature is raised with increasing fuel-air ratio. Isooctane exhibits both an increase and decrease, depending upon the magnitude of the fuel-air ratio.

The author analyzes the results in terms of relative resistances of the pre-flame reactions to self-ignition. He concludes that the increase in ignition temperature of iso-octane occurs in spite of a relatively greater extent of pre-flame reaction. Thus, the relative stability of the pre-flame reactions towards ignition rather than a resistance of a fuel to chemical attack dictates the tendency of a hydrocarbon to self-ignite. A fuel with a great pre-flame reaction may require a very high temperature for ignition; no generalization can be made.

A comparison of these results is made with those of other investigators. The agreements and discrepancies are discussed in regard to differences in the experimental apparatus, techniques and observations.

Subject Headings: ***Ignition, of hydrocarbons; Hydrocarbons, ignition of.***

R. W. Ziemer

Ashman, L. E. and Büchler, A. (Arthur D. Little, Inc., Cambridge Massachusetts) "The Ignition of Gases by Electrically Heated Wires," *Combustion and Flame* **5**, 113–121 (1961)

A study on the ignition of stoichiometric methane-air and hydrogen-air mixtures using constant-temperature tungsten wire ignition sources is presented. The wire is heated by means of a condenser discharge and held at a constant temperature by a feed-back circuit using a photomultiplier tube to monitor the radiation from the wire. The process was studied by means of either schlieren streak photographs or shadowgraphs.

Temperatures higher than 1470°C were found necessary to ignite the 9 per cent methane-air mixture while the 30 per cent hydrogen-air mixture could be ignited by temperatures as low as 800°C. During the pre-ignition period of the methane-air mixture, an exothermic reaction occurred; the velocity and duration of this reaction were found to be dependent on temperature of the wire. Near the end of the pre-ignition period, the reaction accelerated to a more rapidly propagating flame front.

No measurable reaction was found to occur during the pre-ignition period of the hydrogen-air mixture. In contrast to the methane-air mixture a definite point corresponding to the sudden appearance of a flame front was observed in the hydrogen-air mixture. The authors state that this ignition behavior conforms to the theory of Semenov on the ignition of gases by small ignition sources. The nonconformity of the methane-air ignition properties was possibly due to the fact that the ignition temperature was sufficiently high in the presence of small sources for the corresponding high reaction rate to reduce significantly the concentration of reactants near the source. Thus the rate of heat release depends more on the rate of diffusion of fresh reactants into the high-temperature region and less on wire temperature.

Some effects of wire size and gas pressure on ignition delay of the hydrogen-air mixture were also studied. Wire sizes used were 1 and 2 mils, gas pressures 1, ½, and ¼ atm. For a given wire temperature, ignition delay was found to increase with a reduction in either wire diameter or gas pressure. The authors state that the magnitude of change in ignition delay agrees with theoretical considerations of the effect of wire size and gas pressure on ignition delay.

A brief discussion is given on the effect of wire composition on ignition delay. Using platinum wire in hydrogen-air mixtures, temperatures for corresponding ignition delays were found to be 50 degrees higher than for tungsten wire of the same diameter.

The paper concludes with a discussion of the results obtained in the ignition of a 10 per cent propane—45 per cent oxygen—45 per cent nitrogen mixture. The ignition behavior pattern obtained was shown to be similar to the hydrogen-air mixture. The authors point out that even though both of these mixtures have approximately equal quenching distances, quenching distance by itself cannot be a deciding factor in hot-wire ignition since the distance of 30 per cent hydrogen-air mixture at ½ atm is about the same as that of 9 per cent methane-air at 1 atm.

Subject Headings: *Ignition, by electrically heated wires; Gases, ignition of.*

W. Y. Pong

Wadsworth, J. (Gas Dynamics Laboratory, National Research Council, Ottawa, Canada) "Use of Flash Photolysis to Initiate Detonation in Gaseous Mixtures," *Nature* **190,** 623–624 (1961)

The initiation of detonation waves in acetylene-oxygen-nitrogen dioxide mixtures was investigated by flash photolysis. The mixtures contained 8–50 per cent NO_2, 27–40 per cent O_2, and 43–57 per cent C_2H_2 at a total pressure of 13–80 mm. The time between the first peak in the flash and the intercept of the extrapolated detonation wave with the center of the light flash was arbitrarily taken as the ignition delay. The delay decreased with increasing total pressure and increasing concentration of NO_2, e.g., delays of 400 and less than 5 μsec were observed at 40 mm when the NO_2 concentration was increased from 8 to 50 per cent with the C_2H_2 remaining essentially constant at 50 per cent.

Subject Headings: *Ignition, of gases, by flash photolysis Gases, ignition of, by flash photolysis.*

W. G. Courtney

Simms, D. L. (Joint Fire Research Organization, Boreham Wood, England) "Ignition of Cellulosic Materials by Radiation," *Combustion and Flame* **4,** 294–300 (1960)

In this paper, the author presents a summary of the results of much of the experimental research which he has conducted over the past ten years, concerning the ignition of wood, paper, and cotton fabrics. In each experiment, the ignition energy was supplied from one of three radiative sources: a one-foot square, gas-fired, radiant panel; a tungsten filament lamp with an ellipsoidal focusing mirror; and a carbon arc with an ellipsoidal mirror. The time required for ignition (1 to 30 seconds) was recorded as a function of the intensity of the incident radiation.

The samples tested were divided into two groups: (1) thin slabs (0.02 cm to 0.065 cm thick) and (2) thick materials (greater than 1 cm thick). The experimental results were correlated in terms of a model which considered only radiant energy input at the surface, a Newtonian cooling mechanism, and one-dimensional unsteady heat conduction in the solid. For group (1) a linear temperature profile in the solid was assumed, while the heat conduction solution for a semi-infinite solid was used in group (2). By assigning an ignition temperature of 525°C to all samples tested, the author obtained a fair universal correlation between two dimensionless parameters defined as the "energy modulus" (the ratio of the total energy received from the radiation source to the heat content of the specimen at ignition) and the "cooling modulus" (the ratio of the total energy lost by cooling to the heat content at ignition). In the correlation procedure, the value of the Newtonian heat-transfer coefficient was inferred from the ignition temperature by using data at high-heating rates, and reasonable constant thermal and thermodynamic properties were assigned to the material tested. The correlation is better for group (1) than for group (2).

A number of related observations are reported and discussed, and possible effects of various phenomena upon the correlation curves are considered. In particular, the fact that the flame first appears in the gas phase, far-removed from the solid surface, is well documented by clear photographs. The importance of the amount of volatile material contained in the sample is thereby emphasized. The effects of external draughts, diathermancy of the thin slabs, the size of the area irradiated, and the moisture content of the material are among the other phenomena briefly considered. The last two effects, as well as the finite supply of volatile material, are proposed as possible explanations of the fact that the model used in the correlation yields a minimum incident radiation intensity of 0.6 cal/cm^2 sec, above which ignition should occur, while ignition was never observed experimentally for incident intensities below 1 cal/cm^2 sec.

Subject Headings: ***Ignition, of cellulose; Cellulose, ignition of, by radiation; Radiation, ignition of cellulose.***

F. A. Williams

Akita, K. (Fire Research Institute, Tokyo, Japan) "Studies on the Mechanism of Ignition of Wood," *Report of Fire Research Institute of Japan* **9**, 1–44, 51–54, 77–83, 99–105 (1959)

The author notes that the fire hazards of gaseous and liquid flammable materials are usually considered in terms of ignitability and, particularly, in terms of ignition temperature. However, different experimental methods often give different results, and in his work all woods had similar ignition temperatures despite appreciable variation in their actual ignitabilities. He proposes that the criterion for ignitability of a solid material should be igniton lag, the time elapsed between application of heat and the formation of flame.

This report summarizes several years of experimental and theoretical investigation by the author and colleagues of the fundamental problems of ignition, such as heat conduction and thermal decomposition of the solid, mixing of vapor decomposition products with air, and ignition of the vapor mixture. The ignition of wood is divided into autoignition, kindled-ignition, and self-ignition. Autoignition and kindled-ignition involve ignition of vapor decomposition products by either the hot surface of the wood (autoignition) or by a very hot external source such as a flame, hot surface, or spark (kindled-ignition). Self-ignition is the result of the homogeneous accumulation of heat in the bulk solid phase due to slow thermal decomposition and occurs below about 200°C. The different types of ignition lag and various practical problems are interpreted in terms of the fundamental phenomena. The author's method of measuring ignition lag during kindled-ignition with a spark has been adopted as a standard contact flame-testing method in accordance with JIS specifications.

Heat Conduction

The bottom surface of a block of wood was heated by hot air at 200 to 900°C and the temperature distribution in the wood was measured by thermocouples.

The conventional diffusion problem of a semi-infinite slab was approximately solved to obtain:

$$T=T_0+(T_a-T_0)\left\{1-\mathrm{erf}\left(\frac{x+x_0}{2\sqrt{\kappa t}}\right)\right\} \tag{1}$$

where T is the temperature at a distance x in the wood at time t, T_0 is the initial temperature of the wood, T_a is the air temperature, erf is the probability function, κ is thermal diffusivity of the wood, $x_0=K/\alpha$ and is a mathematical extension of the solid into the vapor phase so that the apparent surface of the wood is at T_a, K is the thermal conductivity of the wood and α is the thermal transfer coefficient at the surface.

Only a few millimeters depth of wood underwent a significant temperature rise up to the time when ignition occurred. Satisfactory agreement between experimental data and equation (1) was obtained by adjusting x_0, the only unknown. Values for x_0 increased from 0.5 to 1.2 mm with increasing density of the wood.

Decomposition

The isothermal rate of decomposition was investigated at 150–400°C. Decomposition was slow below about 200°C but was rapid above 270°C.

At the higher temperatures, the decomposition rate in the presence of air was measured by weight loss. Denser woods had faster rates of decomposition. The decomposition rate (Japanese cypress) was independent of sample thickness, moisture, resin content, and grain orientation, but the decomposition of wet wood was much higher than for dry wood. Products were approximately 35% tar and organic vapors, 40% charcoal, and 25% water. The organic vapors included hydrocarbons, ketones, aldehydes, and alcohols, but not CO or H_2. The weight of the final solid residue decreased rapidly with increasing temperature but leveled off at about 400°C.

Since wood involves a variety of constituents, the rate of isothermal decomposition should follow an equation of the type

$$\frac{dN}{dt}=\sum_i k_i(N_{\infty i}-N_i) \tag{2}$$

where N is the total amount of gas evolved at time t, N_i and $N_{\infty i}$ are the amounts evolved at t and infinity from the ith constituent, and k_i is the rate constant for the i*th* constituent. The results for pure cellulose and lignin could each be interpreted by only one term of equation (2). Wood is essentially composed of cellulose, lignin, and hemicellulose, and the results for wood could be adequately fitted by three terms, using the above data and assuming a rate constant for hemicellulose. Hemicellulose decomposed the fastest. Cellulose decomposed the slowest (contrary to common belief), and its decomposition mechanism changed at 340°C. Arrhenius activation energies were 17 for hemicellulose, 26 for lignin, and 36 (270-340°C) and 24 (340-370°C) kcal/mol for cellulose. The average for wood was about 23 and 26 kcal/mol in the higher and lower temperature ranges. The decomposition mechanism, and thus the activation energy, very probably changes outside of the noted temperatures. The decomposition mechanism did not change with pressure, but the rate of decomposition at the same nominal temperature was much faster at 1 atm than at 2 mm, probably because the actual temperature of the surface of the wood in the high-pressure case was higher than in the low-pressure case due to a faster oxidation of vapor and carbon.

Below about 200°C, the heat generated by the slow thermal decomposition of wood is very small. Since direct measurement would be difficult, an indirect method based upon an approximate treatment of the heat-conduction equation was used. The temperature in the center of a sphere of wood heated from the outside surface in the absence of air was measured by a thermocouple. The theoretical equation for heat conduction with homogeneous generation of heat given by one term of equation (2) was approximately solved to obtain

$$T_o = T_a + \frac{2QN_\infty}{c\rho} \sum_{n=1}^{\infty} (-1)^n \frac{a^2k}{\kappa\pi^2n^2 - a^2k} \left\{ \exp\left(\frac{\kappa\pi^2n^2t}{a^2} \right) - \exp(-\kappa t) \right\} \qquad (3)$$

where T_o is the temperature at the center of a sphere of radius a, Q is the heat generated in cal/g, and c is the specific heat and ρ the density of the wood. Equation (3) was fitted to the experimental data (Japanese cypress) by adjusting Q, the only unknown. The best fit gave $Q = 32$ cal/g. The rate of generation of heat typically was about 6 cal/g/min. This heat probably arises from the polymerization or further decomposition of the primary decomposition products.

Autoignition

Autoignition was investigated by heating the bottom surface of the sample by hot air. The temperature distribution in the wood and also in the adjacent vapor was measured. The temperature near the wood initially dropped because of heat loss to the wood and perhaps also because of the cooling effect of evolved gases. These gases contained no condensed phases according to light-scattering measurements. Upon ignition the temperature rise occurred first in the vicinity of the surface and then propagated away. A green-blue flame initially formed and rapidly changed to the normal steady-state diffusion flame, green-blue at the base and yellow at the top. The green-blue base contained C_2 and CH bands and only a faint OH band, suggesting that the various hydrocarbons played a significant role in combustion but not H_2.

The temperature distribution at the time of ignition was calculated by equation (1). For a given wood the distributions at ignition for different air temperatures intersected at one point. The temperature at this point was called the ignition temperature, T_{ig}, and the distance corresponded to x_o, the previously-noted hypothetical surface of the wood. T_{ig} was about 490°C for a variety of woods, while x_0 increased from 0.4 to 0.7 mm with increasing heat conductivity (i.e., increasing density) of the wood. The ignition lag is given by equation (1) if $x=O$ and $T=T_{ig}$. The resulting expression was approximated by taking only the first term of the erf term to obtain

$$\tau=\frac{x_o^2}{\pi\kappa}\left(\frac{T_a-T_o}{T_{ig}-T_o}\right)^2 \tag{4}$$

The experimental data fitted equation (4) quite well. The less dense woods have smaller thermal conductivity, heat faster at the surface, and consequently ignite easier.

Ignition by radiation was also studied and used more intense radiation than previous work. Assuming one-dimensional semi-infinite heat conduction, negligible reradiation, and Newton cooling at the wood surface, the temperature at the surface of the wood is given by

$$\left.\begin{aligned} T_s&=T_o+\frac{2I\beta}{\alpha\sqrt{\pi}}\left(1-\frac{\sqrt{\pi}}{2}\beta\right) && \beta<0.4\\ &=T_o+\frac{2I\beta}{\alpha\sqrt{\pi}} && \beta<0.1\\ &=T_o+\frac{I}{\alpha}\left(1-\frac{\sqrt{\pi}}{2}\beta\right) && \beta>1.4 \end{aligned}\right\} \tag{5}$$

where I is the radiation intensity and $\beta=\alpha\,(\kappa T)^{1/2}/K$. The value of α was 0.025 for a variety of woods. The surface temperature for ignition of various woods was about 500°C with a radiation intensity of 15 cal/cm^2/sec but ranged from 1500 to 2000°C with 70 cal/cm^2/sec. The first value agrees with T_{ig} obtained earlier. The high temperatures obtained with the higher radiation flux is possibly due to slow mixing of the gas product with air, i.e., the surface reachs an abnormally high temperature before the critical gas mixture is established. The total heat absorbed by the wood up to the time of ignition generally increased with increasing density of the wood and with increasing radiation. Contrary to general opinion, this total heat is unimportant in ignition kinetics.

Since T_{ig} roughly corresponds to the ignition temperatures of a number of the organic vapor products from the pyrolysis of wood, T_{ig} is taken as the ignition temperature of the gas-air mixture resulting from the thermal decomposition. The author feels that this gas-air mixture is at or near the lean limit, primarily because the hydrocarbon flame bands observed in the blue zone at the base of the steady-state flame do not occur in the combustion of a rich mixture. Since the initial transient flame is also blue, it also presumably is lean. He concludes that autoignition of wood occurs when the surface temperature of the wood reaches about 500°C and involves ignition of the gases generated by decomposition. Simms[1] also proposed this theory but gave an ignition temperature of 525°C. The author questioned previous work wherein ignition temperatures of woods generally were smaller than the present values and varied appreciably with different woods.

Kindled-Ignition

Ignition lag was measured when a Tesla coil spark was applied to the bottom surface of a wood slab. Results were similar to those obtained in autoignition.

Since an external heat source at high temperature already exists, ignition lag in kindled-ignition was interpreted as the time required for sufficient combustible gas to be generated by decomposition of the wood and for these gases to achieve a proper mixture with air. A theory of kindled-ignition of the gas-air mixture in the turbulent layer near the surface of the wood was based upon four relations:

a) temperature distribution

$$\frac{\delta T}{\delta t}=k\nabla^2 t \tag{6}$$

b) thermal generation of decomposition gases, which is approximately given by

$$\frac{dM_1}{dt}=N_\alpha k_o\int_o^a \exp(-E/RT)\,dx \tag{7}$$

where M_1 is the concentration of the gases, a is the thickness of a thin slab of wood undergoing decomposition, k_o is the kinetic collision factor, and E is the activation energy,

c) dissipation of the decomposition gases,

$$\frac{dM_2}{dt}=f(M_1, D, v) \tag{8}$$

where M_2 is undefined (M_1 and M_2 seemingly should be identical), D is a diffusion constant, and v is the velocity of the air at the surface of the wood, and

d) finally, the condition for ignition is

$$H\phi=\int_o^\tau\left(\frac{dM_1}{dt}-\frac{dM_2}{dt}\right)dt \tag{9}$$

where H is the thickness of the mixing layer, ϕ is the critical concentration of the combustible gas mixture, and τ is the kindled-ignition lag.

The author derived an approximate treatment for τ which corresponded to his experimental conditions of constant temperature, enclosed bottom heating, and one-dimensional heat conduction. The temperature distribution was taken as in equation (1) with the erf term expanded to two terms multiplied by a correction factor $1-\epsilon$. The rate of dissipation was taken as equal to the rate of generation multiplied by a constant λ which is less than 1, and RT_a/E was assumed much less than 1. Ignition lag was then deduced from equations (6) to (9) to be

$$\tau=\frac{3\alpha DC}{2K}\,\frac{F_\tau}{(1-F_\tau)^3}\left\{1-\frac{3}{2}(CZ_\tau)+\frac{3}{2}(CZ_\tau)+\;\ldots\right\}^{-1}\exp C \tag{10}$$

where CZ_τ was assumed to be much less than one and

$$\left.\begin{aligned} D&=\frac{H\phi}{N_\alpha k_o\,(1-\lambda)}\\ F_\tau&=\left(1-\frac{T_o}{T_a}\right)\frac{x_o(1-E)}{\sqrt{\pi\kappa\tau}}\\ C&=E/RT_a\\ Z_\tau&=\frac{F_\tau}{1-F_\tau}\end{aligned}\right\} \tag{11}$$

Since F_τ contains τ but varies much slower than τ with T_a, equation (10) becomes

$$\ln\tau\sim\ln B+\frac{E}{RT_a} \tag{12}$$

where B is approximately independent of temperature. The author's experimental data generally conformed with equation (12) for a variety of woods even though his CZ_τ was not much smaller than one. Activation-evener energies derived from equation (12) ranged from 12 to 14 kcal/mol. These values are smaller than observed in thermal decomposition but were observed at a higher temperature range (450-750°C instead of 290-400°C for thermal decomposition), and the decomposition mechanism may differ in the two ranges. Taking ϕ as 10^{-4} g/cc, the mixing layer H is several centimeters thick for Japanese cedar. The author noted that this value seems somewhat large but probably merely reflects the approximate nature of the theory.

Kindled-ignition occurs when the composition of the combustible gas mixture attains a certain critical limit and does not involve a so-called ignition temperature. While there will be a certain lower limit to temperature which establishes the equilibrium condition relating the rates of gas generation and dissipation, this limit is not basic to kindled-ignition. The apparent absence of an ignition temperature distinguishes kindled-ignition from autoignition.

Self-Ignition

The temperature distribution in a spherical sample of sawdust (Japanese cedar) was measured until ignition occurred. The temperature along a radius decreased monotonically in a parabolic manner until the temperature at the center of the sample reached about 210°C whereupon the central portion began to char and its temperature began to rise.

The critical condition for self-ignition was analyzed with the help of the theory of thermal explosion. The result was

$$\delta_c = \frac{QN_a k_o}{K} r_c^2 \left(\frac{E}{RT_a^2} \right) \exp(-E/RT_a) \tag{13}$$

where δ_c is a dimensionless quantity which depends upon the relative heat transfer coefficient h and the shape of the specimen and r_c is the minimum radius for ignition. If h is very large, δ_c tends to 3.32 (sphere), 2.0 (cylinder), and 0.88 (slab). The results generally agree with the previous values [2] but r_c is larger than expected below 100°C.

The time lag for self-ignition was approximately analyzed to obtain

$$\begin{aligned} \Theta_o = {} & \frac{1}{\beta} \left\{ \frac{\mu q_o}{q_o \cos q_o + (\mu - 1) \sin q_o} - 1 \right\} + \sum_{n=1}^{\infty} \frac{2}{\beta} \left(\frac{1}{p_n^2} (\sin p_n - p_n \cos p_n) \right. \\ & \left. + \left[\frac{\mu}{q_o \cos q_o + (\mu - 1) \sin q_o} \right] \left[\frac{p_n q_o \cos q_o \cos p_n}{p_n^2 - q_o^2} \right] \left[\frac{\tan q_o}{q_o} - \frac{\tan p_n}{p_n} \right] \right) \\ & \left(\frac{p_n}{1 + \frac{\mu - 1}{(\mu - 1)^2 + p_n^2}} \cdot \exp\{-(p_n^2 - q_o^2)\tau\} \right) \end{aligned} \tag{14}$$

where Θ_o is the temperature at the center of the sphere $q_o = \sqrt{\beta\delta}$, p_n is the *nth* root of the equation, $\tan q_i = -q_i/(\mu - 1)$, $\mu = \alpha/Kr$ and is the Nusselt number, r is the radius, and $\tau = K/c\rho r^2 t$. The quantity β is chosen so that the first term of the right hand side (which corresponds to $t = \alpha$) is equal to the temperature obtained by Frank-Kamenetsky. Estimations of τ from equation (14) showed fairly good agreement with the experimental results.

Practical Applications

The above results were used to compare the ignitability, self-ignition and fire-prevention measures for cellulosic materials.

References

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2. Gross, D. and Robertson, A. F. *Journal of Research National Bureau of Standards* 64, 413–417 (1958)

Subject Headings: ***Wood, ignition of; Ignition, of wood.***

W. G. Courtney

Buschman, A. J., Jr. (National Bureau of Standards, Washington, D. C.) "Ignition of Some Woods Exposed to Low Level Thermal Radiation" Technical Report No. 1, ONR Contract NAopr 24–60 and OCDM Contract CDM–SR–60–22 (July 26, 1961)

In the radiant panel flame-spread test described in reference 1 flame spreads to surfaces receiving less than the critical intensity of irradiance for ignition by pilot flame as found in uniform flux tests.[2] To study the seeming anomaly three kinds of tests were arranged with the radiant panel always operated at a radiant output corresponding to that of a black body at 670°C.

1) Flame-spread procedure. A 6 by 18 inch specimen with its upper 6 inch edge 4.75 inches away and its long dimension inclined outward at 30° from the vertical radiant panel is ignited at the top by the pilot flame and the downward rate of spread of the flame front is measured.

2) Delayed ignition test. The pilot flame was withheld for varying lengths of time, then applied for 10 seconds and the position of the flame front observed.

3) Uniform flux test. Specimens 2.25 inches square were exposed with faces at various distances (4.25 to 12 inches) from the radiant panel and the time required for ignition by the pilot flame noted.

For (1) and (2), reference 1 reports the intensity of irradiation, I, as a function of distance from the top of the specimen. For (3) similar calibration was accomplished with a blackened copper sheet calorimeter. At 4.25 inches I was 0.890 and at 12 inches 0.342 cal/cm²/sec.

The materials tested—tempered hardboard, maple, red oak, poplar, spruce, and balsa—represented a wide range in density and thermal conductivity. Specimens were thick enough, 0.25 inch, to be considered semi-infinite solids.

Data from the uniform flux test lead to the relations:

$$(I-I_p)t^n=A$$

in which I_p is the critical intensity and t the time for ignition, n and A are constants characteristic of the species, and

$$\begin{aligned}I_p&=4.24\times10^{-1}-8.75\times10^{-4}(K\rho C_p\times10^6)\\ n&=9.75\times10^{-1}-1.20\times10^{-3}(K\rho C_p\times10^6)\\ A&=K\rho C_p[6.90\times10^2-3.15\times10^4(K\rho C_p)^{\frac{1}{2}}]^2\end{aligned}$$

in which C_p is specific heat, ρ density, and K thermal conductivity. I_p varied from 0.265 (tempered hardboard) to 0.417 cal/cm²/sec (balsa).

Surface temperatures at the time of ignition conformed to the relation

$$T_{\mathrm{ign}} = 667 - 0.527\ (K\rho C_p \times 10^6)$$

and varied from 571°C for tempered hardboard to 664°C for balsa.

For intensities exceeding about 1.0 cal/cm^2/sec the time required for ignition is the same in all three tests but for lower intensities ignition occurs sooner in the flame-spread test by a margin that increases as the intensity falls off. For the denser materials such as hardboard and red oak, ignition times in the uniform flux test and delayed ignition tests are about the same but for the less dense materials such as spruce and balsa ignition times in the delayed ignition test fall closer to those for the flame-spread than for the uniform flux test. The deviation between the uniform flux and flame-spread data is a measure of the heat added to the system by the flame itself, both directly to the specimen and by reflection from the radiant panel and the surroundings.

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Subject Headings: *Wood, ignition of, by thermal radiation; Ignition, of wood.*

F. L. Browne

Palmer, K. N. (Joint Fire Research Organization, Boreham Wood, England) "Preventing Fires Sparked by Friction," *Engineering* **190**, p. 92 (1960)

An analysis of 679 fires attributed to friction or impact sparks was made in an attempt to determine what industries are particularly susceptible, what materials are likely to be ignited, and what proportion of these fires are attributable to the use of nonpowered hand tools.

The highest incidence of friction-initiated fires occurred in solid materials, over 60 per cent involving textile and allied fiber industries, cotton alone accounting for 40 per cent of the total. Most of these fires were caused by power-driven machinery, only 4 per cent being traceable to the use of nonpowered hand tools. Of the materials ignited by low-energy impacts, approximately half involved chemically-reactive substances.

Preventive measures recommended were (1) the avoiding of spark formation, (2) prevention of ignition, and (3) prevention of fire spread if ignition occurs.

Subject Headings: *Fires, initiation of, by friction.*

D. Dembrow

II. Thermal Decomposition

Straus, S. and Madorsky, S. L. (National Bureau of Standards, Washington, D. C.) "Thermal Stability of Polydivinylbenzene and of Copolymers of Styrene with Divinylbenzene and with Trivinylbenzene," *Journal of Research of National Bureau of Standards* **65A**, 243–248 (1961)

The authors investigated the thermal stability of copolymers of styrene with divinylbenzene (DVB) and with trivinylbenzene (TVB), and of polydivinylbenzene (PDVB). These were compared with previous results obtained for polystyrene and polytrivinylbenzene.

The previous results had indicated that the degradation of polystyrene occurred by random scission followed by unzipping at the free radical chain ends, and leading to considerable amounts of monomer in the volatile products. The degradation of PTVB on the other hand resulted in very little styrene or TVB. Analysis of the volatiles and residue suggested that the free radicals formed during the pyrolysis of this cross-linked polymer, led to the abstraction of hydrogen rather than unzipping.

In this work the stability of the polymers was determined by pyrolysis for 30 minutes in vacuum. The temperatures used ranged from 350 to 450°C. The volatiles were fractionated and analyzed. The residue was weighed.

PDVB was found to be intermediate in stability between polystyrene and PTVB. In the copolymers it was found that the stability increased with the per cent of DVB, and the monomer yield decreased. At 50 per cent DVB the copolymer behaved in a manner similar to PDVB homopolymer. One copolymer of styrene with TVB (25 per cent) was examined. It was found to be equal in stability to PDVB, but there was an appreciable amount of styrene in the volatiles.

The degradation rates for the copolymer and for PDVB were also determined gravimetrically at a number of temperatures. The maximum rates were used to calculate activation energies. These were not very different from those calculated using the rates at 35 per cent and at 50 per cent volatilization. The values were between 50 and 60 kcal/mole for the copolymers, 65 kcal/mole for PDVB, and from previous work 55 kcal/mole for polystyrene and 73 kcal/mole for PTVB.

The major conclusion is that the presence of DVB or TVB in large amounts and the resultant cross-linking lead to a blocking of the unzipping process, and result instead in the abstraction of hydrogen by the free radicals and consequent carbonization.

Subject Headings: *Thermal degradation, of polymers; Polymers, thermal degradation of.*

R. H. Atalla

Straus, S. and Wall, L. A. (National Bureau of Standards, Washington, D. C.) "Pyrolysis of Linear Copolymers of Ethylene and Propylene," *Journal of Research of the National Bureau of Standards* **65A**, 221–226 (1961)

The authors made thermogravimetric measurements of the rates of thermal decomposition of polyethylene, polypropylene, and four copolymers of ethylene and propylene at temperatures between 390 and 420°C. Their study also included a fully deuterated polyethylene, and an irradiated linear polyethylene.

The data, in most instances, are presented in the form of plots of the rate of volatilization in per cent per minute versus per cent volatilization. The curves for the linear polymers have maxima typical of the linear polyolefins. They are similar to those expected from random degradation of the chains. In the case of the copolymers the maximum rates were lower than would be calculated from the composition and the assumption of the additivity of the rates for polypropylene and polyethylene.

Activation energies for the chain scission reaction were calculated from the maximum volatilization rates. They are 72 kcal/mole for polyethylene and

59 kcal/mole for polypropylene. These high activation energies suggest that C—C bond dissociation may be the initiating step.

A sample of polypropylene with a high ash content was found to be more stable than the pure polypropylene. When the inorganic ash was isolated and added to pure polypropylene it increased its stability. An increase in stability was also observed when the pure polypropylene was dissolved in xylene and subsequently dried and pyrolyzed. The inorganic impurities had little or no effect on the pure polyethylene. Nor was an increase in stability observed when the polyethylene was dissolved in hot toluene and dried.

Mass spectroscopic analysis of the light volatiles from the impure polypropylene gave results similar to those from a nonlinear polypropylene. Those from pure polypropylene were also similar but indicated more of the monomer.

The deuterated polyethylene degraded in a manner similar to that of the hydrogen polymer, but the maxima were slightly lower. The activation energy calculated for the deuterated polymer is 70 kcal/mole.

The behavior of the irradiated polyethylene was similar to that of the branched polymer. The curves have no maxima.

Subject Headings: ***Pyrolysis, of copolymers; Thermal degradation, of copolymers; Polymers, thermal degradation of.***

R. H. Atalla

Wall, L. A. and Straus, S. (National Bureau of Standards, Washington, D. C.) "Pyrolysis of Fluorocarbon Polymers," *Journal of Research of National Bureau of Standards* **65A**, 227–238 (1961)

The authors investigated the thermal stability of a number of fluorocarbon polymers, and some telomers of hexafluoropropylene. The polymers were pyrolyzed for 30 minutes in vacuum, and the loss in weight was determined. The volatiles were fractionated and some of the fractions analyzed. Rates of volatilization were also measured at various temperatures, and the activation energies calculated. The telomers were pyrolyzed in sealed ampules containing some argon. These were eventually opened, and the products analyzed.

Perfluoroamidine polymers: One homopolymer and two copolymers were degraded at temperatures about 500°C. The major component of the light volatiles was tetrafluorethylene. The decomposition rates were initially high, but decreased as the reactions progressed. Soaking the polymers in methanol for extended periods was found to increase the degradation rates.

Polyhexafluoropentyleneadipate: Degradation at about 340°C gave small amounts of light volatiles. The initial rates were high and decreased as the reactions progressed.

Copolymer of tetrafluorethylene and hexafluoropropylene: Pyrolysis between 450 and 540°C gave less light volatiles than pure tetrafluorethylene. The hexafluoropropylene monomer was the major component initially, while at the conclusion of the pyrolysis tetrafluorethylene was predominant. The rates were again higher initially and slower in the later stages of the process.

Copolymers of vinylidene fluoride with hexafluoropropylene and with chlorotrifluorethylene: Three such copolymers were studied between 370 and 400°C. The major component of the light volatiles was hydrogen fluoride. The rate curves had maxima suggesting random degradation.

Polytrifluorethylene and poly 1, 1-difluorethylene: These were degraded between 400 and 420°C. The major component of the light volatiles was again hydrogen fluoride, and the rate curves had maxima. Only trace amounts of the monomers were detected.

Polytrifluorochloroethylene: This was pyrolyzed between 350 and 370°C. The major component of the light volatiles was the monomer. The rate curves had maxima. Photo-induced degradation of this polymer at about 250°C was appreciable. The decay of degradation in the post-irradiation period was reasonably well described by a second order rate expression.

Telomers of hexafluoropropylene: These were degraded between 200 and 400°C. The major product was hexafluoropropylene, together with parafinic and olefinic fluorocarbons with 1 to 6 carbon atoms per molecule.

To summarize, the polymers fell into two groups: the perfluorinated ones were more stable; those containing hydrogen or chlorine atoms were less stable.

Subject Headings: *Pyrolysis, of polymers; Polymers, thermal degradation of; Thermal degradation, of polymers.*

R. H. Atalla

Holmes, F. H. and Shaw, C. J. G. (British Industry Research Association, Manchester, England) "The Pyrolysis of Cellulose and the Action of Flame Retardants. I. Significance and Analysis of the Tar," *Journal of Applied Chemistry* **11**, 210–216 (1961)

This is the first paper in a series that has as its objective the elucidation of the molecular mechanisms of the pyrolytic reactions of cottons. The method of the investigation was to study the pyrolysis of different cottons (including cottons treated with flame retardants) under a variety of controlled conditions. The products that resulted from pyrolysis of cottons in a vacuum and dry air, mainly at 418°C, were first fractionated and then analyzed for (1) infrared absorption spectra and (2) chemical analysis. Analysis of products included tests for tar, carbonyl compounds, acids, and unsaturated compounds. Also, flammability tests of the materials were conducted.

Flame retardants were: (1) a commercial flame retardant finish based on tetrakis (hydroxymethyl) phosphonium chloride together with urea and methylolmelamine (No. 1 Proban finish, Pn 1); (2) a more recent commercial flame-retardant finish (No. 2 Proban finish, Pn 2); (3) a water-soluble commercial flame retardant (B/BA) containing borax (50 per cent w/w) and boric acid (40 per cent w/w); (4) sodium metavanadate. Materials pyrolyzed were: (1) cotton poplin, freed from impurities by scouring and bleaching treatment; (2) cotton Winceyette, purified in the same way as poplin; (3) cotton Winceyette, as (2), but not scoured or bleached; (4) oxycellulose, prepared by oxidation of the cotton poplin with nitrogen dioxide.

The mean results of the pyrolysis are summarized in Table 1. [At a pressure of 4×10^{-4} mm, the volatile products were separated into the following fractions: V_{-190} (volatile at −190°C), V_{-80} (volatile at −80°C but condensed at −190°C), and V_{rt} (volatile at room temperature but condensed at −80°C).] In general, the experiments show that: (1) when flame retardants are present, the pyrolyzed cottons produce less combustible tar, more gases, and more carbonaceous residues; (2) purification of the cotton cellulose causes more tar to be formed on pyrolysis;

(3) the tar formed in the pyrolysis of cotton cellulose consists mainly of levoglucosan, except in the case of oxycellulose; (4) the smaller the yield of tar on pyrolysis of a treated cotton, the more flame resistant has the cotton been made. As an example of the last conclusion, the total amount of tar decreases from 79.3 per cent for Winceyette 1 to 23.9, 21.4, 18.3, 4.1, and 3.2 per cent for the same cloth treated with Pn 1, Pn 2, $NaVO_3$ (2.8 per cent), B/BA or metavanadate (6.8 per cent). The sequence of flammability of these samples is found to be consistent with the amount of tar in the samples. In another test, a mixture of tar and B/BA that had formed products similar to those from cottons treated with B/BA is not combustible when coated on glass tape.

For the case of cotton heated in dry air instead of vacuum, two new factors arise: (1) oxidation of products, and (2) further decomposition of products because of their longer residence time in the hot zone. Consequently, less total tar but more water and more decomposed tar are formed in dry air pyrolysis than in vacuum pyrolysis.

TABLE 1

MEAN RESULTS OF PYROLYSES

(in vaccum unless stated otherwise)

				% Yield (w/w of dry cloth)						
Cotton cloth	Temp., ° C.	Time, min.	No. of expt.	V_{-190}	V_{-80}	V_{rt}	Tar	Char	Dec. tar**	Total
Poplin	418	15	4	0.9	3.2	13.2	76.3	5.2	0.0	98.8
Winceyette 1	418	15	4	1.0	2.2	7.8	77.3	4.0	2.0	94.3
Winceyette 1	318	130	2	1.05	2.1	16.15	64.5	13.2	.0	97.0
Winceyette 1	318	960	2	2.75	4.25	13.6	65.25	10.2	.0	96.05
Winceyette 1	418*	15	4	—	1.55	24.0	26.3	12.75	18.0	82.65
Winceyette 2	418	15	3	4.0	2.5	12.6	54.6	11.5	—	85.2
1 treated with Pn 1	418	285	4	3.6	3.1	30.3	20.5	38.3	3.4	99.2
1 treated with Pn 2	418	260	4	4.4	5.4	27.6	18.2	37.65	3.2	96.45
1 treated with B/BA (8.3% w/w)	418	160	2	6.65	1.8	21.3	4.1	59.25	.0	93.1
1 treated with B/BA (8.3% w/w)	418*	160	5	—	2.0	41.1	2.7	46.4	5.3	97.5
1 treated with $NaVO_3$ (2.8% w/w)	418	30	1	3.5	—	—	18.3	24.3	.0	—
1 treated with $NaVO_3$ (6.8% w/w)	418	30	1	4.0	—	—	3.2	38.6	.0	—
Oxycellulose	418	45	4	3.2	23.3	17.4	30.1	23.6	.7	98.3

* In dry air at atmospheric pressure.

** "Decomposed tar" is the material, insoluble in methanol, formed by the thermal decomposition of some of the tar remaining in the vicinity of the furnace.

Subject Headings: *Cellulose, pyrolysis of, Pyrolysis, of cellulose; Flame retardants, action of.*

J. M. Singer

III. Heat and Material Transfer

Bailey, H. R. (Ohio Oil Company, Littleton, Colorado) "Conduction-Convection from a Cylindrical Source with Increasing Radius," *Quarterly of Applied Mathematics* 18, 325–333 (1961)

In the process of secondary oil recovery by means of underground combustion, air is injected into a porous earth structure. The air will burn with some of the underground fuel and thereby increase the temperature of the surroundings. As an idealization of this problem, injection of air from a cylindrical line source is considered. The air is assumed to move axisymmetrically outward and heat liberation is assumed to occur at the outer cylindrical surface of the advancing air. It is furthermore assumed that heat is transported by conduction through the solid material as well as by convection between the solid and the adjacent gas. The differential equations describing this process are:

$$\frac{\partial^2 T_s}{\partial r^2}+\frac{1}{r}\frac{\partial T_s}{\partial r}-a^2\frac{\partial T_s}{\partial t}+k^{-1}\,\Phi\,(r,t)=k^{-1}h(T_s-T)=\frac{P(t)}{r}\,\frac{\partial T}{\partial r} \qquad (1)$$

where T_s is the temperature of the solid, T is the temperature of the gas, $1/a^2$ is the diffusivity, h is the convective heat transfer coefficient between solid and gas. The function Φ represents the heat source; for the case of heat liberation at the front of the advancing air, Φ is zero everywhere except at the location of the front. The function P is related to the mass flow rate of air.

An injection rate such that the air front advances at a constant velocity is considered first. The equations are solved for the quasistatic condition which is reached for large values of the time and when the solution is given in a coordinate system which is referred to the instantaneous position of the front. In this approximation the cylindrical character of the solution is lost and the solution becomes equivalent to that of a plane source in a semi-infinite medium. The solution is presented in graphical form and the curves clearly indicate the less abrupt decrease in temperature with distance as the heat release rate increases.

The differential equation is then solved again retaining the transient feature of the problem. A constant injection rate and an infinite heat transfer coefficient, h, are assumed. The solution is obtained by superposition of the temperature distribution which results from an instantaneous cylindrical source. A graph for the temperature at the advancing front is given as a function of injection rate for various values of j, where j depends on the parameters of the problem and is related to the ratio of the heat transfer by conduction to that by gas transport. For the range represented by the graph, the assumption of heat transport by conduction leads to an error of only about 20 per cent in the temperature for the higher injection rate shown and to less of an error at lower injection rates.

The present paper emphasizes the mathematical aspects of the problem, and does not discuss in any detail the physical aspects of the problem or the bases for the simplifying assumptions. For these the reader should consult the references given in the paper.

Subject Heading: *Convection, conduction, from cylindrical source.*

R. H. Sabersky

IV. Diffusion Flames

Thring, M. W. (University of Sheffield, Sheffield, England) "Research on Turbulent Diffusion Combustion," *Journal of the Institute of Fuel* 34, 494–502 (1961)

The author reviews work that has been done to bridge the gap between research scientists and applied engineers in combustion chamber design. He outlines briefly two general paths. The first, which is not discussed in detail, involves aerodynamic studies including (1) flow of simplified shapes such as single-fuel particles, (2) isothermal models of combustion chambers and flow of droplet or particle clouds, and (3) models of actual combustion chambers. The second path, combustion studies, is the main subject.

The author separates work in the combustion field into three "piers" which support the "bridge" between pure scientists and applied engineers. In the first "pier" he includes work on laminar premix flames such as the flat flame of Egerton, particularly valuable in the determination of molecular transport phenomena and spectroscopy. He also mentions work on the burning of single particles or droplets of fuel as belonging to this first "pier," the closest to pure scientists. Results of this work have led to an appreciation of some of the rate-determining processes in industrial flames but have not clarified such problems as physical versus chemical rate-determination for pulverized coal combustion.

Pier III, the one closest to the combustion-chamber designer, is characterized by flames of the same rate-determining steps as industrial ones, but ones which are not concerned with production. The flame must be geometrically and dynamically similar to the industrial flame in order to insure the correct turbulence and recirculation. Some geometric simplification such as in the IJmuiden Flame Radiation Furnace is satisfactory as long as the over-all thermal load is simulated. Scaling-down linear dimensions by ½ to ¼ is often permissible without compromising the necessary simularities. The aims of studies of this type are: first, development of formulae with which soot formation and luminous radiation can be predicted and controlled; second, the establishment of the factors involved in governing flame length and heat release in turbulent diffusion "fluid-atomized" flames of volatile fuels; and, third, the determination of the factors involved in the controlling of temperature and rate of burning of powdered coal.

The work discussed under "pier II" is the experimental link between the simplest possible flames of "pier I" and the extremely complex ones of "pier III." This link is the study of the flame consisting of a cloud of droplets, particles, or vapor, the history of which can be controlled with respect to mixing with air and combustion products and heat extraction. These flames, by proper choice of conditions, can represent characteristics of the flames of "pier III." Work with the homogeneous reactor of Longwell and the controlled-mixing-history flames used at Sheffield are examples of this link between the simple and the complex. Semi-empirical formulae describing the rate of burning of pulverized anthracite, as well as other flames, are being developed and will provide a means for designing much improved experimental burners (pier III) and, later, actual industrial combustion chambers.

With respect to practical applications which have arisen from research in the combustion field, the author cites a number of impressive examples. Work on jet entrainment and flame length has led to the conclusion that the steam or compressed air used in open-hearth oil burners and similar flames serves mainly to provide high jet momentum. Formulae have been developed for the jet momentum obtained when full use is made of high-pressure steam by expanding it adiabatically through a convergent-divergent nozzle. Efficiencies of up to 90 per cent can be hoped for with designs utilizing this concept. Information, obtained at IJmuiden and Sheffield showing that addition of carbon black to oil increases significantly the radiant-heat transfer, has been successfully applied to the design of an open-hearth furnace in the United States with an appreciable increase in output.

Additional applications to industrial design have involved the use of twin burners in the open-hearth furnace, the use of combustion-oxygen, the benefit of an extra 100°C of air-preheat, and a reduction of the amount of infiltrated air. The author points out that the design information obtained through the work discussed in this paper has been a major factor in increasing open-hearth output from 10 tons per hour to 65 tons per hour over the past 15 years.

Subject Headings: *Combustion, turbulent diffusion; Combustion, chamber models; Models, of combustion chambers.*

F. Falk

Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "Buoyant Diffusion Flames," *Combustion and Flame* 4, 382–383 (1960) (Letters to the Editor)

In the case of a fuel issuing from a jet at high velocity the resulting momentum field is determined almost completely by the jet initial momentum. The result is that, for turbulent flow, flame length is independent of volumetric fuel flow and determined solely by orifice size. For piled wood or oil tanks burning in air, the momentum field is determined by buoyant effects and flame height can be predicted to be dependent upon volumetric fuel rate and fire dimension, i.e., base. Experimental evidence is set forth which is correlated very well by a buoyancy parameter. The Reynolds number range was from 2000 to 14,000.

In view of his findings the author questions the explanation offered by Blinov and Khudiakov[1] of their results, namely, that their system was acting as a not fully turbulent fuel jet. The velocity field in the referenced work was dominated by buoyant effects as was the author's.

Reference

1. Blinov, V. I. and Khudiakov, G. W. "Certain Laws Governing Diffusive Burning of Liquids," *Academiia Nauk, SSSR Doklady* 113, 1094–1098 (1957) (See *Fire Research Abstracts and Reviews* 1, No. 2, 41–44)

Subject Headings: *Flame, buoyant diffusion; Diffusion flame.*

H. N. McManus, Jr.

Essenhigh, R. H. and Fells, I. (University of Sheffield, Sheffield, England) "Combustion of Liquid and Solid Aerosols," *Discussions of the Faraday Society, The Physical Chemistry of Aerosols* 30, 208–221 (1960)

The word "aerosol" in the title comprises particle sizes from 1 micron to 1 centimeter. For this range Figure 1 presents burning times of various liquids and solid fuels plotted versus logarithm of particle diameter. Basis of discussion is the "burning constant" defined as $K = s/3qDp$ in sec/cm^2, where s = density of fuel at particle temperature; q = that of air, D = coefficient of oxygen diffusion in nitrogen, the latter two quantities near flame temperature, i.e., above 1000°C; p = oxygen partial pressure in ambient atmosphere. Values of K are listed in Table 1, referring to Figure 1, for a number of liquids (ethanol, tetraline, n-heptane, kerosine, gas-oil) and solids (graphite, coke residues from pitch creosote, heavy fuel oil and production oil, pulverized coals of low and high volatile content). Table 2 compares experimental and calculated K-values for 10 coke residues of different origin. On the average, calculated values are about 50 per cent greater than experimental. The discrepancy is attributed to swelling.

For the "liquid system" the diffusion-controlled burning time is given by Nusselt's equation: $t_b = FKd^2$, where $F > 2$ depends on the fractional excess of air; d = initial drop diameter. However, the authors believe that validity of this relation is restricted to diameters above 8 microns. They state that for smaller drops the heterogeneous nature of the flame vanishes, the drops evaporating completely before reaction starts. No attempt is made to correct for this limitation. On the other hand, thermally-controlled burning according to Godsave's model (Figure 2) is also considered. Here, the reaction zone distance from the evaporating surface is supposed to diminish with decreasing drop radius. However, this assumption is contradicted by Wise and coworkers [1] who advance arguments for a constant distance and by Miesse's theory [2] which predicts an increase of flame/drop radius ratio with decreasing drop size.

In the "solid system," reaction in pores is considered as a characteristic. Pertinent expressions of pore-resistance for reactions of different orders (Wheeler, Popov, Bleyholder, and Eyring) are given. Effects of forced convection due to turbulence are briefly discussed. Under the headline, "rate control," the author claims that for small particles, second order deviations from Nusselt's law are significant (Figures 3 and 4) because the rate of combustion becomes kinetically governed.

In the reviewer's opinion, Nusselt's equation implies physically impossible, i.e., infinite, rates of diffusion if applied to particles burning down to zero diameter. Therefore, chemical control should be taken into account unless, as is most probably the case, the reaction zone distance from the fuel surface remains finite.

References

1. Wise, H. and coworkers, *Jet Propulsion* (March 1958)
2. Miesse, C. C. "On the Combustion of a Liquid Fuel Spray," *Sixth Symposium (International) on Combustion,* New York, Reinhold Publishing Corporation, 732–738 (1957)

Subject Headings: *Combustion, of aerosols; Aerosols, combustion of.*

H. M. Cassel

Williams, F. A. (Harvard University, Cambridge, Massachusetts) "On the Burning Rate of a Fuel Droplet in an Oxidizing Atmosphere," *Combustion and Flame* **5**, 207–208 (1961)

The theory of burning fuel droplets in oxidizing atmospheres affords the following equation for the burning rate

$$\dot{m} = 4\pi\gamma_\ell(\bar{\lambda}/\bar{C}_p)\ln\left\{1+\frac{\bar{C}_p(T_\infty - T_\ell)+QY_{o,\infty}}{L}\right\} \qquad (1)$$

In this equation, $\dot{m}$ is the mass of fuel per second leaving the droplet, γ_ℓ is the radius of the droplet, $\bar{\lambda}$ is the average thermal conductivity of the gas surrounding the droplet, $\bar{C}_p$ is the average specific heat at constant pressure of this gas, T_∞ is the temperature of the oxidizing atmosphere far from the droplet, T_ℓ is the temperature at the surface of the droplet, Q is the heat of reaction per unit mass of oxidizer consumed, $Y_{o,\infty}$ is the mass fraction of oxidizer in the oxidizing atmosphere and L is the heat of vaporization per unit mass of fuel evaporating. This equation is derived assuming spherical symmetry, quasi-steady-state flow, no radiative heating of the droplet, thermal diffusion. Natural convection may be neglected, and there is a single over-all rate-controlling reaction step. It is also assumed the mass fraction of the fuel is zero at infinity and the mass fraction of the oxidizer at the droplet surface ($Y_{o,\ell}$) is zero. If the chemical reaction rate does not approach infinity at some point, the latter may not be true. If $Y_{o,\ell} \neq O$, then the following equation may be derived

$$\dot{m} = 4\pi\gamma_\ell(\bar{\lambda}/\bar{C}_p)\ln\left\{\frac{L+\bar{C}_p(T_\infty - T_\ell)+QY_{o,\infty}}{L+QY_{o,\ell}}\right\} \tag{2}$$

That is, increasing $Y_{o,\ell}$, which is equivalent to decreasing the reaction rate, decreases the burning rate. Estimates of $Y_{o,\ell}$ indicate it is so small the change in $\dot{m}$ will be unobservable. In this case, equation (2) may be expanded in powers of $Y_{o,\ell}$. To first order, this results in a correction to the R.H.S. of equation (1) of an additive term $\left(-\frac{4\pi\gamma_\ell\bar{\lambda}Q}{\bar{C}_p L} Y_{o,\ell}\right)$.

Subject Headings: ***Fuels, droplets, burning rates of; Droplets, burning rates of; Burning rates, of fuel droplets.***

P. R. Ryason

Essenhigh, R. H. (University of Sheffield, Sheffield, England) "Predicted Burning Times of Solid Particles in an Idealized Dust Flame," *Journal of the Institute of Fuel* **34**, 239–244 (1961)

The paper extends the conventional treatment of diffusion-governed burning times to the possibility of dependence on the rate of chemical reaction. The lifetime of (carbon) particles in a monodisperse dust flame, burning in air, is represented by the equation:

$$t_b = \frac{\sigma}{p}(F_D K_D d^2 + F_C K_C d)$$

Here σ = density of fuel; p = ambient oxygen concentration; d = initial particle diameter; $K_D = \frac{1}{3}\rho D$; ρ = density of air; and D = oxygen diffusion coefficient in nitrogen, both near flame temperature T, i.e., above 1000°C; $K_C = (4/3)$-$(2\pi RT/M)^{-\frac{1}{2}} \exp(E/RT)$ with R = universal gas constant, M = mole weight of oxygen, E = activation energy for chemisorption of oxygen on carbon; F_D and F_C, both >2, are functions of excess air alone, graphically represented.

This equation implies that the specific reaction rate above 1000°C is of first order with respect to oxygen concentration, whether reaction is diffusionally or kinetically controlled, or involves burning in pores of the solid. Lifetimes computed according to the above equation are plotted against logarithm of particle diameter for 10 per cent air-excess in flames, and for infinite excess in the burning of isolated particles. However, the value assumed for the activation energy E is not given, so that it is difficult to form a judgment regarding deviations from the Nusselt "square law" that the author claims to be significant.

The main contribution of the paper lies in the consideration of the dependence of the diffusional term on the thickness of the boundary layer around particles. This might be reduced by microturbulence that will scavenge the film. The maximum percentual decrease in lifetime was calculated as close to 90 per cent, this percentage being relatively insensitive to excess air and to particle size over the range 10 to 100 microns. However, since scavenging is unlikely to be complete, the probable decrease in burning time may be less than 50 per cent. This figure is in agreement with experiments by Atkins.[1]

Essenhigh's treatment is open to the criticism that it considers the burning of carbon as a one-step reaction, i.e., $C+O_2=CO_2$. Blyholder and Eyring[2] have convincingly shown that in the range from 600 to 800°C, the heterogeneous reaction yields exclusively CO. At higher temperatures this should be true *a fortiori.* Coffin and Brokaw[3] have developed a more realistic model of carbon combustion in which CO originates from the Boudouard reaction at the solid surface due to back-diffusion of CO_2 that forms in the oxidation of CO at a distance, L, from the solid. Accordingly, the oxygen diffusion rate-determining diameter is $d+2L$, and greater values of the burning time result than estimated by Essenhigh.

References

1. Atkins, B. R., *Fuel* 29, 76 (1950)
2. Blyholder and Eyring, *Journal of Physical Chemistry* 61, 682 (1957)
3. Coffin and Brokaw, *NASA Technical Note 3929* (1957)

Subject Headings: *Particles, burning rates of; Burning rates, of particles.*

H. M. Cassel

Fleischer, H. O. (Forest Products Laboratory, U. S. Forest Service, Madison, Wisconsin) "The Performance of Wood in Fire," *Forest Products Laboratory Report No. 2202* (November 1960)

This is a general review of current knowledge of the combustion of wood and wood structures. The author points out that fire often causes greater structural damage in nonwood buildings that are more quickly affected by heat from the burning contents. Building contents and furnishings are often primary contributors to serious fire damage regardless of structural material and design. Heavy timber construction often survives fire because wood burns slowly, is a good insulator, and retains most of its strength until actually consumed by the fire.

Tests conducted by the Forest Products Laboratory to determine characteristics of ignitability, flame spread, and fire penetration of building materials are described. The results of these tests on typical wood products are given. Suggestions are made for the best use of natural and treated wood in construction, based on present knowledge of how wood burns.

The author decries the lack of basic research in combustion of cellulosic materials. The problem is a chemical one and he predicts that future research will provide treatments for wood that will interrupt or modify the burning process to reduce production of flammable tars and gases.

Subject Headings: *Wood, combustion of; Combustion, of wood.*

O. P. Cramer

V. Combustion Principles

Lawson, D. I. (Joint Fire Research Organization, Boreham Wood, England) "Trends in Fire Research in the United Kingdom," *The Institution of Fire Engineers Quarterly,* **XXI**, 220–240 (1961)

The organization and research activities of the Joint Fire Research Organization in the United Kingdom are outlined in this paper. This organization is a joint venture between government and insurance and was organized specifically for conducting research on the prevention of loss of life and property in fire. Its research program is dictated primarily by information obtained from a continuous watch, by the Fire Brigades, on fire patterns throughout the country, and by the needs of government and industry. Information obtained by the Fire Brigades is sorted as to cause, type, and size of fire, and the direction of research activities is determined to a large extent by these findings.

In carrying out its research program, the organization is divided into five sections. The first of these is the Operational Research and Intelligence Section whose primary concern is collecting and processing as much information on fires as possible. This information is obtained through the Fire Brigades. Normally, reports of about 120,000 fires are processed per year, one-half of which involve buildings. Results of these reports show that about one-half of all fires in buildings are caused by use of electricity, oil, gas, or solid fuels for purposes of heating, and the number of fires associated with each fuel depends to a large extent on the way it is used. Major research is concerned with electricity and oil.

The Ignition and Growth Section is concerned primarily with growth, since conditions for ignition are fairly well understood. A survey of time-temperature histories of a large number of fires has shown that the first few minutes are the most important in determining how rapidly the fire will spread and how much damage will be done. Although sprinkler systems in large factories offer the best protection, roof ventilation systems are of great importance in removing heat and smoke so that fire brigades can fight the fire more effectively.

In the Building Materials and Structures Section, the major emphasis is on tall buildings and the effect of fire on the structural strength of various materials. Means of escape from such buildings is also being investigated with particular emphasis on the spread of smoke and toxic gases on stairways and landings.

In the Extinguishing Materials and Equipment Section, considerable research is being done on the effective use of water in extinguishing flames, since water is the most commonly used fire-extinguishing agent. Dry powder extinguishers are also being investigated and the most effective salt is being sought. Studies are in progress on how to prevent aggregation of powders using a minimum of flowing agent. Survival of oil-tanker crews is also being investigated. Findings show that by spraying a canopy in the life boat with water at a rate of 460 liters per minute it is possible to hold the temperature under the canopy below 50°C for a period of 5 minutes while the boat moves through a sea of burning oil.

The Chemistry and Chemical Engineering Section is concerned with industrial hazards such as dust explosions, flame traps, and venting of ducts. Experiments are underway to use a modified jet engine to generate an inert atmosphere for use in fire fighting. The engine is capable of generating 1500 cu m/min of inert gas, an increase of 200 over conventional systems.

The Joint Fire Research Organization is now in its fifteenth year of service.

Recently, other countries have begun participating in this endeavor. Only by international cooperation will it be possible to make rapid progress against one of man's deadliest enemies—fire.

Subject Heading: ***Fire research, in United Kingdom.***

I. R. King

Langdon-Thomas, G. (Joint Fire Research Organization, Boreham Wood, England) "The Science of Fire Protection. Structures, Materials and Their Resistance," *The Times Review of Industry* (October 1960)

The author presents an informative discussion on materials of construction, and their characteristics with respect to fire resistance. He points out that organic, combustible materials can not be made noncombustible by impregnations or surface coatings.

Four classes of fire hazard of materials are defined as follows:

Class I, consisting of materials such as plasterboard having a very low rate of flame spread in combustion.

Class II, materials such as resin-bonded paper and fabric, having a low rate of flame spread.

Class III, materials such as wood timber and plywood of density greater than 0.4 gm/cc, having a medium rate of flame spread.

Class IV, materials such as fiberboard and wood of density less than 0.4 gm/cc, having a rapid flame spread rate.

The classification of a given material may be altered to a less hazardous category by impregnation or coating; however, the effect is lost once the material is involved in a fully-developed fire. The British Standard 476, Part 1, 1953, is referenced in discussing fire resistance of structural elements, where structural strength under heating is a critical factor in determining fire resistance. Properties of various materials are discussed. For example, the temperatures (550 and 250°C respectively) are cited, above which steel and aluminum alloy structural members can not be expected to support their design loads. The importance of research, such as that carried out at the Fire Research Station, Boreham Wood, England, is discussed. For example, fire-resistance standards must be developed such as will not unduly restrict the development of new and more economical materials of construction, and model studies must be exploited in order to enable study of the many factors concerned in improving fire safety in buildings.

Subject Heading: ***Fire resistance, of materials.***

J. E. Malcolm

Eckhaus, W. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "Theory of Flame-Front Stability," *Journal of Fluid Mechanics* **10,** 80–100 (1961)

The stability of a plane flame front in laminar flow is a problem of unsteady dynamics of a fluid in which heat conduction, multicomponent diffusion, and complex reactions resulting in heat transfer take place. Much experimental evidence is available on the behavior of distorted flame fronts. Theoretical studies, however, have failed to produce a satisfactory explanation of the observed phenomena.

Experimentally, Markstein has shown, with a series of hydrocarbon fuels premixed with air, that in a large number of cases the flame has a cellular structure. The plane flame front breaks down into small cells which remain in the plane of the original flame, but which dance around and oscillate. With the exception of methane as a fuel, practically all fuels produced cellular structure for rich mixtures, but no breakdown occurred for lean mixtures leaving the flame planar.

Thus, the transition from stable to unstable flames occurs at the stoichiometric composition. Landau's theory does not explain the experimental evidence.

Eckhaus uses a highly idealized model of the flame structure in that he employs the concept of thermal flame propagation. Thus, the flame zone is composed of two regions (preheat and burning). The rates of reaction in the preheat region are neglected. In the burning zone, Eckhaus assumes that the rates of reaction are very high, leading to a very thin region, and that the rate of reaction can be approximated by a constant which is not temperature dependent. The boundary between the two zones is given by a fictitious ignition temperature which is assumed to be close to the final flame temperature.

Next, he considers that the flame is slightly curved which allows the use of a one-dimensional flame structure with the addition of some small perturbations. Heat conduction and diffusion are changed which, in turn, affect the local composition and rate of heat release in the burning zone. In the following steps, Eckhaus sets up the various equations for diffusion and heat conductivity. After imposing the model of the combustion mechanism and defining the perturbation quantities, he linearizes the equations for them.

A formula for the perturbation of the flame-propagation velocity is derived. It depends on the curvature of the flame and on the rates at which the fluid velocities change at the flame boundary. The coefficient of heat conductivity and the various coefficients of diffusion greatly affect the flame stability. Estimating certain parameters, Eckhaus shows that the theoretical results agree with the general trend of the experimental data, which is an advancement compared to previous theoretical attempts.

Subject Heading: ***Flame front, stability of.***

L. E. Bollinger

Adler, J. and Spalding, D. B. (Imperial College, London, England) "Flame Propagation by Non-Branching Chain Reactions," *Combustion and Flame* **5**, 123–134 (1961)

A steady, one-dimensional laminar flame was considered, whose mode of propagation was determined by the following reaction scheme:

(i) $A \rightarrow 2B$ (radical generating)
(ii) $A + B \rightarrow B + D$ (chain propagating reaction)
(iii) $tB \rightarrow D$ (chain breaking)

subject to the following assumptions:

(a) Ignore (i) compared to (ii) as destroyer of A
(b) Ignore effect of (i) on temperature
(c) Ignore (iii) completely

Analytical solutions to the conservation equations for particular systems of reaction-rate functions were determined in two ways: (1) Assume for the dimensional temperature gradient and radical concentration, analytical functions of the dimensionless temperature which satisfy the boundary conditions. The corresponding rates of consumption of reactant A, θ_A, and generating rate of product B, θ_B, were determined by direct substitution. Typical reaction-rate functions θ_A and θ_B, as well as the dimensionless temperature gradient and radical concentration, were plotted against the dimensionless temperature. The second approach to the solution of the conservation equations was to consider simplified functions for θ_A and θ_B for which an analytical solution of the energy and continuity equation was possible. The eigenvalues were plotted against the centroid of the normalized reaction-rate function, τ_A, with the temperature centroid, τ_B, of θ_B as a variable. The centroid was previously shown to be an important characteristic for single-step reactions.

Approximate solutions, based on the centroid rule, assumed that the radical concentration for non-branching chain reactions was a monotonic function of the temperature and rises from zero to an upper value as the dimensionless temperature increases from zero to unity. This approximate solution was applied to the hydrazine decomposition flame.

The two exact solutions gave distinct eigenvalues, λ, versus τ_A relationships for fixed values of τ_B, the agreement becoming worse as τ_B approached unity. It was concluded that for non-branching chain reactions, the centroids of the reaction rate curves were of less dominant importance than with single-step reactions. The approximate solutions fell above and below the corresponding λ versus τ_A relationships obtained from the exact solutions.

Subject Heading: *Flame, chain propagation of.*

L. A. Povinelli

Bonne, U., Grewer, T., and Wagner, H. G. (University of Göttingen, Göttingen, West Germany) "Measurements in Reaction Zones of Hydrogen-Oxygen and Methane-Oxygen Flames," *Zeitschrift für Physikalische Chemie* NF **26**, 93–110 (1960)

In a flat-flame burner (diameter 11.5 cm) operating at pressures from 1 to 20 mm Hg the authors describe measurements of temperature and OH-concentration in H_2—O_2 and CH_4—O_2 flames. The temperatures are determined by means of a Pt—Pt, Rh thermocouple (inside a quartz capillary) which is heated to compensate for heat losses [1] and by measurements of the rotational temperature of the OH radical. In addition the OH radical concentration is evaluated by absorption spectroscopy. The determinations are carried out at different pressures but at constant mass flow rate of unburnt gas and therefore varying flame velocity.

From the measured rate of change of OH concentration with distance above the burner, the rate of formation of OH is computed taking into account diffusion $\left[D_{OH}\cdot P_{mm\,Hg}=300\left(\frac{T}{T_0}\right)^{3/2}\right]$. Good agreement is observed between the temperatures measured spectroscopically and with the thermocouple. As observed by others the peak in the OH emission curve does not coincide with the maximum in the unexcited OH concentration. Rather the OH emission intensity due to OH* is approximately proportional to the rate of formation of OH (in the ground state). Some estimates are made of the ratio of the rate of formation of OH* (R_{OH^*}) to that of OH (R_{OH}). The data yield a value of $R_{OH^*}/R_{OH}\simeq 10^{-6}$. In hydrocarbon-air flames $OH^*(^2\Sigma)$ may be formed[2] by $CH+O_2=CO+OH+156$ kcal; in H_2—O_2 flames, three-body collision processes may play an important role.[3]

References

1. Berkenbusch, F. *Wied. Ann.* 67, 649 (1899)
2. Gaydon, A. G., and Wolfhard, H. G. *Fourth International Symposium on Combustion,* Baltimore, p. 211 (1953)
3. Kaskan, W. E. *Journal of Chemical Physics,* 31 944 (1959)

Subject Headings: ***Flame, reaction zones of hydrogen and methane; Temperature, in hydrogen and methane flames.***

H. Wise

Yang, C. H. (Convair Scientific Research Laboratory, San Diego, California) "Burning Velocity and the Structure of Flames Near Extinction Limits," *Combustion and Flame* **5**, 163–174 (1961)

This paper is another in a series whose purpose is to obtain a theory which can be applied to flammability limits, quenching distances, and flame velocities of premixed flames. Since all flames lose heat to their surroundings, the model proposed is a non-adiabatic one which for very small heat losses reduces to the idealized adiabatic model.

Recent contributions to the theory of non-adiabatic flame theory have been made by a number of authors.[1, 2] In a previous paper[3] the author used the Gaussian error function as an approximation to the flame profile, and obtained flame-extinction limits from a one-dimensional mathematical model. In the present paper solutions are obtained through the use of an analogue computer.

A reacting medium ($A+B\rightarrow$Products) is assumed to flow in an infinitely long tube. The tube wall is assumed to be kept constant while a flame exists in the tube establishing steady-state temperature and concentration profiles. Neglecting pressure variations and the kinetic energy of flow, the energy equation and the two diffusion equations are formulated. All three equations include a rate-function term, while the energy equation, in general, has a heat-loss term.

The upstream boundary conditions express the fact that the temperature of the gas is equal to the wall temperature, the temperature gradient is zero, and the concentration of each reactant is unity. The downstream boundary conditions are: the gas temperature is equal to the wall temperature, the temperature gradient is zero, and the concentration gradients are zero. For an adiabatic flame, in addition to the above conditions, the heat-loss term in the energy equation becomes zero.

The rate-function term is an Arrhenius type of rate function. Calculations are made for the propane-oxygen reaction. Average values of the specific heat and thermal conductivity are used. Calculations are made for three values of the Lewis number, $D\rho_c/k$, where D is the diffusion coefficient, ρ is the density, c is the specific heat, and k is the thermal conductivity. The problem is to find solutions of the three equations subject to the two boundary conditions. This will only be possible for certain particular values of the mass flow G. Thus, the parameter G, and hence the burning velocity become solutions of the equation which the computer will seek.

Curves are shown giving the temperature, concentration, and heat-release pattern for propane-air flames at atmospheric pressure. The flames are adiabatic flames, and burning velocity (40 cm/sec) is in good agreement with the experiment.[4]

The non-adiabatic case near the quenching limit of the flame is calculated and is in good agreement with the experiment. The lower values of burning velocity may be associated with the minimum ignition energy.

Heat-release curves are presented from which the flame depth can be estimated. The flame depth is quite dependent on whether or not the conditions are near a quenching condition.

References

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3. Berlad, A. L. and Yang, C. H. *Combustion and Flame 4,* 325 (1960)
4. Bootha, J. P. and Spalding, D. B. *Proceedings of the Royal Society A225,* 71 (1954)

Subject Headings: ***Flame, structure of; Burning rates, of flame near limit.***

W. C. Johnston

Seakins, M. (Oxford University, Oxford, England) "Peroxides and Peroxy Radicals in Propane Oxidation," *Proceedings of the Royal Society* **A261,** 281–291 (1961)

Consideration of a reaction scheme for the oxidation of hydrocarbons based on the usual form of peroxide mechanism has aided to interpret the reaction mechanism in the "low-temperature" and in "higher-temperature" regions. The essential steps in the reaction were taken as:

$$\begin{array}{rl}
RH+O_2\rightarrow R\cdot+HO_2\cdot & (1)\\
R\cdot+O_2\rightarrow RO_2\cdot & (2)\\
RO_2\cdot+O_2\rightarrow \text{end of chain} & (3)\\
RO_2\cdot\rightarrow \text{end of-chain} & (3')\\
RO_2\cdot+RH\rightarrow ROOH+R\cdot & (4)\\
ROOH\rightarrow RO\cdot+OH\cdot\rightarrow R'CHO+R''+OH\cdot & (5)\\
ROOH\rightarrow \text{end of chain} & (6)\\
R\cdot+O_2\rightarrow \text{end of chain} & (7)\\
R\cdot\rightarrow \text{end of chain} & (7')
\end{array}$$

Assuming that the reaction is past the induction period $[K_1(RH)(O_2)]$ plus other assumptions and simplifications, it was shown that

$$\frac{\text{rate}}{(\text{total peroxide})}\sim\frac{C(RH)}{\dfrac{\Sigma K_7[\Sigma K_3+k_4(RH)]}{k_2(O_2)}+\Sigma K_3} \qquad (1)$$

This relationship indicates the following effects on the ratio of rate/(total peroxide):

1) The ratio is proportional to (RH), when ΣK_3 is large (Reaction steps 3 and 3′)

2) The ratio is either proportional to, or independent of (O_2) depending on the form of ΣK_7, as ΣK_3 gets close to zero.

3) The ratio is reduced, if the addition of a salt as KCl or KF causes destruction of $R\cdot$ or $RO_2\cdot$, i.e., increases ΣK_7 or ΣK_3.

4) The ratio is unchanged, if the salts destroy the peroxide molecules, since the rate and (peroxide) are reduced in the same proportion.

Initial tests with propane/oxygen (60mm/120mm) from 284 to 430°C and using a peroxide initiator in the low temperature region (ca. 280 to 330°C) validated the use of ρ max. in subsequent studies, since ρ max. (maximum pressure rise per unit time) and Φ[net branching factor, defined as $d(\ln\Delta p \text{ init.})/dt$] behaved in a near parallel fashion. In plots of logarithms of these functions versus 1/T°K, both functions possessed the sinusoidal form peculiar to hydrocarbon oxidations and passed through respective maxima and minima values at 327 and 382°C. Subsequent studies were made to determine:

1. The relation of reaction rate (ρ max.) to reactant concentrations.

Oxygen was varied between 0 to 400 mm at propane levels of 100, 140, and 200 mm and propane was varied between 0 to 400 mm at oxygen levels of 50 and 100 mm.

2. The effect of potassium chloride and fluoride surfaces on reaction rate (ρ max.).

A propane/oxygen (100 mm/200 mm) mixture was studied from ca. 280 to 430°C for both salts. In addition, at 280°C, (O) was varied from 0 to 400 mm at a (PrH) of 200 mm with a salt-coated and uncoated Pyrex vessel.

3. The relation of reaction rate to aldehyde concentration.

A PrH/O_2 (100 mm/160 mm) mixture was studied at 280°C.

4. The relation of reaction rate to peroxide concentration.

Propane/oxygen mixtures of 100/160, 100/300, 150/160, and 150/300 and propane/oxygen (150/160 and 150/300) in KCl-coated vessels were studied to relate total peroxide and aldehyde peroxide with reaction rate at 280°C. In addition, the influence of temperature on the relation of ρ max. and peroxides was determined from ca. 280 to 372°C.

Since, generally, a linear relation existed between rate and peroxide concentration, the ratio of rate/(peroxide) proved convenient to draw conclusions of the studied systems. In terms of this ratio, equation (1), interpretation of the results at 280°C were:

1) The ratio is independent of (O_2) but proportional to (PrH); i.e., there is a competing degradation of $RO_2^{\cdot}$ indicating that the nonchain destruction of peroxy radicals is important,

2) The rates are much lower in the presence of KCl and KF, but the kinetics are similar to the uninhibited system,

3) The ratio is almost unaffected by KCl indicating inhibitory action by destruction of peroxide molecules rather than radicals. In addition, when considering the decay in ρ max. in the region of 330 to 380°C, three factors may play a role in the decay. Two factors, the destruction of $RO_2^{\cdot}$ and, by a cited analogy, increasing temperatures may progressively destroy ROOH. These factors will alter respectively the C(RH) and $[\Sigma K_3 + k_4(RH)]$ of equation (1). In addition, if predominance of ΣK_3 over ΣK_7 at 280°C is reversed at the higher temperatures, R· will be increasingly destroyed by oxygen leading to the rise in the production of olefins.

Subject Headings: *Propane, oxidation of; Oxidation, of propane.*

R. A. Gorski

Palmer, K. N. and Tonkin, P. S. (Joint Fire Research Organization, Boreham Wood, England) "The Flammability Limits of Moving Mixtures of Propane and Air," *Journal of Applied Chemistry* **11,** 5–7 (1961)

This work extends our knowledge of the lower and upper flammability limits of gas mixtures flowing in horizontal tubes under both streamline and turbulent conditions. For propane/air mixtures under static conditions, the lower limit, between 2.0 and 2.25 per cent propane, corresponded to that of other investigators. For moving mixtures, the lower limit dropped to 1.75 to 2.0 per cent propane, then rose to the original value as the rate of flow was increased to over 400 cm/sec. Simultaneously, the upper limit increased and then decreased but remained at all times within static limits measured elsewhere, of 9.5 per cent propane for upward propagation in an open vertical tube, to 7.3 per cent for propagation in a large closed globe.

Subject Headings: *Propane, flammability limits of; Flammability, of propane.*

G. S. Cuff

McKellar, J. F. and Norrish, R. G. W. (University of Cambridge, Cambridge, England) "The Combustion of Gaseous Methyl Iodide Studied by Flash Photolysis and Kinetic Spectroscopy," *Proceedings of The Royal Society* **A263,** 51–57 (1961)

A spectrographic study of the combustion of gaseous methyl iodide initiated by flash photolysis was undertaken to elucidate the reaction between oxygen molecules and methyl radicals. Also, some observations were made of the reaction between iodine atoms and oxygen molecules.

When an equimolar mixture of methyl iodide and oxygen (at a total pressure of 1 cm Hg) is flash-ignited, an explosive reaction results. The spectrum of methyl iodide is intense at a time delay of 0.03 ms (milliseconds) following the flash but is no longer present at 0.095 ms. The spectrum of OH appears at about 0.20 ms, reaches maximum intensity by 0.4 ms, and disappears by 4.8 ms. At 0.03 ms some additional structure is present which could be part of the formaldehyde spectrum; this structure does not appear at longer time delays. The I_2 spectrum is very weak at 0.03 ms but after 5 ms it becomes stronger, reaching an intense state at about 30 seconds.

When the amount of methyl iodide in the vessel is maintained constant and the oxygen is increased tenfold (i.e., a total pressure of 5.5 cm Hg), slow combustion is obtained. The OH intensity (now lower) reaches its maximum by 0.03 ms and falls to zero at 0.1 ms. Under these conditions the IO spectrum appears having a maximum intensity by 0.03 ms; it disappears at about 0.4 ms. The I_2 spectrum appears at 0.4 ms, reaching a maximum intensity after 30 seconds. The maximum intensity is greater in the explosive combustion; hence the amount of I_2 formed is greater. When the total moles of methyl iodide in the reaction vessel is increased eightfold and the relative excess amount of oxygen is maintained (resulting in higher total pressure), then the formaldehyde spectrum is apparent at 0.03 ms, with its maximum intensity occurring long (30 sec) after the flash, and OH is not observed at all.

The experimental observations are taken to indicate the following mechanism for the reaction between methyl radicals and molecular oxygen:

$$CH_3+O_2\rightarrow H_2CO+OH$$

The failure to observe H_2CO in slow combustion at the lower pressure is attributed to the smaller amount present. On the other hand, the OH spectrum is not evident at the higher pressure because the higher temperature causes the CH_3I spectrum to extend to longer wave lengths, thus obscuring the OH structure.

During explosive combustion, the disappearance of the CH_3I spectrum by 0.095 ms implies that CH_3I no longer is participating in reactions. The subsequent increase in OH in the period 0.2 to 0.4 ms can be explained by the generation of OH in the rapid combustion of formaldehyde. This view receives some support from the structure observed at 0.03 ms which is thought to represent formaldehyde not yet consumed.

Under the slow combustion conditions an appreciable delay is experienced before molecular iodine appears. This delay indicates that the iodine atoms produced by the dissociation of CH_3I react with oxygen to form the IO observed. The successive intensity changes in the spectra of IO and I_2 suggest that the IO radicals react to form iodine:

$$2IO \rightarrow I_2 + O_2$$

The absence of IO during explosive combustion suggests that the formation of some other radical such as IOO may predominate prior to the production of I_2.

Subject Headings: ***Methyl iodide, combustion of; Combustion, of methyl iodide.***

G. A. Agoston

Rasbash, D. J. and Rogowski, Z. W. (Joint Fire Research Organization, Boreham Wood, England) "Gaseous Explosions in Vented Ducts," *Combustion and Flame* 4, 301–312 (1960)

This paper aims directly at a solution to the practical problem of industrial explosions in large ducts. The ducts were vented at one end, either near or remote from the ignition source. Numerous pipe dimensions (lengths and diameters) were used, and some ducts were square in cross section. Quiescent mixtures of pentane and propane with air were employed as the explosives. Concentration of fuel in the mixture was varied over a very narrow range, e.g., from 1.17 to 1.33 per cent stoichiometric.

Two important parameters will be helpful to the plant design engineer: the ratio of the cross-sectional area of the duct to the area of the vent, and the length-to-width ratio of the duct. The first factor varied from 1 to ∞, and the latter from 6 to 30. An induction spark served as the ignition source. Pressure traces were obtained for each explosion. In addition, flame speeds were deduced from measurements made with ionization gaps placed at 3-feet intervals along the duct. Results are reported for closed ducts; for relief vent remote from ignition source; and for relief vent near ignition source.

In the discussion, the authors attempt to interpret their results on a quantitative basis. Factors controlling the maximum pressure reached in a vented vessel are divided into two groups: (1) those which govern the rate at which the volume in the vessel is increased or expanded, and (2) those which govern the rate at which the gas may be discharged. The most important factor in the first group is the rate of combustion; in the second group, friction and inertia of the gases and the discharge characteristics of the vent are pertinent. These governing factors are discussed in some detail.

The paper concludes with suggestions for applying their results. Users are cautioned that the results are valid only for open vents in the end of ducts; for initially quiescent gas in empty ducts; and for a narrow range of combustible-mixture strengths. An important practical principle expressed by the writers is that vents should be so placed in a duct that burnt gas rather than unburnt gas will be discharged. To accomplish this, frequent small vents along the duct rather than large vents at infrequent intervals should be installed. The work reported in this paper should be helpful to those concerned with gaseous explosions in closed or vented ducts.

Subject Headings: *Gases, explosion of, in ducts; Explosions, of gases in ducts.*

C. O'Neal, Jr.

Burgoyne, J. H. and Long, V. D. (Imperial College, London, England) "Some Measurements of the Burning Velocity of Coal-in-Air Suspensions," Paper 28 *Conference on Science in the Use of Coal—Institute of Fuel* (1958)

Coal dust flames are investigated for three reasons: (1) to understand industrial flames; (2) to understand explosion flames; and (3) for the intrinsic value of understanding fundamental flame mechanisms. The experiments in the paper under review partially satisfied all these three reasons. Burning velocities of coal-in-air suspensions were studied to provide basic information on flame behavior; from the safety angle, salt was added to the suspension to examine its influence on the burning velocity and low limit; and finally, some extrapolation of the results was made to explain behavior of large industrial flames.

The experimental apparatus was a water-cooled down-pointing burner tube, of ⅝″ i.d. carrying the premixed coal-air suspension; and buoyancy was therefore countered by a suction device. The dust flame formed was of the bunsen type with a conical inner zone defining the flame front, and this dust flame was supported by a surrounding flame of premixed coal gas and air. The dust flame itself had two zones: the short inner one had intense luminosity from burning volatiles, and it was followed by the outer one of residue combustion.

The burning velocity was defined as the air velocity (corrected to cold conditions) normal to and at the flame front, and averaged over the flame-front area. The dust concentration was measured kinematically as the weight of dust filtered from a measured volume of cloud. The coal was Silkstone, of 36 per cent V.M., finely ground and cut into six fractions of mean mass diameter 11, 22, 33, 45, 62, and 120 microns. Salt was added only to the 11 micron fraction.

Measured burning velocities were in the range 3 to 10 cm/sec. From the lower values at the low limit, the velocities were found to rise steadily with dust concentration, leveling off to a plateau at about 2 times the coal-stoichiometric concentration, this being about ½ that of the volatiles stoichiometric. The rate of rise and maximum value increased with smaller particle size, but was reduced by salt addition, this apparently influencing the volatiles combustion. Linear plots were alternatively obtained by plotting the specific mass flow rate (per unit area of flame surface) against kinetic concentration. (The reviewer therefore deduces that burning velocity is inversely proportional to concentration, though this would seem to contradict the existence of the burning velocity plateau.) The slope of the lines rises with particle size, but they all converge reasonably convincingly at a common point, thus denoting a common low-limit and low-limit flame-speed (these have also been observed in moving flames [1]). Less convincing to the reviewer is the plot of burning velocity relative to the ambient gas, obtained by adding in the sedimentation velocity. The reviewer is not personally convinced that direct extrapolation from the motion of a single particle sedimenting in a stationary fluid to multitudes in a moving one, has yet been validated.

Mention is also made of large flame behavior. These generally have flame speeds in the region of 10 to 15 m/sec, or about 100 times that found by the authors. This difference they ascribe to turbulence; current work would seem rather to favor recirculation but the point is not yet proved.

Reference

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Subject Headings: ***Burning rates, of coal; Coal, burning rates of.***

R. H. Essenhigh

VI. Radiation

Hottel, H. C. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "The Melchett Lecture for 1960: Radiative Transfer in Combustion Chambers," *Journal of the Institute of Fuel* **34,** 220–233 (1961)

The many different aspects of the problem of calculation of the radiative transport of heat in furnaces were described and discussed by the author in the Melchett Lecture for 1960. To facilitate the presentation of the many important results and new developments which the paper contains this abstract follows the subheadings employed by the author.

1) Furnace Gas Radiation

Previous results for the emissivity of the important gaseous constituents (CO_2 and H_2O) of furnace gases are presented in the form of graphs of ϵ vs. gas temperature for various values of the parameter pL, where p is the partial pressure of the radiating constituent and L is the path length (beam length) for radiation through the gas. The use of pL as a measure of the number of molecules traversed by the beam, instead of the more logical parameter CL (where C is the concentration of the radiating species), is found to be more convenient for engineering applications.

The author raises the question of the permissibility of analyzing radiative performance by using the concepts of multiple reflection and Beer's law absorption of a beam of radiation as it bounces around in an enclosure containing gray gas, in view of the fact that the contributions of different bands may vary differently with path length (variation as L, $L^{\frac{1}{2}}$, and log L are all possibilities). It is shown that the difficulty can be resolved by expressing the emissivity in the series form

$$\epsilon_G = \sum_n a'_n (1 - e^{-K_n L})$$

This is equivalent to treating the gas as a mixture of gray gases, each present in fractional amount and having absorption coefficient K_n. By comparing with the experimental curves described previously for CO_2+H_2O (equimolar mixture) at 2500°K it is shown that excellent agreement may be obtained by employing four terms of the series (3 gray gases and 1 clear gas, i.e., with $K=0$) over a 2500-fold range of pL.

The short cuts developed to allow for the shape of the gas mass include the use of shape factors and mean-beam lengths. Methods of calculating these quantities are described and charts are included to illustrate their variation with KD (where D is some characteristic dimension of the gas shape), based on both the gray-gas model (i.e., using one term in the above series) and the three gray gas-clear gas mixture. Recommended beam-lengths for cylinders have been computed and are presented in a table. From the table it follows that when interest is in flux to the whole bounding area of the gas mass, of whatever shape, the average beam-length is approximately 0.88 x (the mean hydraulic radius of the shape).

2) *Simplified Furnance Equations*

A mathematical model of combustion chamber performance which, though departing seriously in many ways from reality, succeeds strikingly in preserving the correct relation among the dominant variables finally leads to the result

$$\mu' D' + \tau^4 = (1-\mu')^4$$

where

μ' = reduced furnace efficiency $= \dfrac{q}{H_{in}}\left(\dfrac{T_{AF}-T_O}{T_{AF}}\right)$

τ = ratio of sink temperature T_s to pseudo-adiabatic flame temperature T_{AF} (which ignores dissociation)

D' = reduced firing density $= \dfrac{H_{in}}{\sigma A_T T_{AF}^3 (T_{AF}-T_O)}\left(\dfrac{1}{\epsilon_G}+\dfrac{1}{C\epsilon_1}-1\right)$

q = rate of heat radiation from gas to sink

H_{in} = hourly input of enthalpy in the air and fuel with reference to a base temperature T_O

A_r = total surface area of furnace (sink and refractory)

C = fraction of chamber wall occupied by sink.

This result applies to the idealized "well-stirred, speckled-wall, gray-gas, combustion chamber." Speckled walls have sink and refractory surfaces intimately mixed so that the view-factor to sink surfaces is the same from any point on the walls. The equation is plotted as curves of μ' vs. D' for various values of τ and corresponding experimental results for various furnace types are superimposed for comparison. The full range of operating variables covered by the well-stirred combustion-chamber equation makes the graphs attractive for use in the thermal classification for furnaces. Modifications of the equation to allow for departure from perfect stirring and non-speckled-walls are described. In particular the modification to allow for plug flow instead of perfect stirring is derived and plotted to compare with the corresponding well-stirred approximation. How much one modifies the plug-flow results downwards or the well-stirred flow result upwards to match industrial practice is a subject for further investigation.

3) *Rigorous Treatment of Furnace Chamber Performance*

This section consists of a progress report on the problem of predicting furnace performance more rigorously than in the past or in the previous section. Real-gas absorptivity is represented as that of a sum of gray-gases, just as was described for emissivity in section 1. The indices on the exponential terms are identical with those for the corresponding emissivity but the values of a'_n differ. The agreement of calculated and measured absorptivities for a specific case is found to be within 5 per cent. Allowances for temperature gradients in a chamber are made by splitting up both the gas mass and the walls into zones, and the calculation of the direct radiant interchange between solid-solid, gas-solid, and gas-gas zones is described. Equations are also derived for the calculation of the net radiant transport away from any surface zone in the presence of gray gas or from any gray-gas zone. The modifications necessary to allow for real gases are indicated. Finally, the sequence of operations to be followed in handling a complex problem of interaction of radiation and other transport mechanisms in a furnace chamber is summarized.

The whole paper represents a concise and lucid resume of the present state of knowledge in the field of calculation of radiative transport in combustion chambers, to which the author and his co-workers have made such major contributions.

Subject Headings: *Radiation, in combustion chambers; Combustion chambers, radiation transport in.*

R. G. Sidall

Bell, E. E., Burnside, P. B., and Dickey, F. P. (Ohio State University, Columbus, Ohio) "Spectral Radiance of Some Flames and Their Temperature Determination," *Journal of the Optical Society of America* **50,** 1286–1292 (1960)

Radiation from flames of several different fuel-oxidizer combinations were examined in the wave-length interval 2–15 microns. A Meker burner was modified to permit metering the air. The primary flame zone was studied. To determine flame temperature the spectral emissivity and the actual flame spectral radiance were measured. Knowledge of these two quantities provides the black body spectral radiance. Comparison of the experimentally determined black body curve with the curve calculated using Planck's law yields the temperature. To facilitate comparison of the two curves log-log plots are used; with a log-log plot the black body curve has a shape independent of temperature.

Careful experimental technique is required to obtain meaningful measurements. Slit-width calibration was determined, using the fact that recorder-deflection varies as square of slit width. Diffraction effects are accounted for. To calibrate the recorder-deflection in terms of spectral radiance, a black body source (a capped iron pipe with a very small hole in one end) was used. Apparent or observed quantities differ from the actual quantities due to the slit function. As a result of the slit function, effective values of spectral emissivity were measured. The effective value of spectral emissivity equals the product of actual spectral emissivity and slit-function integrated over all wave lengths. A correction for the influence of atmospheric and instrument transmission was included in the procedure.

Flame radiance was measured directly by illuminating the slit with flame radiation. The experimental setup uses a flame-chopper-slit. To measure spectral emissivity the readings from two experiments are compared. The first experiment used a globar-chopper-slit setup giving a reading of R_G. The second experiment involved a globar-chopper-flame-slit setup giving a reading R_A. Emissivity equals $(R_G - R_A)/R_G$.

A wide variety of flames was studied. For the hydrocarbon-air flames, the emission bands of water and carbon dioxide were observed, as expected. An ammonia-oxygen flame has water bands but, naturally, no CO_2 bands. A carbon monoxide-oxygen flame has CO_2 bands. A diffusion flame of hydrogen-chlorine was also studied, and in addition CS_2-air flames were examined.

This experimental method for determining temperature has a significance in regard to departures from equilibrium. If chemiluminescence were dominant, the data points, adjusted for emissivity, could not be fitted to a black body curve. Since the points do fit reasonably well, it indicates that there have been sufficient collisions to distribute the energy among the excited species. Compared to rotational or vibrational temperatures, this method should yield a more meaningful, effective temperature.

Subject Headings: *Flame, spectral radiance of; Radiance, from flames.*

A. E. Fuhs

VII. Suppression of Combustion

Bardwell, J. (University of Saskatchewan, Saskatoon, Canada) "Inhibition of Combustion Reactions by Inorganic Lead Compounds," *Combustion and* Flame **5**, 71–75 (1961)

In a study of the inhibition of the oxidation of n-butane by lead oxide, lead tetroxide, and lead chloride, the author found that lead oxide was the most powerful inhibitor. Using coated vessels, he studied the suppression by these oxides of cool flames and low-temperature ignitions in equimolar n-butane-oxygen mixtures over a pressure range of 200–500 mm Hg and temperatures up to 500°C. The powerful inhibition found with lead oxide is used to help explain the mechanism of the anti-knock action of lead tetraethyl. The results of this investigation lend support to the mechanism proposed by Walsh and co-workers that the anti-knock action is the consequence of the destruction of free radicals at the surface of lead oxide smoke particles formed from lead tetraethyl in the cylinder.

Although, with n-butane, lead oxide greatly lengthens the induction period preceding a cool flame and lead tetraethyl has little effect with n-heptane,[1] the explanation advocated by the author of the effect of lead tetraethyl on the combustion of paraffins is not materially contradicted. He merely argues that the true inhibitor can still be lead oxide if its formation from lead tetraethyl is appreciably delayed.

The author compares the inhibiting action of lead oxide on n-butane with results obtained by Chamberlain and Walsh[2] on diethyl and diisopropyl ether. Oxidation of n-butane is found to be more affected by lead oxide than oxidation of the ethers. This is especially apparent in the low-temperature reaction where lead oxide suppresses cool flames in n-butane over a wide range of experimental conditions, but has little effect with ethers. An explanation of this difference is offered by considering that the length of the free-radical chains in butane oxidation is much greater than in ether oxidation.

The possibility that lead oxide vaporizes and that the observed inhibition is due to lead oxide molecules in the vapor state was considered. However, this was rejected because in butane oxidation with a lead-oxide-coated vessel, inert gas additions accelerate rather than inhibit the reaction. Besides, available data indicate that the vapor pressure is very low and, in addition, the magnitude of the observed inhibition does not increase sharply with temperature as would be the case if vapor molecules were responsible for the inhibition. The effect at temperatures above 500°C is not considered.

References

1. Pahne, A. J., Cohen, P. M., and Sturgis, B. M. *Industrial Engineering Chemistry* 46, 1024 (1954)
2. Chamberlain, G. H. M. and Walsh, A. D. *Proceedings of the Royal Society* A215, 175 (1952)

Subject Headings: ***Inhibition, by lead compounds; Lead, inhibition of combustion by; Combustion, inhibition of, by lead compounds.***

A. Strasser

Creitz, E. C. (National Bureau of Standards, Washington, D. C.) "Inhibition of Diffusion Flames by Methyl Bromide and Trifluoromethyl Bromide Applied to the Fuel and Oxygen Sides of the Reaction Zone," *Journal of Research of the National Bureau of Standards. A. Physics and Chemistry* **65A**, 389–395 (1961)

During preliminary studies on the inhibition of propane diffusion flames by methyl bromide, it was noted that extinguishment was more readily achieved when the inhibitor was supplied to the air-side of the reaction zone than when added to the fuel. This effect had been noted by Simmons and Wolfhard during some spectroscopic studies of diffusion flames.

Creitz undertook this study to see if the inhibitor interferes with some reaction involving oxygen or oxygenated intermediates. The inhibitor effect was studied as a function of the oxygen concentration in the oxygen-nitrogen mixture supplied to a diffusion flame. In addition, the flames were inhibited with nitrogen added to the fuel so that a datum could be established for estimating the relative efficiencies of other inhibitors used under similar conditions.

The diffusion flame was burned on the end of a Pyrex tube (7 mm o. d. by 0.8 mm wall thickness) which was contained within a Pyrex outer jacket 5 cm in diameter. Glass beads at the base distributed the air flow evenly.

Diffusion flames are extinguished by a number of factors including the fuel flow rate and the linear velocity of the secondary air past the flame. Creitz found this latter effect to be relatively unimportant except at rather high or very low flow rates. An optimum fuel flow rate was determined for each fuel and inhibitor combination to prevent extinguishment or lift off because of the rate of fuel addition. Fuels employed were hydrogen, natural gas, ethane, propane, butane, and carbon monoxide. The inhibitors utilized were methyl bromide, trifluoromethyl bromide, and nitrogen.

Results of the study were presented in the form of curves which define the boundary between burning and extinguishment conditions. For fuels burning in air at the start of the experiment, results showed that the inhibiting effect of nitrogen is different on the opposite sides of the reaction zone. Less nitrogen had to be added to the fuel in order to obtain extinction than was necessary when nitrogen was added to the air. Using nitrogen as a basis of comparison, relative efficiencies were then calculated for the other two inhibitors.

Diffusion flames are peculiar in that the amount of nitrogen they tolerate is dependent upon whether it appears at the lean or rich boundary, according to these results. Neglecting chemical effects and differences in the rates of diffusion, halogenated inhibitors would be expected to behave similarly. Results show that the percentage of the halogenated inhibitor needed to extinguish the flame was much less when added to the oxidizer side than to the fuel side.

This study and others indicate that gases known to capture electrons have shown strong influences on the combustion processes. These gases are oxygen, water vapor, nitrogen dioxide, and halogenated organic compounds. Only OH^-, O^- and the negative halogen ions appear to have important effects. It appears that poor halogen inhibitors are strongly bonded or that they produce no halogen ions in a mass spectrometer.

Methyl bromide is less effective than trifluoromethyl bromide except at oxygen concentrations below that of air and when added to the fuel. Inhibitors are more effective under conditions of low oxygen concentrations when mixed with the air supplied to a fire.

Subject Headings: ***Inhibition, of flame, by bromides; Flame, inhibition, by bromides.***

L. E. Bollinger

Fehlner, F. P. (California Institute of Technology, Pasadena, California) "Inhibition of a Low-Pressure Flame by Halogen Atoms," *Technical Report No. 32–122, National Aeronautics and Space Administration Contract No. NASw–6* (August 14, 1961)

In attempting to test the hypothesis that halogen atoms inhibit the burning characteristics of certain flames, a flash photolysis technique was employed to dissociate molecular chlorine which had been introduced into a low-pressure acetylene-oxygen flame. Earlier work on similar flames with halogenated compounds had indicated that halogen atoms were released in the flame and that the latter subsequently reacted to reduce flame speed. Rather than depend on breaking the bonds of a halogenated hydrocarbon within the flame, it was felt that a better measure of the flame-quenching capabilities of the halogens could be obtained by attempting to introduce the halogen directly.

The acetylene oxygen flame, burning at 10 mm Hg pressure, was stabilized on a quartz tube. The chlorine was dissociated when a krypton lamp, mounted below the flame, was flashed by capacitor discharge. High-speed photography with a Fastax camera, hot-wire anemometry and absorption and emission spectroscopy techniques were used to measure the burning characteristics of the resultant flame.

Fastax photographs clearly showed the reduction of flame speed as the flame rose above its equilibrium position. The duration of flame inhibition after the lamp flash, measured by the variation in light intensity, was found to be greater than the lifetime of a chlorine atom at 10 mm Hg pressure. It was concluded that a chlorinated hydrocarbon rather than the chlorine atom was causing the flame inhibition.

Absorption spectroscopy measurements confirmed the photographic analysis. When chlorine and acetylene were subjected to flash photolysis, a compound was produced which absorbed less light than chlorine. Data were presented which showed how the degree of flame inhibition varied inversely with pressure and directly with fuel-oxidizer ratio.

In a similar experiment using methane in place of acetylene, high-speed photographs showed that very little inhibition took place. Apparently chlorine atoms were recombining before entering the flame because of the difficulty in removing hydrogen from methane. The fact that there was no resultant change in the species entering the flame explains why no flame inhibition took place.

Studies of the flame using an optical schlieren system proved of little value. Emission spectroscopy proved difficult because of the transient nature of the flame caused by the intermittent flashing of the krypton lamp.

Since the spectrographic results failed to indicate that chlorine was entering the flame, the author made specific recommendations for improvement of the experimental apparatus. A lower pressure flame to increase the life of the chlorine radicals, a larger flame holder and a steady state source of atomic chlorine were recommended. In order to prevent the combination of halogen and fuel prior to reaching the flame, methane or hydrogen were recommended as fuels. Direct sampling via a mass spectrograph or infrared spectrometer was also suggested.

Subject Headings: ***Flame, inhibition, by halogen atoms; Inhibition by halogen atoms.***

A. L. Goldstein

van Tiggelen, A. (University of Louvain, Louvain, Belgium) "Experimental Investigation on the Kinetics of Flame Inhibition," *Final Technical Report No. 2, Office, Chief of Research and Development, U. S. Department of Army, European Office Contract DA–91–591–EUC–1072* (March 1960) *

The studies undertaken in this report were designed to broaden the understanding of the mechanism of flame inhibition, but not to attempt a definite interpretation of a general flame-inhibition mechanism at this time. A summary of the four parts of the report is as follows:

1. Qualitative Observations on the Influence of Chlorine in Hydrogen-Oxygen Flames

a) In tests containing 40% H_2+O_2 with a ratio variation of $H_2/(H_2+O_2)$ from 0.62 to 0.72 and 60% N_2+Cl_2 with a ratio variation of $Cl_2/(N_2+Cl_2)$ up to 0.04, the $Cl_2/(N_2+Cl_2)$, dilution of 0.01 or less inhibited the flame, whereas values above 0.01 appeared to accelerate the flame.

b) In tests containing 42.5 to 37.5% of $H_2/O_2/Cl_2$ and 57.5 to 62.5% of N_2 where the stoichiometric mixture of H_2/Cl_2 was varied from 0 to 80% of the total stoichiometric mixture of H_2/Cl_2 and H_2/O_2, the chlorine appeared to act as a promoter.

c) In tests where maximum-burning-velocity, binary mixtures of H_2/O_2 $[H_2/(H_2+O_2)=0.70]$ and H_2/Cl_2 $[H_2/(H_2+Cl_2)=0.64]$ were mixed together and diluted with 50 to 60% N_2, practically no inhibition effect was noted.

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* See FIRE RESEARCH ABSTRACTS AND REVIEWS, 1, 196–199 (1959) for Report No. 1

d) In tests where binary mixtures of H_2/O_2 $[H_2/(H_2+O_2)=0.70]$ and H_2/Cl_2 $[H_2/(H_2+Cl_2)=0.53]$ were mixed and diluted with 52.5 to 60% N_2, some inhibition was observed.

e) In tests where the binary mixture of H_2/Cl_2 $[H_2/(H_2+Cl_2)=0.64]$ containing 30 and 35% N_2 were mixed in increasing amounts with a binary mixture of H_2/O_2 $[H_2/(H_2+O_2)=0.7]$ containing respectively, 65 and 67% N_2, a strong promotion was observed.

2. Inhibition Effects in Ethylene/Vinylchloride/Oxygen Flames

Earlier studies have shown the over-all activation energies of C_2H_4/O_2 and $CH_2{=}CHCl/O_2$ flames to be 36 and 53 kcal, respectively. These studies were extended in this report to flames containing both compounds with stoichiometric amounts of oxygen. The stoichiometry of the vinylchloride oxidation was defined as follows:

$$2\,CH_2{=}CHCl+5O_2 \rightarrow 4\,CO_2+2HCl+2H_2O$$

The results of these tests at nitrogen dilutions of 62.5 to 70% showed that as the C_2H_4 was replaced by the $CH_2{=}CHCl$, (1) the flame velocity decreased almost linearly, (2) the flame temperature remained about the same, and (3) the activation energies varied regularly from 38 to 57 kcal (C_2H_4 to $CH_2{=}CHCl$ flames). These data show only a possibility of an inhibiting effect by the halocarbon.

3. A New Ionization Measuring Device

According to the author, many difficulties and limitations are inherent to the classical methods by which the ion concentration in flames are usually measured. Thus an apparatus has been developed and tested which appears to (1) permit exclusive measurement of the ionization in the flame front only, (2) allow temperature measurement over a broad range, and (3) does not disturb the flame front. The essential part of the apparatus is the burner, which consists of two coaxial tubes (Tube I.D.'s of 2.79 and 2.99 cm, annular space of 1 mm, and tube lengths of ca. 50 cm) which are electrically insulated from each other. The gaseous mixtures are fed and burned in the annulus. A DC voltage (range of 1.5 to 1200 volts) is applied across the two tubes to permit measurement of the current intensities in the flame front with a galvanometer, sensitive up to 10^{-9} amp).

This apparatus has been applied to studies with C_2H_4/O_2 and $CH_2{=}CHCl/O_2$ flames to show that (1) the apparent activation energies of the ion formation for the respective compounds are ca. 65–80 kcal and 140–200 kcal, (2) at flame temperatures of about 2500°K, the total ion concentrations in both flames are not much different, and (3) with cooler flames (higher N dilution) the C_2H_4 flames contain more ions than the $CH_2{=}CHCl$ flames. It is of interest to note, as the author points out, that in hydrocarbon flames about 95 per cent of the ions in a flame front consists of H_3O^+. In $CH_2{=}CHCl/O_2$ flames, additional ions as HO_2^+, $H_3O_2^+$, and H_2Cl^+ have been identified. The concentration of each of these ions is about 1/10 of the H_3O^+ ion concentration formed with $CH_2{=}CHCl$.

The above circular slit burner has also been used to determine the upper flammability limit for $CH_4/O_2/N_2$ mixtures. These data give an upper limit of about 14 per cent in air and of 56.2 per cent in oxygen. The results are consistent with published data.

Subject Headings: ***Flame, inhibition kinetics; Inhibition, of flame.***

R. A. Gorski

van Tiggelen, A. (University of Louvain, Louvain, Belgium) "Inhibition Processes in Methane-Oxygen Flames," *Final Technical Report No. 3, Office, Chief of Research and Development, U. S. Department of Army, European Office Contract DA–91–591–EUC–1425* (April 1961)

In these recent studies by the author, the oxidation studies were altered from ethylene and vinylchloride systems to simpler systems containing methyl chloride/oxygen, methane/methylchloride/oxygen, and also methane/methyl bromide/oxygen. In this study measurements of burning velocities and flame temperatures have been combined with measurements of the intensity of the bands which are emitted by the flame.

Initially, the flame velocities of the CH_3Cl/O_2 system were determined. Via mathematical analysis, the flame velocity (V_o in cm/sec) was determined to be

$$V_o \cong 10^{5*} \sqrt{\frac{(CH_3Cl)^{0.7}(O_2)^{0.3}e^{-47000/RT_m}}{PT_m}}$$

where

(CH_3Cl) and (O_2) = initial partial pressures of the compounds in atmospheres
P = total pressure (one atmosphere)
T_m = mean temperature of flame front
$= T_i + 0.74\ (T_f - T_i)$
T_i = initial temperature of unburned gases (293°K)
T_f = maximum flame temperature (°K)
0.7 and 0.3 = orders of reaction of CH_3Cl and O_2, respectively
$-47{,}000$ = activation energy of the branching process

In comparison to the flame velocities determined by the author at a previous occasion for the CH_4/O_2 system,

$$V_o = 10^6 \sqrt{\frac{(O_2{}^{1.4}\ e^{-38000/RT_m}}{P\ (CH_4)^{0.4}\ T_m}}$$

it can be seen that the orders of reaction of CH_4 and CH_3Cl and the activation energies are markedly different. The difference may be ascribed to the chain carriers. By use of the relationship

$$\frac{V_o\,S}{\sqrt{T_m}} = K\ (\text{constant}),$$

where S = distance between luminous cone and schlieren image and assuming a mean molecular of 17 (OH) in the CH_4/O_2 flames, a value of 32 (~Cl) is found for the CH_3Cl/O_2 flames.

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* If E = —47000 Kcal were —52000, this constant would have a value of 10^{11}. The latter value would be more consistent with theory as discussed by the author.

In the determination of the flame velocities of ternary flames of $CH_4/CH_3Cl/O_2$ systems, it was found that the over-all activation energy of chain-branching does not vary regularly from 38 kcal as the ternary system becomes richer in CH_3Cl, but rather the activation energy passes through a maximum which indicates a strong interaction between the two combustion mechanisms with a resulting strong inhibition.

In one case, where the stoichiometric mixtures were taken as $4\,CH_3Cl+6\,O_2 \rightarrow 4\,CO_2+4H_2O+4\,HCl$ to give a $CH_3Cl/(CH_3Cl+O_2)$ ratio of 0.4, and $CH_4+2\,O_2 \rightarrow CO_2+2H_2O$ to give a $CH_4/(CH_4+O_2)$ ratio of 0.333, the fraction of stoichiometric mixture of (CH_3Cl and O_2) in the total mixture (α), at which the maximum activation energy of ca. 62 kcal occurred, was about 0.6. In a second case, where the stoichiometry of the CH_3Cl/O_2 was considered as $4\,CH_3Cl+7\,O_2 \rightarrow 4\,CO_2+6H_2O+2\,Cl_2$ to give a $CH_3Cl/(CH_3Cl+O_2)$ ratio of 0.364, an α value of ca. 0.65 gave a maximum activation energy of ca. 68 kcal. In an extension of the second case, different proportions of CH_4+O_2 and CH_3Cl+O_2 were separately diluted with nitrogen to yield separately the same burning velocities. Mixing of these two ternary mixtures, gave a minimum burning velocity at about an α of 0.5.

Supplementary to the above measurements, the intensities of the radicals C_2, CH, and OH were measured, respectively, at 4680, 4315, and 3089 Å for $CH_4/CH_3Cl/O_2$ systems based on the stoichiometric ratios of

$$\frac{CH_4}{CH_4+O_2}=0.33$$

$$\frac{CH_3Cl}{CH_3Cl+O_2}=0.4$$

In these studies it was shown that as α increased, the intensity of the OH radical decreased, the C_2 radical increased, and the CH radical increased and attained a maximum value at $\alpha=0.4$. In addition, the activation energies in the flame front of the OH, C_2, and CH radicals were found to be approximately 30, 40 and 40 kcal.

The analyses of the results in the report by the author are beyond the scope of this review. These excerpts, however, cannot be overlooked:

1) A good correlation exists between the diminishment of flame velocity and OH radical, emission intensity and
2) Chances are good that CH_3 radicals are formed from CH_3Cl and that by a succession of undefined reactions, CH, C_2, and OH radicals are produced as in the CH_4/O_2 flames.

During the above studies, some properties of $CH_4/CH_3Br/O_2$ flames were investigated also. Difficulties were experienced in the measuring of flame velocities in this work due to the marked flame inhibition exerted by small quantities of CH_3Br. These data were considered semiquantitative, but nevertheless of significance. The studies dealt with CH_3Br/O_2 and CH_4/O_2 mixtures using the following stoichiometry:

$$4\,CH_3Br+7\,O_2 \rightarrow 4\,CO_2+6\,H_2O+2\,Br_2$$

to give a ratio of $CH_3Br/(CH_3Br+O_2)=0.364$, and

$$CH_4+2\,O_2 \rightarrow CO_2+2\,H_2O$$

to give a ratio of $CH_4/(CH_4+O_2)=0.333$.

These data showed:

1) The maximum over-all activation energy was 130 kcal when α was equal to 0.3,

2) The mean molecular weight of the chain carriers for α values of 0, 0.1, 0.3, and 0.5 were respectively 17, 28, 36, and 45 (transition from OH radicals to the bromine atoms),

3) The variation of CH, C_2, and OH radical emissions were similar to the $CH_4/CH_3Cl/O_2$ systems. In this instance, however, the intensity of the CH radical reached a maximum at an α value of 0.3. The results showed that CH_3Br was a more effective inhibitor than CH_3Cl since (1) the maximum over-all activation energy in the flame front was higher, and (2) less CH_3Br was required to get to the point at which the former was obtained.

Subject Headings: ***Flame, inhibition kinetics; Inhibition, of flame.***

R. A. Gorski

Skinner, G. B., Miller, D. R., Katon, J. E., and Hedley, W. H. (Monsanto Research Corporation, Dayton, Ohio) "A Research Program for the Understanding of the Mechanisms of Flame Inhibition," *Aeronautical Systems Division Contract AF 33(616)–7757.* 1st Quarterly Progress Report (March 1961), 2nd Quarterly Progress Report (June 1961), and 3rd Quarterly Progress Report (September 1961)

These reports describe a research program in which studies aimed at an understanding of the processes involved in the extinguishment of propellant fires will be performed. The hydrazine-nitrogen tetroxide system is the first propellant system selected for study. The program involves (a) a literature survey of present knowledge in the field—the survey is completed and should be available soon; (b) screening experiments in which the effects of various additives on the hydrogen-air flame will be measured; (c) mechanistic studies by shock wave and spectroscopic techniques; and (d) a computer program in which it is hoped some correlation between structure and inhibiting power can be established.

In the screening experiments to date, measurements have been made of the effect of thirty-five gases and thirty vaporizable liquids on the flame speed of premixed hydrogen-air flames burning on a conical burner. The bulk of the measurement was made with hydrogen:air equal to 41.5:56.5. The additives studied have included hydrocarbons, organic and inorganic halides, and other compounds of interest, both organic and inorganic. The amounts of additives ranged from 0.5 to 4.97 volume per cent, the bulk being at 2.0 per cent. Every additive, except water, lowered the flame speed, some quite sharply. Water increased the flame speed somewhat. Future plans call for the study of the effect of solid powders on the flame speed.

In the shock tube studies the general approach is to subject gaseous mixtures with and without inhibitors to shocks of varying strength in the hope that conditions corresponding to different points along the combustion profile can be approximated. Spectroscopic measurements and product composition studies would be made. To date some shock tube studies have been made on hydrogen-oxygen-argon mixtures with and without added methane. (Methane was selected because of its relatively strong inhibiting power indicated in the screening studies.) From product analyses and emission spectra, induction periods for reaction were found as a function of temperature. Induction times varied from about 20 milliseconds at 950°K to about 0.2 milliseconds at 1100°K. The inhibitor had no noticeable effect on induction time. Measurement of hydroxyl radical concentrations in the uninhibited flame by emission spectroscopy showed that these increased exponentially during the induction period. The above results suggest to the authors that inhibition occurs by reaction of inhibitors with active species upstream of the flame front.

Some experiments have been performed in which the hydroxyl emission near 3100Å was measured for hydrogen-air and hydrogen-air-methane flames on the conical burner. It was found that the emission intensities were much stronger in the reaction zones than in the hot product gases. The presence of methane resulted in somewhat lowered emission; this was more noticeable for a lean flame than for a rich or stoichiometric one. Future workout on a flat flame burner is planned. The parts of the project devoted to the computer program and to studies with hydrazine-nitrogen tetroxide are still in a preliminary stage.

Subject Headings: *Inhibition, of flame; Flame, inhibition.*

J. B. Levy

Atlantic Research Corporation (Alexandria, Virginia) "A Program to Advance the Technology of Fire Extinguishment," *First Quarterly Progress Report, Wright Air Development Command Contract AF33(616)–8110* (July 15, 1961)

This is the first progress report in a twelve-month program to investigate the mechanism of combustion processes in fires resulting from spills of liquid hydrogen and liquid hydrogen in the presence of liquid oxygen. The ultimate goal of this program is to develop procedures and materials to reduce the combustion volume of such spill fires, reduce or eliminate the danger of detonations, and ultimately to find the best way to extinguish these fires.

A three-part program was designed to attain these objectives: (1) evaluation of agents to reduce or suppress detonation in the gaseous phase; (2) determination of the characteristics of fires resulting from spills of liquid hydrogen (with and without liquid oxygen); and (3) evaluation of suppressing agents including those found to be effective in (1) on liquid hydrogen spill fires.

During the first quarter, literature describing hydrogen-oxygen-nitrogen systems was surveyed for information on the use of additives for deflagration and detonation suppression. Information was obtained on liquid-hydrogen spill fires, and techniques for storing and handling liquid hydrogen.

A liquid-hydrogen laboratory was designed, and construction has been essentially completed. A storage facility for 100 liters of liquid hydrogen, a transfer line, hood, inert gas manifold, and explosion-proof electrical outlets, lights, and blower-motors are provided.

Equipment has been designed and constructed for conducting the gaseous hydrogen-oxygen detonation studies. Detonation-suppression testing will be carried out in a 4.5 liter stainless steel spherical bomb at a pressure of one atmosphere. The hydrogen-oxygen additive mixture will be premixed in a 17 liter chamber and then allowed to flow into the bomb. An exploding wire system will be employed for initiation of detonations. Pressures will be recorded by a rapid-response pressure gauge mounted in the wall of the bomb to determine whether a spherical detonation has occurred. The effectiveness of candidate suppressing agents will be determined by measuring the increase in initiation energy required to cause spherical detonations.

In the fire-extinguishment phase of the program, initial tests are planned to determine liquid hydrogen burning rates in stainless steel Dewars. The small 4.8 and 44 sq in (surface area) Dewars used for initial testing will be equipped with thermocouples to aid in determining burning rates by sensing changes in the level of the liquid hydrogen. Extinguishment tests will be conducted on these small 4.8 and 44 sq in fires, and then if suitable agents are found, extinguishment of large spill tests will be attempted at the Pine Ridge test site. Delivery of a 550 gallon liquid hydrogen Dewar is expected soon.

Experimental work on both gaseous detonation suppression and scaled fires will begin early in the next period.

Subject Headings: ***Fires, hydrogen, extinguishment of; Extinguishment, of hydrogen fires.***

B. Greifer

Atlantic Research Corporation (Alexandria, Virginia) "A Program to Advance the Technology of Fire Extinguishment," *Second Quarterly Progress Report, Wright Air Development Command Contract AF33(616)–8110* (October 15, 1961)

During this quarter, the literature survey was continued to obtain additional data on fires involving the hydrogen, oxygen, and air. The Anacostia Naval Air Station was visited to view demonstrations of dry chemical extinguishment of gasoline fires. Valuable information on extinguishment techniques was obtained at the demonstrations and the discussions which followed.

The construction of the liquid-hydrogen laboratory was completed, and experiments on small-scale fires were conducted. The site for large spill tests was selected and concrete pads for the large Dewars were designed.

Detonation tests of gaseous hydrogen-oxygen are essentially complete. Methane, methyl chloride, and iron pentacarbonyl as additives suppress detonation moderately but carbon tetrachloride acts as a sensitizer. The apparatus for the condensed-phase explosion studies with liquid hydrogen and solid oxygen was designed and is being constructed. Small-scale tests will begin early in the next quarter.

Scaled fires with liquid hydrogen have been conducted with the 2.75-and 7.5-inch-diameter Dewars. Regression rates were measured and found reasonably consistent. Initial attempts to extinguish a fire with a dry chemical (sodium bicarbonate) were not successful.

Further extinguishment tests employing various dry chemicals with modifications in application techniques are planned. Other types of extinguishment agents, e.g., water fog, steam, vaporizing liquid, and foam, will also be evaluated.

Subject Headings: ***Fires, hydrogen, extinguishment of; Extinguishment, of hydrogen fires.***

Note: This is a summary extracted from the report.

Coleman, E. H. (Joint Fire Research Organization, Boreham Wood, England) "Non-Flammable Liquid Mixtures and Safety Solvents," *The Industrial Chemist* 36, 211–214 (1960)

The effects of non-flammable liquids on the flammability limits of combustible vapors are discussed. Halogenated hydrocarbons added as non-flammables to combustible liquids cannot be presumed to reduce the fire hazards of such mixtures. Consideration must be given both to the process in which the mixture is to be used and to the respective volatilities of the components making up the mixture. Thus, the more volatile constituent may evaporate as part of a process leaving a mixture richer in the less volatile which, if the non-flammable constituent is that volatilized, may be highly flammable. Methods for calculating the limiting safe mixture ratios and examples of such calculations are given for carbon tetrachloride and hexane, methyl bromide and ethylene oxide, carbon tetrachloride and ethylene dichloride, and acetone and methylene chloride.

The criterion for a safe liquid mixture is that the vapor be non-flammable at all stages in the process for which the mixture is used. Inasmuch as the standard flash-point tests are inadequate, recommended are additional tests made on samples evaporated to 50 per cent of the original volume. Attention is also drawn to toxic problems with halogenated hydrocarbons and the hazards of inadvertent mixture with either metals or alkalies to produce dangerous reactions or combustibles.

Subject Heading: *Flammability, limits, of vapors.*

D. Dembrow

Gracie, J. D. and Droher, J. J. (Atomics International, Division of North American Aviation, Inc.) "A Study of Sodium Fires," *AEC Research and Development Report NAA-SR-4383, Contract AT(11–1)-Gen-8* (October 1960)

The study reported was undertaken to develop information on the extinguishment and handling of sodium fires. This information is required in connection with liquid sodium cooling systems used in nuclear reactors. In such systems, a typical accident might be represented by a molten sodium spray, or leak, emanating from a pressurized coolant pipe line, and the study reported included extensive tests set up to simulate such liquid spill and spray conditions, as might be realized in actual accidents.

Sodium (m.p. 97.8°C, b.p. 883°C) initially oxidizes by:

$$2Na+\tfrac{1}{2}O_2 \rightarrow Na_2O \qquad \Delta H \cong -104 \text{ kcal/g mole}$$

Na_2O when pure is white, but when impure, or with metallic sodium dispersed therein, it is grey or red. It sublimes at *ca.* 1260°C, and in the presence of excess oxygen at temperatures from around 240° to 400°C it is converted to the peroxide:

$$Na_2O+\tfrac{1}{2}O_2 \rightarrow Na_2O_2 \qquad \Delta H \cong -20 \text{ kcal/g mole}$$

The peroxide melts at 645°C (1210°F), and in the liquid phase evolves oxygen. The authors give data for approximating the heats of combustion for sodium within limits of accuracy of about ten per cent.

The combustion characteristics of sodium are described. In liquid pools, fires are characterized by low flames, and dense clouds of white smoke. The peroxide forms in nodules, incorporating particles of unreacted sodium, which glow in the burning process. The peroxide behaves somewhat as a tar, and on cooling and congealing forms a solid residue with a hollow core. In the molten state, it acts as a wick for the molten metal. Initiation of the oxidation reaction in undisturbed heated metal pools may occur in the temperature range of 260 to 420°C. The pool-fire burning rate was found to be *ca.* 75 to 150 mg $cm^{-2}min^{-1}$, with the highest value for the greatest pool depths (25 cm), and the lowest for the greatest surface areas (1000 to 1500 cm^2) investigated.

The dense white smoke contains both particles of the monoxide and the peroxide, and is highly caustic. Therefore, the inhalation of the smoke is to be avoided.

Temperature versus time profiles for sodium pool fires are presented. Burned as a spray in an atmosphere containing five or more per cent oxygen, sodium produces a shower of sparks and dense clouds of white smoke. In an atmosphere (dry) of less than five per cent oxygen concentration, no flames or incandescence are produced. In neither spray- or pool-type fires is the oxidation of sodium complete, but the proportion of unreacted sodium is the highest in the pool fires. Substantial quantities of reacted sodium, particularly in the spray-type combustion, are carried away in the smoke.

Studies reported revealing the combustion and ignition characteristics in an atmosphere of reduced oxygen concentration indicate that hydrogen or water as additives to the combustion system exert a critical influence. For example, liquid sprays at 104.4°C ignited and reacted on contact with an atmosphere containing as little as 10 mm Hg oxygen partial pressure in the presence of traces of water vapor (0.01 mm Hg) or hydrogen. Rates of pressure-rise, resulting from the injection of a molten spray into closed chambers, were investigated.

As a result of their studies, the authors present techniques for detecting leaks, preventing damage to equipment in the event of leakage of liquid sodium, and for accident cleanup. In addition, the results of an extensive empirical study of sodium fire-extinguishing methods are reported. The most effective agent found was a proprietary sodium chloride base powder (Met-L-X). Sodium carbonate and sodium stearate were also effective. Sand and calcium carbonate powders extinguished sodium fires, though they reacted exothermally with burning sodium (perhaps due to moisture content). Sodium bicarbonate powder was not effective, and cadmium carbonate powder, sodium phosphate powder, and a liquid mixture of equal portions of bromochloromethane and motor lubricating oil, all reacted explosively with burning sodium. A technique was also discussed for smothering certain types of sodium fires using a stainless steel foil blanket.

Seventeen references are cited, seven of which concern earlier investigations of the characteristics of sodium combustion.

Subject Headings: ***Fires, sodium; Sodium, fires of.***

J. E. Malcolm

Nash, P., Hird, D., and French R. J. (The Joint Fire Research Organization, Boreham Wood, England) "Base Injection of Foam for Fuel Storage Tanks," *The Institution of Fire Engineers Quarterly,* **XXI,** 116–122 (1961)

Foam is the most effective extinguisher of fires in large storage tanks containing low flash-point products if the foam can be properly applied to the burning liquid surface. Three methods of application of foams are considered.

1) Each tank can be equipped with a permanent installation. This method is regarded as the most reliable; it is also expensive.

2) A portable system serving several tanks requires that the foam be applied to the burning surface from outside the tank. This method may prove both slow and difficult to manage.

3) Foam can be carried to the burning tank through existing product lines which enter the tank. After entering the tank, the foam rises to the surface where it quenches the flames.

This paper discusses the problems associated with this third approach and describes experiments testing the approach in a 45-foot diameter tank.

There are four principal problems associated with base injection of foam. If the foam carries more than 10 volume per cent petrol to the burning surface, the intensity of the fire may be reduced but not completely extinguished. Physical properties of the foams may change between the time they are injected into the petrol stream and the time they arrive at the surface. Circulatory currents caused by the rising foams may cause problems in distributing the foam over the entire burning surface. Only a limited number of compounds can be used to make foams which can be successfully injected into existing petrol lines under typical conditions.

Fire tests were not made, but conclusions were drawn from observations of the behavior of the foams as they reached the surface of the petrol. Also, the petrol content of the foam on the surface was analyzed to help predict the ability of the foam to extinguish a fire. These observations were repeated for different inlet configurations and locations.

It was found that both the way in which the foam blanket is formed and the petrol content of the foam depend strongly on the location and number of the points of injection of the foam. A foam of the desired properties could probably extinguish fires in a 45-foot diameter tank if it is applied through a central swing arm or other centrally located inlet. Side injection would probably not be effective.

The authors suggest that the high petrol content of the foam blanket when using side injection is due to the way in which the foam blanket forms. Further experiments are needed to clarify this point.

Subject Headings: *Foam, base injection of; Extinguishment, by foam.*

L. R. Griffith

Jablonski, E. J. (U. S. Naval Research Laboratory, Washington, D.C.) "The Influence of Temperature on the Viscosity and Drainage Rates of Mechanically Produced Fire-Fighting Foams," *N.R.L. Report 5598* (March 1961)

Within the past twenty years, the use of mechanically produced fire-fighting foams has increased tremendously. The Bureau of Yards and Docks, under whose sponsorship the present work was carried out, has maintained an active and continued interest in this field. The majority of the work which has been done by the Naval Research Laboratory on aqueous foams is in the temperature range of 70 to 80°F. The purpose of this report is to extend the range of investigation from 40 to 100°F and to determine the effect of the temperature on the physical properties of the fire-fighting foam.

The foam concentrate liquid was made with protein hydrolyzates as the basic foaming material, in accordance with the standard government specification.[1] All foams described were made using this liquid in the conventional concentration of six per cent in an aqueous solution.

The three physical properties of a fire-fighting foam which are considered here are: its expansion ratio, its stability or rate of drainage, and its apparent viscosity. These properties in turn are dependent on the basic nature, temperature, and concentration of a foam liquid, and on the type of generating apparatus. The property of bubble size and bubble size distribution were not considered.

The apparatus and experimental methods described in this report were developed and standardized at the Naval Research Laboratory[2] and have been accepted as a standard by both military and commercial activities.[1]

The term "expansion ratio" denotes the ratio of the volume of foam produced to the initial volume of foaming solution used under a given set of operating conditions. Foam sampling containers were used 7⅜″ ID x 2″ deep.

The rate of drainage of the liquid aqueous foam from the sampling containers into a graduate is indicative of the stability of the foam. Bubbles of these foams do not ordinarily coalesce or collapse during the decay; rather the solution drains slowly out, leaving a skeletal form of the original bubbles. The stability of the foam is indicated by the time required for 25 per cent of the foam's original liquid content to drain out from the foam body. Since this time will vary with the relationship between sample cross-sectional area and depth, the apparatus has been standardized.[1]

The sphere viscometer used to measure the apparent viscosity is an adaptation of Amsel's ball method.[3] The term "apparent viscosity," when applied to a foam, is an empirical one and is used to denote the foam's resistance to shear when a sphere is moved up through the body of the foam at a constant speed of 1 ft/sec. Readings are taken on a spring balance of the force expressed in grams.

The mechanical foam generator consists of a foam solution pump, a source of air pressure, and a mixing chamber. The premixed six per cent foam solution is pumped into the mixing chamber at 0.50 gal/min and the air rate varied to obtain expansion ratios from 4 to 12. Two types of mixers can be used: a packed-column type employing aluminum metal turnings, and a nozzle-tailpiece type. The nozzle-tailpiece type has the advantage of yielding foams which are more uniform and reproducible. Therefore it was used in all of the tests.

Conclusions and recommendations may be summarized as follows: (1) It was found that as the solution temperature is lowered from 100 to 40°F, less energy is required to produce a foam of a given drainage time and apparent viscosity value within the 4 to 12 expansion range. (2) The effect of solution temperature on the viscosity of various expansion foams is somewhat similar to that found for the drainage times of these foams. (3) It is recommended that foam solution temperatures above 100°F not be used in foam generating equipment producing foams in the expansion 4 range because of the rapid decrease in foam stability and reduction in fire-extinguishing effectiveness.

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1. *U. S. Joint Army-Navy Specification JAN–C–266* (1945)
2. Tuve, R. L. and Peterson, H. B., "A Study of Some Mechanical Foams and Their Use for Extinguishing Tank Fires," *N.L.R. Report 3725* (August 23, 1950)
3. Amsel, O., *Oel u. Kohle* 38: 293–310 (1942)

Subject Heading: *Foam, viscosity and drainage rate.*

W. C. Johnston

VIII. Model Studies and Scaling Laws

Putnam, A. A. and Speich, C. F. (Battelle Memorial Institute, Columbus, Ohio) "A Model Study of the Interacting Effects of Mass Fires," Summary Report (November 9, 1961)

A mass-fire model burning gaseous fuels at controlled flow rates was used to study the merging of flames (primarily as merging affects flame height) from individual sources into a mass fire. The model consists of arrays of gas jets in which the effects of jet spacing, fuel flow rate, and jet-array geometry can be investigated. A theoretical analysis was undertaken to provide information on the parameters and dimensionless groups which best describe the changes in flame arrays which result from merging effects.

The first step was to determine the gas-flow velocities and jet diameters which would produce buoyancy-controlled diffusion flames. A recent equation of Spalding[1] gives the mass flux of air entrained into a jet for free convection conditions. For a jet in which a chemical reaction occurs, Ricou and Spalding[2] give an equation for a modified Froude number. Combining these two equations yields an equation for the flame height Z_1 for a single jet which may be written as

$$\frac{Z_1}{d_o}=K\left(\frac{Q_o^2}{gd_o^5}\right)^{1/5}$$

where K is a numerical constant, d_o the jet nozzle diameter, Q_o the volume flux of gas fuel, and g the acceleration due to gravity. When Z_1/d_o is plotted as a function of Q_o^2/gd_o^5 on a log-log scale, their data fall around a line with a slope of 1:5. The value of K as calculated from this line is 29. Another check on the requirement that the flames be buoyancy-controlled was a comparison of the measured central temperature at the flame tip with the central temperature as computed from the free convection equations.

In studying the merging effects in arrays of individual flames, three basic assumptions were made. First, the rate of entrainment of air into any given jet is decreased by the shielding or blocking effects of surrounding jets. Second, the ratio of the mass flux of air entrained throughout the height of the flame to the mass flux of injected gas fuel is constant for a jet whether it is isolated or in close proximity to other jets. The third assumption is that there is no significant deviation of a jet from the vertical because of the influence of surrounding jets. The mass flux equation of Spalding[1] can be written in the form

$$\rho_1 Q=\rho_o Q_o(0.165)z^{5/3}\left(\frac{\rho_1}{\rho_o}\right)^{5/6}\left(\frac{I}{d_o}\right)^{5/3}F_r^{-1/3} \tag{1}$$

where Q is the volume flux and ρ_1 the density of the air entrained throughout the height z, Q_0 is the volume flux and ρ_0 the density of the injected gas, and F_r the modified Froude number of Ricou and Spalding.[2] This number is defined by the equation

$$F_r = \frac{C_1 T_1}{m_{fu} H + C_0 (T_0 - T_1)} \left(\frac{U_0^2}{g d_0} \right) \left(\frac{\rho_1}{\rho_0} \right)^{1/2} \qquad (2)$$

where C_1 and C_0 are the specific heats of the ambient air and injected gas, respectively, T_1 and T_0 are the temperatures of the ambient air and injected gas, U_0 is the nozzle velocity of the injected gas, and H is its heat of combustion. (If the injected gas contains inert fractions, H is multiplied by m_{fu} the mass fraction of the gas fuel in the injected gas.)

By combining equations (1) and (2) and introducing a term to account for the partial blocking of the air supply of one jet by another, equations are derived which give the dimensionless flame heights of jet arrays in terms of the distance S between jet centers and Q_0. For two jets the dimensionless flame height Y is

$$Y = \frac{Z_1}{Z_2}$$

where Z_1 is the flame height for a single jet and Z_2 the flame height for the two-jet array. Y is expressed as a function of X where X is given by the equation

$$X = G \left[\frac{S}{(Q_0^2/g)^{1/5}} \right]$$

in which S is the distance between jet centers and G is a constant. When X is large the approximate relationship between X and Y is

$$X = \frac{Y}{4\pi (Y - 1)}$$

When X is small, Y can be obtained as a function of X from the equation

$$Y^{-5/3} = \int_0^{Y/X} (5/3)(y/x)^{2/3} \left(1 - \frac{\Theta}{\pi} \right)^{2/3} d(y/x)$$

where $y = 2/Z_1$. The function $\left(1 - \frac{\Theta}{\pi} \right)^{2/3}$ is introduced to account for the blocking effect of one jet on the air supply of the other. Θ is the half angle subtended by the diameter of one jet at the central axis of the other jet.

Similar equations are developed for greater numbers of jets and different patterns of arrangements. Plots of these equations do not agree well with the data based on flame height measurements. The most noticeable discrepancy is the sudden increase in flame height as jet spacing decreases. This is not indicated by the theoretical curves.

Recommendations are given for future work.

References

1. Spalding, D. B. "The Theory of Turbulent Jets of Nonuniform Momentum," April 1960 (to be published).
2. Ricou, F. P. and Spalding, D. B. "Measurements of Entrainment by Axisymmetrical Turbulent Jets," *Journal of Fluid Mechanics* 11, 21 (1961)

Subject Headings: *Models, of mass fires; Fires, mass, models of.*

G. M. Byram

Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "Research on Fires Using Models," *The Institution of Fire Engineers Quarterly* **XXI,** 197–219 (1961)

The author briefly describes recent work on the behavior of building fires using small-scale models at the Joint Fire Research Organization Laboratory at Boreham Wood. The paper presents some results of a continuing study, which the author believes may have immediate application in establishing fire regulations on a firmer scientific basis.

Types of studies discussed are: Fire in Single Compartments; Radiation from Fires; Flames from Windows; Effect of Wind.

Fire in Single Compartments

For a fire in single compartments in scale from 1/2 to 3 meters, the period of maximum flaming (or the second period of burning) is considered to be of prime importance by the author. It is during this period that the bulk of combustible material is consumed, which results in major structural damage. The air flow into a compartment is proportional to $A \sqrt{H}$, where A and H are the window area and height, respectively. The results of experimental fires show that the rate of burning is proportional to $A \sqrt{H}$. The author suggests that this finding is somewhat at variance with the fire-grading concept which uses the amount of fuel per unit floor area in determining fire resistance.

The effect of large windows, based on earlier work, is briefly discussed. The author points out that when the window area becomes very large in relation to the total area of the compartment the fire burns like an open fire, and the rate of burning is approximately proportional to the surface area of the fuel.

Radiation from Fires

Small-scale wood crib fires in open-front cubic boxes were used to evaluate the radiation intensity at a point in front of the window of a compartment fire. For cubes from 31 to 93 cm and where the window area is the same as the floor area, the ratio of radiation intensity to the rate of burning resulted in a value of 390 cal/g. This value is in agreement with that found by others.

Flames from Windows

Crib fires were burned in cubical enclosures, with one side open for estimating the height of flame emerging from windows of a burning compartment. The results are presented on a log-log plot of two-dimensionless quantities, which shows that L/D is a function of $R^2/\rho^2 g D^5$; where, L is flame height; D is a linear dimension of the fire; R is rate of weight loss; g is gravitational constant; and ρ is the density of volatile fuel at ambient temperature.

Effect of Wind

Wood cribs constructed to represent an infinite strip were burned to study the effect of wind and burning rate on flame height. Results are presented on a log-log plot of the product L/D and U^2/gD as a function of $r^2/\rho^2 gD^3$; where, U is wind speed and r is the burning rate.

The important conclusion the author makes is that the present basis of fire grading is somewhat deficient in not considering the importance of window area in compartment burning.

Subject Headings: *Fires, models of; Models, in fire research.*

W. L. Fons

Spalding, D. B. (Imperial College, London, England) "A Model for Studying Pulverized-Fuel Combustion," Paper No. 27 *Conference on Science in the Use of Coal—Institute of Fuel* (1958)

The use of cold models for quantitative measurements in combustion research generally requires the employment of tracer techniques. A tracer is injected into a carrier fluid flowing in the model, and its concentration throughout the model relative to the carrier is then determined with respect to either time or position. Such measurements provide information on flow patterns, mixing behavior, transit times, retention factors, and so on. In the past measurements generally have been made in one of two ways: (1) by steady-state tracer injection with point-position measurements of the time-mean concentration, to determine the steady concentration contours in space; or (2) by pulse injection with time-variable measurement of the space-mean concentration across a plane.

In the paper under review, the author suggests a new variant by combining the transient elements of both standard systems, i.e., pulse injection of the tracer with the time-variable concentration being observed point-by-point in space. To meet the requirements of instantaneous point measurements, the suggested tracer is salt in a water carrier so that relative concentrations can be measured by electrical conductivity.

The proposal is illustrated by order-of-magnitude calculations applied to a hypothetical model simulating a pulverised-fuel-fired boiler. This was assumed to be bottom-fired, burning anthracite, and of dimensions, 15 x 15 ft in plan section by 30 ft high. The proposed model would be scaled geometrically to ⅒th, i.e., reduced to 1 ft 6 in side by 3 ft high, with burners scaled by the Thring-Newby criterion. The calculations then call for water circulation of about 2 tons per min, flowing in the model at about 30 ft per min, supplied through the burners at approaching 500 ft per min. The expected salt concentrations to be detected by the point-conductivity probe are in the range N/1000 to N/10,000.

This was only proposed; no experiments were carried out, so the workability of the scheme has yet to be demonstrated.

Equations are then quoted that are said to relate salt concentrations to: rate of burnout; particle size; particle size distribution; and cloud emissivity. The validity of this claim is difficult to assess as the equations are quoted without derivation, and the assumptional basis can, therefore, only be inferred. The basis would seem to be that the time-distribution of the salt-pulse concentration (σ) can be used to infer the distribution in injection time that would be required in steady-state flow for a set of particles all to arrive at the sampling point simultaneously. If they all start with different initial radii (r_0), their different transit times can enable them to burn down to the same radius (r). By knowing the original relative number of a specific radius (r_0) at injection, from the Rosin-Rammler distribution [$\exp(-r_o/r_m)$], the fractional relative number that each initial radius (r_o) (now reduced to radius r) will give at the sampling point is the product of the R-R distribution factor and the salt density for the given radius, i.e., [$\sigma \exp(-r_o/r_m)$]—radius is related to time at the sampling point by an assumed burning-rate equation integrated over the transit time. Integrating then the (σ exp) product over all relevant initial radii thus gives the number of particles that have burned down to the specified radius, r; this can then be done for all other radii in turn to give the complete size distribution.

If this inferred basis is correct, two minor points need correcting: in the first, the residue form of the Rosin-Rammler distribution has been used when it would appear that it should have been the frequency distribution form; and in the second, the bottom limit of the (σ exp) integration should not be zero, it should presumably be the initial radius r_o that just burns down to the specified radius r in the shortest possible transit time.

The weakest theoretical point of the paper is accurately pinpointed by the author: the assumed constancy of specific reaction rate. This is certainly not true if reaction control is by diffusion, as assumed for the reaction-rate equation. For variable reaction rate, the increased labor required for both experiment and computation, as the author indicates, could well make the evaluation prohibitively tedious.

Subject Headings: *Combustion, of powders; Powders, combustion of.*

R. H. Essenhigh

Jewell, W. S. and Willoughby, A. B. (Broadview Research Corporation, Burlingame, California) "A Study to Analyze and Improve Procedures for Fire Damage Assessment Following Nuclear Attack, Part I," *Final Report under Contract with Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service* (October 1960)

This timely study seeks to make determinable the probable extent of fire damage resulting from nuclear bombs. The dual objectives are to develop a simplified calculation method for predicting total burnt-out area, emphasizing computational feasibility, and to develop improved fire-spread models for more accurate methods of estimating the damage area.

The initial premise is that the total burnt-out area comprises a region of initial ignition resulting directly from a nuclear weapon explosion, and a subsequent fire-spread area. The radius of initial ignition depends on the thermal radiation properties of the nuclear explosion, atmospheric transmission, and ignitibility of exposed fuels. The total thermal energy of air bursts (i.e., the fireball does not touch the ground) has been found equal to ⅓ the explosion yield; surface detonations produce a smaller thermal energy ratio, assumed as 1/4.5 in this study. Spectral distribution approximates a 6000°K black body for an air burst and a 3000°K body for a surface burst.

A blast of W kiloton yield produces Q thermal energy at a distance of D miles given by the relation:

$$Q = \frac{10^{12}\, W\, \overline{T}}{12\, \pi\, D^2}, \text{ cal/cm}^2 \qquad (1)$$

where $\bar{T}$ represents the atmospheric transmission fraction. Absorption and scattering processes diminish atmospheric transmission which can be evaluated in the form:

$$\bar{T}=(A+B\,t_1)\,T_\beta \qquad (2)$$

The constants A and B are dependent on the explosion color temperature equalling 0.52 and 0.48 respectively, for an air burst, and 0.08 and 0.92 for a surface burst. The value of t_1 is controlled by the amount of precipitable water vapor in the air, but for long distances is of the order of 0.5 to 0.6. The determination of diffuse transmittance, T_β, which includes scattering phenomena, has a great deal of uncertainty. Stewart and Curcio give a relation yielding a constant value of 0.6 for large distances, whereas Gibbons suggests a strong decrease with distance. The present authors bypass critical evaluation of this aspect of determining radiation transmission by averaging the values of T_β from both investigators.

The critical ignition energy of materials is defined as the minimum thermal energy to produce a sustained flow or glow. It is assumed that the average critical energy varies as the ⅛ power of weapon yield up to 1 MT, and as the ¼ power of megaton range yields (up to 20 MT). A "reasonable" average value for various ignitible materials is taken as 3 cal/cm^2 for a 20 KT weapon in a low humidity environment. Then, the average critical ignition energy, including yield and moisture variations, is given by:

$$Q=3(1+0.005H)\,(W/20)^{\frac{1}{8}} \quad \text{for } 20\text{ KT} \leqq W \leqq 1\text{ MT} \qquad (3)$$

and

$$Q=5(1+0.005H)\,(W)^{\frac{1}{4}} \quad \text{for } 1\text{ MT} \leqq W \leqq 20\text{ MT} \qquad (4)$$

H is the per cent relative humidity.

Initial ignition radius is computed and plotted, using the above four equations, for H=10%, 50%, and 90%, air and surface blasts and yields from 20 KT to 20 MT. The smallest explosion produces ignition at a 5 to 7 mile radius, while the 20 MT yield extends the initial ignition radius to between 14 miles (10% humidity, air burst) and 21 miles (90% humidity, surface burst). Considering the major uncertainties in the computation (i.e., diffuse transmission, thermal yield from surface bursts, and critical ignition energy for large weapons) the expected radius variation is about 15%.

The simplified method for fire-damage assessment is a rapid computational scheme for ultimate burnt-out area under the most probable conditions following a nuclear attack. It begins with the 1957 Forest Damage Assessment Study estimates of ultimate extensions from the initial ignition area in the four cardinal directions (denoted by N,E,S,W,) for 421 homogeneous areas in the United States. Based on "reasonable" assumptions about fire spread, the total burnt-out area, A, equals:

$$A=\pi(R+r)^2+\epsilon \qquad (5)$$

where: R is the initial ignition radius, r is the average extension = ¼ (N+E+S+W), and ϵ is an eccentricity correction factor related to N,E,S, and W.

The simplified method suffers, as does the more cumbersome 1957 graphical method, from a dependence on human estimates and inexact knowledge of fire-spread variation with the month, homogeneous region, and direction. Also the burnt-out mechanism is undefined and overlapping regions are not considered.

A preliminary inquiry is made into better prediction methods for ultimate fire boundaries. The major difference from normal peacetime fire fighting is that fuel, weather, and topography will be controlling factors rather than human efforts. The lack of a macrophysical understanding of massive fires, as well as inadequate fire data estimating and processing, preclude inclusion in a realistic fire-spread model. Therefore, the present emphasis is on a methodology to give correct and workable schemes for over-all prediction capability rather than detailed regional descriptions.

Accordingly, the authors suggest an improved model of ultimate fire spread which is based on:

a) the selection of a small number of pertinent parameters by experienced fire fighters for only a finite number of probable target areas (rather than homogeneous regions),

b) the use of wind, weather, and topography as the model variables, rather than month,

c) the introduction of statistical uncertainty for predicting degree of destruction,

d) the representation of areas by discrete (quantized) locations. In addition, the application of automatic computational machines is strongly indicated in order to handle data processing and the calculations.

Properly implemented, the model determines the average burnt-out area, $\bar{A}$, as the sum of the burnt-out probability, P_i, for all discrete locations (each representing an area of N^2 square miles), or:

$$\bar{A}=N^2\sum_i P_i \tag{6}$$

The variance from this average has an upper limit of

$$\begin{aligned}\sigma_A{}^2 &\leqq \bar{A}(A_{min}+A_{max})-A_{min}\,A_{max}-(\bar{A})^2\\ &\leqq \tfrac{1}{4}[(A_{max}-A_{min})^2]\end{aligned} \tag{7}$$

where $A_{min}=\pi(R+r_{min})^2$ and $A_{max}=\pi(R+r_{max})^2$, within 90% confidence.

The new method also accommodates overlapping burnt-out regions resulting from multiple nuclear bursts.

In summary, the present art of describing fire spread is dependent largely on the judgment of experienced fire fighters and is not likely to change for many years. For better fire-damage estimates, physical research is recommended to obtain data on the thermal yield and transmission of multi-megaton blasts into the initial ignition area, statistics of fuel distribution, and macrophysics of large-scale fire spread. Operational research is indicated in the areas of improved models for the ultimate extent and the dynamics of fire spread.

Subject Headings: *Fires, caused by nuclear attack, assessment of; Nuclear attack, fires caused by.*

K. M. Foreman

IX. Atomization of Liquids

Wilcox, J. D. and June, R. K. (Army Chemical Center, Maryland) "Apparatus for Study of the Breakup of Liquid Drops by High Velocity Airstreams," *Journal of The Franklin Institute* **271**, 169–183 (1961)

This paper contains a description of experimental apparatus constructed by the authors for investigating the disintegration mechanism of drops at approximately sonic velocities in air streams. A few experimental results are also briefly presented.

Two experimental techniques are reported. In the first, a drop was supported in a stationary position by means of a low-speed, vertical, open jet, powered by a variable-speed blower. The velocity distribution in the jet was tailored by means of contoured screens at the exit of the blower tube and a funnel placed above the drop. A blast gun, consisting of a tube with a high-pressure section, separated by a frangible diaphragm from a section open to the atmosphere, was directed toward the stationary drop. The response of the drop to the shock wave and the high-velocity flow from the exit of the blast gun was photographed by single-flash and double-flash shadowgraph techniques. Photographic results are presented for a 4 mm diameter drop of diethylene glycol monobutyl ether at an air speed of roughly 1290 ft/sec. Reflection of the shock front from the surface of the drop is evident, and the "surface stripping" breakup mechanism is clearly indicated.

In order to eliminate inaccuracies caused by the non-uniform velocity field and super-atmospheric pressure at the exit of the blast gun, a second experimental technique was developed. Conditions in a vertically-mounted conventional shock tube were adjusted to obtain atmospheric pressure behind the incident shock. A liquid drop was injected into the upper (low-pressure) end of the shock tube and allowed to fall freely down the tube. An elaborate timing mechanism burst the diaphragm at the right instant to insure that the drop and the shock wave would meet and the spark-light source would flash when the drop was adjacent to the photographic window. Photographs for a water drop, 4 mm in diameter, at a relative velocity of 1450 ft/sec, show details of the "surface stripping" mechanism.

Subject Heading: *Drops, break up of.*

F. A. Williams

X. Meteorological Interactions

Morton, B. R. (University of Manchester, Manchester, England) "On a Momentum-Mass Flux Diagram for Turbulent Jets, Plumes, and Wakes," *Journal of Fluid Mechanics* **10**, 101–112 (1961)

In many cases a sophisticated method of attack is not available for columnar flows involving diffusion and convection along the column. However, in this paper the author presents a simplified analysis of the turbulent axisymmetric flow of jets, wakes, and plumes (this last case is restricted to those in which the buoyant force acts in an axial direction only). Sufficient information for a variety of purposes may be obtained from this analysis to within an order of magnitude or better with a minimum of effort.

The author assumes that the mean profiles across the column are similar in shape at all axial stations and neglects molecular and longitudinal diffusion compared to turbulent and lateral diffusion. The flow is independent of the Reynolds number and the inflow speed across the mean boundary of the column is taken to be proportional to the velocity difference between the ambient fluid and the columnar fluid. For convenience the author has assumed top-hat (or constant) radial profiles within the column.

For the flow described above, the relationship between the dimensionless mass and momentum fluxes, M and V, may be written

$$\frac{dM}{dV}=A+\frac{BV}{M^{\frac{1}{2}}(M-AV)}$$

where A is the ratio of the free-stream velocity to the mean velocity of the column at the initial point of fully developed turbulent flow and B represents the buoyancy term evaluated at the same point. This equation thus describes the character of appropriate columnar flows without giving their distribution in space. A separate equation for spatial distribution is presented and may be integrated if so desired.

The treatment is based upon fully developed turbulent flow and thus the initial conditions, $V=1$ and $M=1$, have been set at the initial onset of turbulent flow. This corresponds to the assumption of a virtual source, located by extrapolating backwards from the end of the development region. The distinction between jets and wakes has been made on the basis of their relative motion with respect to the surroundings, jets having $A<1$ and wakes having $A>1$. In general it may also be said that a virtual source of momentum corresponds to jet flow and a virtual source of mass corresponds to wake flow.

The author specializes this description to a variety of cases; the simple jet, the jet in a uniform stream, the forced plume, the simple plume, the plume in a uniform stream, the forced wake, the simple wake, and the buoyant wake. In all cases either exact closed-form solutions or relatively simple numerical integration yields the characteristics of these flows. Some difficulty is encountered in determining the value of A for wakes but an approximate expression in terms of the drag coefficient may be used with good results.

The simplicity of this analysis insures the fact that the physical significance of all of the assumptions is exposed and allows acceptable results to be readily determined.

Subject Heading: ***Jets, momentum and mass flux in.***

T. P. Anderson

Ricou, F. P. and Spalding, D. B. (Imperial College, London, England) "Measurements of Entrainment by Axisymmetrical Turbulent Jets," *Journal of Fluid Mechanics* **11,** 21–32 (1961)

The motion of a turbulent jet through another gas at rest results in entrainment of ambient gas in the jet. For example, this phenomenon is the basis of the so-called "fire storms" which occur around large conflagrations. From dimensional analysis, it may be shown that the mass rate of flow across a section at right angles to the jet varies as the axial distance from the jet origin, if the axial distance is large compared to the jet diameter at the origin. The constant of proportionality must be found experimentally, and previously this has been done by many investigators. Generally, it is found by one of two methods: (1) Measure the velocity profile and find the mass flow by numerical integration, and (2) Assume a functional form for the velocity profile and integrate analytically to find the mass flow in terms of average velocities at two radial positions. With method (1) it is difficult to measure the velocity far from the jet axis. With method (2) the value depends somewhat on the choice of velocity profile. As a consequence, there is considerable divergence in results, indicating that a new method of measuring mass flow is desirable.

The authors present a new experimental method for measuring directly the mass flow entrained in the jet. Instead of flowing into an ambient atmosphere, the jet is surrounded by a porous-walled chamber through which gas is injected radially. The amount of gas injected is varied until the pressure in the chamber is uniform and atmospheric, at which point the mass rate of flow of injected gas is taken to be equal to that which would have been entrained under equivalent ambient conditions. Before employing the method, experiments were made to determine both the proper chamber-exit diameter and the lower limit to the Reynolds numbers which may be considered.

As a result of many experiments, a value for the above-mentioned constant of proportionality was found, which lies within the range of values found by other investigators. It is believed that this given value is the most accurate, since mass-flow measurements were made directly.

The effects of buoyancy and chemical reaction were investigated experimentally, and a general entrainment law was deduced from the results. However, the spread in the experimental points was too large to prove the validity of this relation.

Subject Heading: ***Jets, entrainment by.***

T. C. Adamson, Jr.

Gifford, F. (U. S. Weather Bureau Office, Oak Ridge, Tennessee) "Peak to Average Concentration Ratios According to a Fluctuating Plume Dispersion Model," *International Journal Air Pollution* 3, 253–260 (1960)

Large, short-period fluctuations in concentration levels are consistently measured in studies of atmospheric pollution from point sources. They are a permanent and characteristic feature of the atmospheric dispersion process. A fluctuating plume model is represented by two Gaussian distribution equations. One gives the mean concentration distribution and the other the instantaneous distribution within the plume. Dispersion due to the spreading of the plume in the y and z directions is represented by $\overline{Y^2}$ and $\overline{Z^2}$. Dispersion due to the meandering of the plume about its mean position is represented by $\overline{D_y^2}$ and $\overline{D_z^2}$.

The fluctuating plume is assumed to be composed of an infinite number of overlapping disk elements. The distance of the center of mass of such an element from the plume axis (considering dispersion in one lateral direction) is

$$D = \frac{1}{n}(y_1 + y_2 + \cdots y_n) \qquad (1)$$

where n is the number of particles in the element. The mean square distance of all the particles from the center of the element is

$$Y^2 = \frac{1}{n}[(D - y_1)^2 + (D - y_2)^2 + \cdots + (D - y_n)^2] \qquad (2)$$

The ensemble average of Y^2 is $\overline{Y^2}$ which from equations (1) and (2) is

$$\overline{Y^2} = \overline{y^2} - \overline{D^2} \qquad (3)$$

From equation (1) it follows that

$$D^2=\frac{1}{n}\overline{y^2}+\frac{(n-1)}{n}\overline{y_i\,y_j},\ i\neq j \tag{4}$$

so for large values of n

$$\overline{D^2}\rightarrow\overline{y_i\,y_j} \tag{5}$$

Hence, the plume dispersion parameter $\overline{D^2}$ (for large n) depends only on $y_i\,y_j$, that is, upon the statistics of two particles. Combining equations (3) and (4) gives (for large values of n)

$$\overline{Y^2}=\overline{y^2}-\overline{y_i\,y_j}$$

Batchelor's (1950) work showed that the plume-spreading parameter becomes independent of the two particle statistics for large values of travel times (i.e., large distances downwind from the source). This can be so only if $\overline{y_i\,y_j}$ approaches a constant value. Consequently, $\overline{D^2}$ must be constant for large travel times.

The peak concentration occurs when the receptor is at the centerline of the instantaneous plume. If atmospheric turbulence is such that the rates of horizontal and vertical mixing are about equal and if the source and receiver are at the same height, the ratio of peak to average concentration is shown to be

$$P/A=\frac{\overline{Y^2}+\overline{D^2}}{\overline{Y^2}}$$

$\overline{D^2}$ approaches a constant value for large travel times whereas $\overline{Y^2}$ continues to grow. Hence P/A→1 for large distances from the source.

Data from several investigators are presented which show the range of P/A and how it depends on sample time. At large distances from the source, measurements indicate that P/A→1 as the mathematical model predicts.

Subject Heading: ***Plumes, dispersion of.***

G. M. Byram

Ayer, H. S. (U. S. Weather Bureau, Portland, Oregon) "On the Dissipation of Drainage Wind Systems in Valleys in Morning Hours," *Journal of Meteorology* **18,** 560–563 (1961)

This brief report, based on eight double-theodolite balloon runs, agrees with other studies on the lowering of the top of the down-valley drainage current during its dissipation after sunrise. Observations were made between 0500 and 0840 local time on August 8, 1958, in the 1000 m deep U-shaped Carbon River Valley that flows northwestward for 30 km from the north side of Mt. Rainier to the flat lands between Puget Sound and the Cascade Mountains.

The top of the down-canyon drainage lowered from 560 m above the valley floor at 0500 to 360 m at 0800, though it rose to 440 m by 0840. Down-canyon speeds of 3 m/sec were noted in the layer while opposing westerly winds 5 to 6 m/sec prevailed only 3–400 m above. The observed 40–50 m/hr lowering of the drainage layer top is less than that reported by two other investigators. A broken layer of stratocumulus that moved in at 0730 may have slowed the dissipation process by reducing radiation.

Erosion of the top of the drainage current by mixing with the air above is suggested as a possible mechanism for dissipation of the drainage current.

Reversal of the pressure force along the valley and deepening of convective mixing from the valley floor also may contribute. Simple draining away of the cold air after its source is eliminated by warming would also cause the upper surface of the cold air to lower.

The title implies a much broader study. Although the author's interpretation of the data is probably correct, one could be more certain if the conditions reported were shown to be unique to the Carbon River Valley and not an extension of the prevailing weather pattern this particular morning.

Subject Heading: ***Wind, dissipation of.***

O. P. Cramer

XII. Instrumentation

Loftus, J. J., Gross, D., and Robertson, A. F. (National Bureau of Standards, Washington, D. C.) "Potential Heat—A Method for Measuring the Heat Release of Materials in Building Fires," *Proceedings of the American Society for Testing Materials* (1961)

The determination of the extent to which building materials burn and release heat during fires involving buildings is a complex problem. Considerable uncertainty exists as to exactly which material property is the significant factor of combustibility. Whereas surface flammability is concerned with the rate at which flames travel along the surface of materials, it is the extent to which the bulk of a wall, ceiling, or floor element may contribute heat to support active combustion which represents the degree of its combustibility or, as defined by the authors, its potential heat.

This paper describes modifications of a method that is currently a standard of the French Government for the assessment of the combustible characteristics of building materials. The method makes use of standard differential bomb calorimetric techniques in which the burning of small quantities of combustibles in an otherwise inert material is assured by use of a combustion promoter added prior to the test. By performing calorimetric measurements both before and after exposure to a "standardized fire," the difference may be considered as the potential heat of the material.

Experience with the test procedure indicates that it is applicable to a wide variety of building materials. It appears to provide a useful tool for determining potential heat, which is a measure of that portion of the gross heat of combustion liberated during exposure to a simulated standard fire at 750°C. The method has the advantage over previously used combustibility test methods of providing a quantitative measurement of the heat release during such exposure and is particularly suited for measurements on metals and on materials of low combustibility.

The experimental method is described in detail and the potential heats of a variety of building materials, including metals and materials of low combustibility, are presented. The results are in general agreement with fire experience, though little correlation was observed between the potential heat and flame spread index properties of the materials tested.

A complete discussion is included on the precision of the test method.

Subject Headings: ***Fires, heat release rates in; Heat release, rates in fires.***

E. C. Woodward, Jr.

McGuire, J. H. and Wraight, H. (Joint Fire Research Organization, Boreham Wood, England) "Radiometer for Field Use," *Journal of Scientific Instruments* **37**, 128–130 (1960)

To determine the hazard to buildings exposed to fires, an instrument is required which will measure thermal radiation in the ranges 0.05 to 1.5 cal cm^{-2} sec^{-1} and be insensitive to wind and ambient temperature effects.

An instrument for such field use was developed consisting of a lampblack-coated gold disc exposed to the incident radiation through a mica window, a second disc which was shielded, and thermocouples connected differentially to the two discs to provide the instrument output. The instrument can be water-cooled, if long exposure-times are anticipated.

The instrument has a response time of about 10 sec, is insensitive to ambient temperature, and is affected less than 8 per cent by winds up to 25 mph. It can measure intensities up to 1.2 cal cm^{-2} sec^{-1} for periods of exposure up to 5 minutes.

Subject Heading: *Radiation, measurement of.*

A. E. Noreen

Coleman, E. H. (Joint Fire Research Organization, Boreham Wood, England) "The Performance of Some Portable Explosimeters," *British Chemical Engineering* **5**, 500–502 (1960)

Determination of whether the concentration of flammable vapors is sufficient to be hazardous is important, in at least the mining and petroleum industries.

Portable instruments to measure gas concentration were tested. Two instruments which burned the gas catalytically on a heated platinum filament were evaluated, the filament temperature being a measure of the concentration. In another instrument the flame of a lamp became enlarged in the presence of flammable gas and operated the thermal switch of an alarm.

The filament instruments were sufficiently accurate to be used as an effective warning device on simpler hydrocarbons, lower alcohols and esters, which constitute most of the gases commonly encountered in industry. The flamelamp appears to be a less versatile instrument.

Subject Heading: *Explosions, in gas, measurement of hazard.*

A. E. Noreen

French, R. J. (Joint Fire Research Organization, Boreham Wood, England) "Foam Viscometer," *Journal of Scientific Instruments* **37**, 307–308 (1960)

Foams for fire-fighting use, although non-Newtonian fluids, do exhibit a well-defined critical shear stress. After an initial shear at the critical stress, a lower continuous stress can be measured. The critical shear stress is used as an indicator of the surface energy and flow properties of the foam.

A torsional-vane viscometer used in measuring shear stresses is described. This appears to be a relatively simple and inexpensive technique. It permits rapid evaluation of the shear stress; readings can be taken ten seconds after collection of the foam.

No sample data are shown to indicate reproducibility or sensitivity of the instrument.

Subject Heading: *Foam, viscometer for.*

A. E. Noreen

Wraight, H. and Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "A Comparison between Two Methods of Measuring the Flammability of Fabrics," *Journal of the Textile Institute* **51**, 203–207 (1960)

An important problem in establishing performance standards for fabrics is the choice of a suitable test to assess their flammability. The British Standards Institution recommends two tests: in the first, which is the method prescribed in the performance standard, a strip of cloth hanging vertically is burned from the bottom upwards; in the second, which is not referred to in the performance standard (BS 3121), a cloth strip held at 45° is ignited on the upper surface. In both cases the ignition source is of a standard intensity, and in both cases the time taken by the flame to travel a specified distance is taken to be a measure of the flammability of the material. The paper by Wraight and Thomas describes a comparison between the two methods. Standard apparatus was used to determine the relation between the "flame-resistance rating," M, defined as the time for the flame to propagate 100 inches vertically, and T_{45}, the time taken for the flame to propagate 5 inches along the fabric when held at an angle of 45°. The comparison was made for a variety of fabrics, including cotton, viscose, cellulose acetate, paper, and wool of various weights and weaves. For most substances, the results of the two tests may be correlated by the relation

$$M = 3.4\,T_{45}$$

Certain materials, however, did not conform to this equation, and the use of a measured T_{45} to calculate M for all forms of cellulose acetate and for wool-cotton mixtures would appear to lead to an incorrect result. Also, woolen materials which have a finite value of M, failed to ignite satisfactorily when used in the 45° test apparatus. The authors compare their results with the relation

$$M = 2.5\,T_{45}$$

quoted in BS 2963 and find that the use of this relation, given a measured T_{45}, leads in most cases to a conservative estimate for the flame-resistance rating.

Subject Headings: *Flammability, of fabrics; Fabrics, flammability of.*

D. G. Martin

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FOREWORD

The Ninth Symposium (International) on Combustion was held at Cornell University, August 27–September 1, 1962. In covering all current research areas in this extensive field a number of papers of direct concern to Fire Research were included. Since the Proceedings of this Symposium will not be available for several months, eight papers of particular interest to the readers of *Fire Research Abstracts and Reviews* have been singled out and are presented in this issue, either in the form of an Author's Summary (with a more detailed abstract to follow in a subsequent issue) or as a more extensive Author's Abstract. The papers by Thomas, Fons *et al.,* and Putnam and Speich were part of a Colloquium on Modeling Principles, arranged by Professor D. B. Spalding (Imperial College, London). The Proceedings will include all the papers, together with pertinent discussions of them.

A discussion on "Dust Explosions" was held at the Department of Fuel Technology, The Pennsylvania State University, under the general chairmanship of Professor M. W. Thring (University of Sheffield), September 4–5, 1962. It is hoped that a more detailed account of the Proceedings on this important subject will be published in an early issue of *Fire Research Abstracts and Reviews.*

A new section dealing with "Fire-Fighting Techniques, Equipment Design, Materials of Construction" is being added to this and subsequent issues. It will include those papers on the borderline between research and development which contain sufficient quantitative data to be of interest to the readers of *Fire Research Abstracts and Reviews.*

An observation by Professor D. B. Spalding and a reply thereto is reprinted in the section on "Comments and Discussions." The pages of this journal are always open to such contributions. Vigorous exchange of views can be published rapidly and presented to a wide readership. Similarly, reports of meetings having a bearing on the Fire Research problem will be gratefully accepted.

WALTER G. BERL,
Editor

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COMMENTS AND DISCUSSIONS

ABSTRACTS

I. Ignition Phenomena

Thomas, P. H. and Bowes, P. C. (Joint Fire Research Organization, Boreham Wood, England) "Thermal Ignition in a Slab with One Face at a Constant High Temperature," *Transactions of the Faraday Society* 57, 2007–2017 (1961)

The authors present a theoretical description of the thermal ignition of an axisymmetrically heated solid reactive material. The physical model is a slab of the material of finite thickness with one face at a constant high temperature and the other face in contact with surroundings of a constant lower temperature, with the cold surface temperature dependent upon the heat transfer rate to the surroundings. Application, for example, is the ignition of a thick layer of combustible dust in contact with a hot surface. As in the case of the symmetrical heating of a slab, there is a critical contact surface temperature above which the heat release in the media exceeds the loss by conduction to the hot and cold surfaces and the reaction rate accelerates until ignition or explosion occurs.

In the analysis an approximate solution for a range of variables of practical interest is obtained. An asymptotic form of the solution is given for the range which cannot be calculated.

The theoretical model of the system is as described above. An exothermic reaction occurs locally in the slab depending upon the local temperature and the reaction rate is related by the Arrhenius equation for a zero order reaction.

The equations for the steady-state heat transfer and steady-state temperature distribution are written in dimensionless form. An approximation is made, which is good only in the high temperature region, to facilitate a solution. The equation is solved for the critical depth in the slab, the point of maximum temperature at which the temperature gradient is zero. The conditions which result in ignition or explosion of the solid are those for which a maximum value of temperature in the slab exists for the steady state. Hence, a solution for ignition is obtained in terms of the hot surface temperature, the cold surroundings temperature, the film heat transfer coefficient, and the physical and chemical properties of the slab material. The solution is presented graphically as functions of only three dimensionless parameters.

In addition to the mathematical details of the solution, the authors present justifications for the approximation, and give the solution for the temperature distribution at critical conditions.

Other physical models are also considered. It is shown that if the hot surface is a perfect insulator, i.e., the temperature gradient at the hot surface is made zero, the resulting solution differs by only 1 to 5 per cent from the case of perfect thermal contact. The reason is that in the latter case, the critical point occurs very close to the hot surface for a wide range of values of the physical properties. For the case where the temperature gradient at the cold surface is zero, i.e., the heat transfer film coefficient approaches zero, the solution reduces to that of one half of a symmetrically heated slab.

Subject Headings: *Ignition, thermal, of slab; Thermal ignition, of slab.*

R. W. Ziemer

Simms, D. L. (Joint Fire Research Organization, Boreham Wood, England) "Experiments on the Ignition of Cellulosic Materials by Thermal Radiation," *Combustion and Flame* 5, 369–375 (1961)

In experiments to examine the ignition of cellulosic materials by thermal radiation, the temperatures in the stream of gases emitted from the irradiated surface have been measured by thermocouples placed both in and at varying distances above the surface. Various types of radiative source were used including a gas-fired radiant panel, tungsten and carbon arcs focused by ellipsoidal mirrors.

The effect of turbulence above the surface has been closely studied photographically and by the temperature distribution. The radiant panel and carbon arc sources produce convection currents so that the stream of volatiles from the heated specimen becomes turbulent regardless of the rate of heating. With tungsten filament no such draught occurs and the minimum radiation intensity required to ignite blackened fiber board insulation is higher with the tungsten source than with the other two.

Superimposing a draught on the laminar part of the volatile stream produced turbulence near its point of emission and hence ignition where otherwise turbulence would develop too far from the heated surface for the volatiles to be sufficiently hot to ignite. Where turbulence occurred naturally very near the point of emission of the volatiles, an imposed external draught had no effect on the ignition time. The results suggest a reason why large irradiated areas of the same cellulosic material are more quickly ignited than small ones at the same intensity of radiation. The smaller area emits a smaller plume of volatiles and for a heated plume of inert gas, the smaller the total amount of gas in the originating plume the further away from the source is the onset of turbulence and the lower the temperature at this point. The same effect would be expected for reacting gases up to the point at which heating as a result of the reaction in the gas becomes significant. This means that the smaller areas require a longer heating time to raise the temperature of the volatiles to a given value at the greater distance where turbulence begins. Hence the ignition time is longer.

Several experimental difficulties associated with mounting the specimen are discussed and it is suggested that work is required on much larger irradiated areas.

Subject Headings: ***Ignition, of cellulose by thermal radiation; Radiation, thermal, ignition of cellulose by; Cellulose, ignition of, by thermal radiation.***

G. L. Isles

Bowes, P. C. and Townshend, S. E. (Joint Fire Research Organization, Boreham Wood, England) "Ignition of Combustible Dusts on Hot Surfaces," *British Journal of Applied Physics* 13, 105–114 (1962)

Experimental

Two methods of determining the ignition temperatures of dust layers were applied:

I. A flat cylindrical sample of dust was deposited on a plane circular plate of aluminum alloy, 19 cm in diameter, heated electrically, and temperature-controlled within 1°C. Temperature rise in the dust layer was measured by a chromel-alumel thermocouple stretched parallel to the plate with junction over the center at a distance half the sample thickness. Deposits of higher density were prepared by compression.

Tests were made at a series of hot plate temperatures differing by 5°C. Ignition temperature was defined as that plate temperature at which ignition, as judged by observation, occurred, and which was 5°C higher than the maximum plate temperature without ignition in three to five repeated tests.

A typical temperature-time record is presented for a 2.5 cm layer of beech sawdust with maximum plate temperature of 275°C attained after 15 minutes. The dust temperature rose 200°C after 45 minutes when the T-t curve showed an inflection point. Between 75 and 90 minutes temperature rise was more rapid but lessened at 350°C, resuming speed after 100 minutes at temperatures above 400°C. In that stage smoldering at the top surface was observed. With 270°C plate temperature, sample temperature rose only to 216°C, whereafter it dropped. Layers less than 0.5 cm thick were tested only with fine fractions. Layers 0.3 cm thick could not be ignited unless deposited upon a preheated plate. For 0.5 cm thick layers, or thicker, ignition temperature was independent of preheating. Diameter/height ratio had no effect, provided it was greater than 5. Therefore, edge cooling seemed to be insignificant. Increase in layer density or particle size had little effect. In general, ignition temperatures increased with decreasing layer thickness, e.g., for beech sawdust from 275 at 2.5 cm to 350°C at 0.5 cm.

II. For comparison, some tests were made at uniform ambient temperature, samples being suspended inside an electric furnace. Thus determined ignition temperatures are slightly greater than in test I.

Theoretical

Interpretation of experiments is based on Thomas' generalization[1] of the Semenov[2] (infinite thermal conductivity) and Frank-Kamenetzkii[3] (infinite heat transfer coefficient) theories of thermal explosion. The present treatment[4] expresses critical parameter δ as function of dimensionless heat transfer coefficient $\alpha \cong (T_p - T_s)/2(T_s - T_0)$ and relative ambient temperature $E(T_0 - T_p)/RT^2_p$, where $T_0 = 300°K$, T_p = plate temperature, T_s = temperature of cool surface, and E = activation energy in a zero order Arrhenius-type reaction.

Conclusion

The theory permits predictions, though with larger errors, of critical conditions for ignition on hot surfaces from data on ignition in uniform ambient temperature, and vice versa.

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Subject Headings: ***Dusts, ignition of; Ignition, of dusts.***

H. M. Cassel

Bowes, P. C. and Hinkley, P. M. (Joint Fire Research Organization, Boreham Wood, England) "Spontaneous Heating and Ignition in Esparto Grass," *The World's Paper Trade Review* (August 17, 1961)

The authors obtained a continuous record of temperature and CO_2 concentration during early stages of self-heating of a sample of wet North African esparto grass placed in a specially adapted calorimeter. They calculated rate of heat and CO_2 evolution. Maxima of these rates occurred about 50 hours after wetting the grass and the maximum temperature of 67°C occurred at about 90 hours. Tests have shown that 75°C is possible from microbiological activity in other materials. Only hay from forage grasses and alfalfa are known to reach ignition by self-heating. But by analogy the authors conclude there is risk of self-ignition in a stack of esparto grass that becomes wet and begins to heat.

Subject Heading: *Ignition, of esparto grass.*

W. G. Morris

II. Thermal Decomposition

Laidler, K. J. and Wojciechowski, B. W. (University of Ottawa, Canada) "Kinetics and Mechanisms of the Thermal Decomposition of Ethane. I. The Uninhibited Reaction," *Proceedings of The Royal Society* **A260**, 91–102 (1961)

The ethane decomposition in the absence of inhibitors was studied between 550 and 640°C. The reaction was found to be accurately first order in an unpacked quartz reaction vessel as pressures above about 50 mm and under these conditions the rate constant, in agreement with other investigations, was $k=1.07\times10^{15}\exp(-73060/RT)\text{sec}^{-1}$. In a vessel packed with quartz tubes the rates were slightly lower, and the order was somewhat greater than unity (about 1.15). The effect of pressure on the order of reaction was investigated at 640°C down to low pressures. The order changed from unity to 3/2 at about 60 mm.

The results have been used to try to decide the initiating and terminating steps in the reaction chain. Two mechanisms have been proposed, the first by Rice and Herzfeld [1] consisting of reactions (ix), (x) and (xiv)–(xvi)

$$\begin{array}{rl}
\text{(xiv)} & C_2H_6 \rightarrow 2CH_3 \\
\text{(xv)} & CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \\
\text{(ix)} & C_2H_5 \rightarrow C_2H_4 + H \\
\text{(x)} & H + C_2H_6 \rightarrow H_2 + C_2H_5 \\
\text{(xvi)} & H + C_2H_5 \rightarrow C_2H_6 \text{ or } H_2 + C_2H_4
\end{array}$$

and the second, due to Küchler and Theile,[2] comprising reactions (with second order initiation) (ix), (x), (xiva), (xv) and (xvii),

$$\begin{array}{rl}
\text{(xiva)} & C_2H_6 + X \rightarrow 2CH_3 + X \\
\text{(xvii)} & C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \text{ or } C_2H_4 + C_2H_6
\end{array}$$

Consideration of the results of a theoretical investigation by Gill and Laidler [3] of the recombination of methyl radicals at 200°C leads the authors to the conclusion that the initiating reaction forming methyl radicals is second order under the conditions of the present experiments (reaction xiv a). Next, the chain terminating step is considered and it is predicted from consideration of the steady-state radical concentrations, that reaction (xvii) will predominate at high pressures, irrespective of which mechanism is assumed. In this case the experimentally observed first order pressure dependence is only given by the Küchler-Theile mechanism with second order initiation. At lower pressures reaction (xvi) becomes the chain terminating step, and the observed transition to 3/2 order occurs. The Küchler-Theile mechanism also predicts the observed activation energy better than that of Rice and Herzfeld, besides giving a reasonable prediction of the rate constant itself.

Inhibition of the reaction by its products and the inhibiting effects of additions of ethylene and hydrogen may be explained by the inclusion of reactions (xviii) and (xix) into the Küchler-Theile mechanism.

$$\text{(xviii)}\quad H+C_2H_4 \rightarrow C_2H_5$$
$$\text{(xix)}\quad C_2H_5+H_2 \rightarrow C_2H_6+H$$

Increase in the surface area of the reaction vessel (by packing) caused a decrease in reaction rate, attributed by the authors to H atom recombination on the surface. H atom recombination in the gas phase is neglected compared with the termination involving C_2H_5, for the reason that H atoms require a three body collision.

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Subject Headings: ***Ethane, thermal decomposition; Thermal decomposition, of ethane.***

G. Dixon-Lewis

Laidler, K. J. and Wojciechowski, B. W. (University of Ottawa, Canada) "Kinetics and Mechanisms of the Thermal Decomposition of Ethane. II. The Reaction Inhibited by Nitric Oxide," *Proceedings of The Royal Society* **A260,** 103–113 (1961)

The rates of decomposition of ethane when fully inhibited by nitric oxide were studied between 610 and 680°C. The rates are reduced to a limiting value for mixtures containing about 10 per cent nitric oxide and over, and the limiting rates are the same as those obtained when propylene is the inhibitor. The inhibited reaction has frequently been interpreted as a direct molecular decomposition of ethane into ethylene and hydrogen. However, a number of observations quoted in the paper are inconsistent with this view, and the authors propose an alternative mechanism in which nitric oxide both initiates chains by reaction (xx) whilst chain termination is by reaction (xxii) as at the beginning of the reaction, and by reaction (xxi) in the later stages.

$$\text{(xx)}\quad C_2H_6+NO \rightarrow C_2H_5+HNO$$
$$\text{(xxi)}\quad C_2H_5+HNO \rightarrow C_2H_6+NO$$
$$\text{(xxii)}\quad H+HNO \rightarrow H_2+NO$$

Experimentally, the pressure-time curves have initially a point of inflexion. The *initial* rates are proportional to the first power of the pressure at high pressures, and to the 3/2 power at lower pressures. *At the inflexion point* the rates are proportional to the pressure to a power slightly greater than unity. At pressures above about 200 mm the two rates are essentially the same, the induction period having vanished. In this first order region the rate constant is $k=3.12\times10^{15}$ $\exp(-77{,}500/RT)\text{sec}^{-1}$. The induction period disappears when 10 per cent ethylene is added to the mixture, and the rate of reaction is increased by about 10 per cent.

The observations are consistent with a mechanism for the steady-state reaction involving reactions (xx) and (xxi) together with reactions (ix) and (x) as propagating steps, and reactions (xxiii) and (xxiv) involving H, NO and HNO.

$$\text{(xxiii)}\quad H+NO\rightarrow HNO$$
$$\text{(xxiv)}\quad HNO\rightarrow H+NO$$

This is a mechanism in which the NO plays the same part as does the allyl radical in the propylene inhibited decomposition of ethane. Here the reactions involving NO serve to maintain the equilibrium $C_2H_5+H\rightleftharpoons C_2H_6$, and the decomposition rate is the same as that with propylene inhibition, giving first order kinetics. The reactions producing and removing C_2H_5 are much more rapid than in the uninhibited Küchler-Theile mechanism, so that the latter is essentially eliminated.

During the induction period at lower pressures the chain ending step is assumed to be reaction (xxii), leading to the order of 3/2 for the initial rates in this region. Above some transition pressure reaction (xxi) takes over even in the initial stages, and the initial rates become first order. At the end of the induction period, when ethylene has accumulated in the reaction vessel, a shift occurs in the ratio $(C_2H_5)/(H)$ with the result that the chain ending step is now always reaction (xxi). The inflexion point rates are therefore first order at all pressures. The elimination of the induction period when ethylene is added initially supports this view.

Subject Headings: ***Ethane, thermal decomposition; Nitric oxide, inhibition of ethane decomposition; Thermal decomposition, of ethane.***

G. Dixon-Lewis

Laidler K. J. and Wojciechowski, B. W. (University of Ottawa, Canada) "Kinetics of the Thermal Decomposition of Propylene, and of Propylene-Inhibited Hydrocarbon Decompositions," *Proceedings of The Royal Society* **A259**, 257–266 (1960)

The main products of the thermal decomposition of propylene studied between 580 and 640°C, were found to be ethylene, methane, and hydrogen, in the approximate ratio 2:2:1. Smaller amounts of ethane, propane, butenes, benzene, toluene and diallyl were found. The results are in agreement with those of Hurd and Meiner[1] and Ingold and Stubbs.[2] In contrast with the findings of Szwarc[3] at about 800°C and 10 mm pressure, no allene was found.

The order of the reaction between 580 and 640°C was 3/2. The rate constant, calculated from the maximum rates of pressure change, could be expressed by

$$k=2.2\times10^{13}\exp\left(\frac{-56{,}700}{RT}\right)\text{ml}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{sec}^{-1}$$

During the propylene decomposition in the presence of CD_4, which by itself undergoes no appreciable decomposition in this temperature range, steadily increasing amounts of CD_3H were produced, and significant amounts of $CH_2DCH=CH_2$ were also formed.

The rates of formation of the individual reaction products, and the observed activation energy may be satisfactorily explained by the proposed reactions (i) to (vii) which include abstraction reactions by H and CH_3.

(i) $CH_3CH=CH_2 \rightarrow CH_2-CH=CH_2+H$
(ii) $H+CH_3-CH=CH_2 \rightarrow CH_3-CH_2-CH_2$
(iii) $CH_3-CH_2-CH_2 \rightarrow H_2+C_3H_5$
(iv) $CH_3-CH_2-CH_2 \rightarrow C_2H_4+CH_3$
(v) $CH_3+CH_3-CH=CH_2 \rightarrow CH_4+CH_2-CH=CH_2$
(vi) $CH_2-CH=CH_2+CH_3-CH=CH_2 \rightarrow \text{higher hydrocarbons}+H$
(vii) $H+CH_2-CH=CH_2 \rightarrow CH_3-CH=CH_2$

If, at higher temperatures, reaction (vi) is replaced by reaction (via), then the production of allene (observed by Szwarc) may be explained.

(via) $CH_2-CH=CH_2 \rightarrow CH_2=C=CH_2+H$

Finally, a kinetic study was made of the decomposition of ethane at 600°C when fully inhibited by propylene. The inhibition is of the type where the first small additions of propylene to the ethane cause the rate to decrease until a rate characteristic of the propylene inhibited decomposition is reached: further additions of propylene have no effect. The order of the decomposition reaction when fully inhibited by propylene was unity.

The mechanism suggested by the authors for the fully inhibited decomposition involves initiation by H atom abstraction from C_2H_6 by allyl radicals, (reaction viii), and termination by the reaction of the ethyl radical with propylene (reaction xiii). The complete mechanism is:

(viii) $C_2H_6+C_3H_5 \rightarrow C_2H_5+C_3H_6$
(ix) $C_2H_5 \rightarrow C_2H_4+H$
(x) $H+C_2H_6 \rightarrow C_2H_5+H_2$
(xi) $H+C_3H_5 \rightarrow C_3H_6$
(xii) $C_3H_6 \rightarrow C_3H_5+H$
(xiii) $C_2H_5+C_3H_6 \rightarrow C_2H_6+C_3H_5$

This leads by the conventional steady state treatment to an overall reaction rate $v=(Kk_{11}k_{12})^{\frac{1}{2}}[C_2H_6]$, which is independent of the inhibitor concentration and first order in ethane concentration. In the steady state reactions (viii), and (xi) to (xiii), serve to maintain the equilibrium $C_2H_6 \rightleftharpoons C_2H_5+H$, and the constant K is the equilibrium constant. The propylene serves to maintain the equilibrium, provided that sufficient is present. Hence the limiting rate corresponding to the fully inhibited reaction.

The above approach to the propylene inhibition is different from that of previous workers, who have taken the alternative view that the propylene inhibits solely by removing radicals, and that the limiting rate is that of the direct molecular decomposition of ethane.

Nitric oxide, acting as an inhibitor, gives the same limiting rate as propylene, but smaller quantities of NO are required to establish this. Either hypothesis of the action of the additives is able to explain the phenomenon. In the radical mechanism, similar roles would be allotted to NO and the allyl radical.

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Subject Headings: ***Propylene, thermal decomposition; Thermal decomposition, of propylene; Hydrocarbons, decomposition, inhibited by propylene.***

G. Dixon-Lewis

Holmes, F. H. and Shaw, C. J. G. (Brunel College of Technology, London, England) "The Pyrolysis of Cellulose and the Action of Flame-Retardants. I. Significance and Analysis of the Tar," *Journal of Applied Chemistry* **11,** 210–216 (1961)

A study has been made of the pyrolysis of different cottons in vacuum, and in dry air, primarily at 418°C, and the products have been fractionated and analyzed. When cotton or any nonvolatile solid polymeric fuel burns it undergoes thermal decomposition (pyrolysis) and yields volatile products of lower molecular weight which in turn support combustion. The authors have shown that flame retardants added to the fabrics react with the cellulose at or below the burning temperature, altering the course of the pyrolysis so that the volatiles found are primarily noncombustible and are largely composed of water vapor.

The pyrolysis tests were conducted on cotton poplin, oxycellulose and two prepared strips of cotton Winceyette. The flame retardants tested were No. 1 Proban finish (P_n1), No. 2 Proban finish (P_n2), water soluble borax (50% w/w) and boric acid (40% w/w) and sodium metavanadate. The fabrics at reduced pressures (10^{-4} mm) were immersed into a preheated electric oven at 418±3°C and the resulting gases and vapors collected and fractionated in cold traps at 25°, −80°, and −190°C. The gases that were not condensed at −190°C were collected in a gas collection bulb. Each of the above fractions were analyzed on a Perkin-Elmer "Infracord" recording double-beam spectrophotometer, Model 137. Elementary carbon and hydrogen analysis was conducted on the tars condensed at 25°C and molecular weights were determined by elevation of the boiling point of acetone. The infrared spectrum of the tars from the pyrolysis of cotton poplin was found to be very similar to that of laevoglucosan except for the presence of a small peak probably due to the presence of a carbonyl group. A methanolic solution of the tar was smeared on Whatman No. 54 chromatography paper and after development the resulting chromagram showed 5 distinct zones. The fraction that moved at the same rate as pure laevoglucosan was extracted with a methanolic solution and recrystallized from ethanol. The crystals had very nearly the same melting range (180–182°C) as pure laevoglucosan (182–183°C). The quantitative analysis of laevoglucosan in each tar was determined from the infrared spectrum. Those strips treated with the flame retardant showed considerable decrease in the laevoglucosan content. Acids, carbonyl groups, and unsaturates were also shown to be present in the tar in each case, although no attempt was made to determine their exact composition.

In all cases, the −190°C fraction contained primarily carbon monoxide and the −80°C fraction, for the cottons, had an infrared spectra characteristic of carbon dioxide and a small maximum near 1700 cm^{-1} probably due to carbonyl groups. The Winceyette treated with P_n1 showed the presence of ammonia and possibly phosphene. The fraction volatile at room temperature that condensed at −80°C showed the presence of water only in each case.

The infrared spectra of the tars from the air and vacuum-pyrolysis were similar except the air-pyrolysis showed stronger carbonyl peaks. The tar from the oxycellulose had a spectrum bearing no resemblance to that of laevoglucosan. Finally the char, analyzed with infrared and X-ray spectroscopy, showed the presence of aromatic or unsaturated groups and the complete absence of any crystal structure.

Subject Headings: *Cellulose, pyrolysis of; Pyrolysis, of cellulose; Tars, in pyrolysis of cellulose; Flame retardants, effects on cellulose.*

H. E. Perlee

Roberts, A. F. and Clough, G. (Safety in Mines Research Establishment, Derbyshire, England) "Thermal Decomposition of Wood in an Inert Atmosphere," *Paper presented at Ninth Symposium (International) on Combustion, Cornell University, August 27–September 1, 1962.* (To be published in the Proceedings)

Introduction

The thermal decomposition of wood has up to now been represented by an overall first order reaction with a definite heat of reaction.[1] There is now sufficient experimental evidence to show that such a treatment is too simple, since values obtained for activation energy and heat of reaction vary with experimental conditions. [2, 3]

The present paper describes a series of experiments in which cylinders of wood were decomposed under controlled heating conditions in an atmosphere of nitrogen in a furnace. During each experiment, the specimen was weighed continuously and its temperature was measured at several points. Data were analyzed in terms of the above theory to examine its validity and shortcomings.

Experimental Arrangement

Experiments were carried out on cylinders of oven-dried beech, 2 cm in diameter, 15 cm in length and 25 gm in weight, into which five thermocouples were inserted along fine holes drilled parallel to the axis of the cylinder. A cylinder was mounted on a supporting rod which formed part of a continuous weighing system, the specimen being maintained at the axis of the furnace throughout the experiment by means of a servo system. This system could follow changes in weight of 0.2 gm.

A cylindrical muffle furnace, with a zone of uniform heating 40 cm in length, was used for heating the specimens. When switched on, the temperature of the furnace rose at approximately 20°C/min to a preset control temperature which it maintained to within ±5°C.

To carry out an experiment, the specimen, mounted on its supporting rod, was inserted into the cold furnace through which nitrogen was passing. A furnace control temperature was selected and the furnace switched on. The weight of the specimen was recorded at 15 second intervals and each thermocouple reading at 30 second intervals until five minutes after the decomposed specimen had reached constant weight. The furnace was then switched off and the specimen left to cool in an atmosphere of nitrogen.

Summary of Data Obtained

		Experiment No.				
		1	2	3	4	5
Maximum temperature achieved by specimen	°C	445	353	505	394	282
(Final weight/Initial weight) × 100	per cent	30.9	52.5	28.0	39.7	78.6
Maximum rate of weight loss	mg/sec	92	26	193	40	8
Surface area of specimen	cm^2	97	88	88	88	85

The variations in the percentage loss of weight and maximum rate of weight loss demonstrate how sensitive the decomposition of wood is to changes in the heating conditions.

From the temperature records graphs of temperature against distance from surface were plotted at one minute intervals. These records illustrate the effects of exothermic reactions on the temperature distribution within the specimen, as the center temperature rises above that of the surface in the later stages.

Calculations Based on Results

1. *The Overall Kinetics of the Reaction*

The data were used to test the suggestion that the thermal decomposition of wood can be represented by a first order reaction, i.e.,

$$-\frac{dw}{dt}=k(w-w')\exp(-E/RT)$$

where

w = weight at time t
w' = final weight

Since the temperature distribution in the specimen was known throughout the period of decomposition, a weight/time curve could be calculated for particular values of k and E. For the first four experiments, good agreement between experimental and calculated weight/time curves was obtained with values of $k=9.1\times10^4\ \text{min}^{-1}$ and $E=15{,}000$ cal/mole, while for the fifth experiment better agreement was obtained with $k=2.6\times10^9\ \text{min}^{-1}$ and $E=25{,}000$ cal/mole.

2. *The Heat of Reaction*

A heat balance can be written on any cylindrical surface within the specimen as heat transferred across the surface + heat generated within the surface =

sensible heat within the surface. The first and third of these terms were calculated from the measured temperature distribution, while values for the second term were obtained by assuming a value for q, the heat of reaction. For the first four experiments agreement was obtained with values of q in the range 55–75 cal/gm whereas for the fifth experiment a value of $q = 280$ cal/gm was obtained.

Discussion

The weight/time data could be represented satisfactorily by a first order reaction law. However, this law made use of the final weight of the specimen, a quantity which is not determined *a priori* but which is determined by the course of the reaction. The need for an alternative law which obviates this difficulty is discussed.

The fifth experiment gave exceptional values both for activation energy and heat of reaction. These values did, however, agree with others obtained in self ignition experiments,[4] which were also carried out at temperatures less than 300°C. The other experiments gave self consistent values.

It is suggested that the first decomposition reaction to take place has an activation energy of 25,000 cal/mole. As the wood temperature rises, this reaction proceeds rapidly to completion, whereupon the effects of a further reaction, activation energy 15,000 cal/mole, predominate.

Differences in the heat of reaction could arise if the primary decomposition had a low heat of reaction and the bulk of the heat release came from a secondary decomposition of volatile matter, a theory that has previously been suggested.[5] The total heat release would then depend on the residence time of volatile matter within the specimen after its production. Gentle heating conditions would permit more time for secondary reaction and would give rise to a higher heat of reaction, such as that in the fifth experiment.

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Subject Headings: ***Wood, thermal decomposition of; Thermal decomposition, of wood.***

Authors' Abstract

Arseneau, D. F. (Xavier Junior College, Sydney, Nova Scotia) "The Differential Thermal Analysis of Wood," *Canadian Journal of Chemistry* 39, 1915–1919 (1961)

Differential thermal analysis was made of 5-milligram samples mixed with equal volume of aluminum oxide against aluminum oxide at a heating rate of 5.8°C a minute between 50 and 420°C in a brass-block furnace with air circulated around the sample. Balsam fir filings were screened for particles between 70 and 200 mesh and were tested in the air-dry and the "bone-dry" conditions. In addition, alcohol-water and benzene-alcohol extracts, sulfuric acid lignin, potassium hydroxide hemicellulose, and extract-free wood were prepared from the powdered wood and tested.

The differential thermogram for balsam fir in air is simply a composite of the individual thermograms of the wood components, with little or no interaction between them. All thermograms run predominantly endothermically to somewhere between 250 and 300°C after which all but that for alcohol-water extract turn more or less sharply exothermic to a peak somewhere between 300 and 330°C. For air-dry wood feeble peaks at 145° and 163°C are attributable to the alcohol-water extract, a peak at 210°C remains unexplained, one at 265°C may be due to lignin, at 285°C to the benzene-alcohol extract, at 300°C to both hemicellulose and lignin, at 330°C to cellulose, and at 360°C to both lignin and benzene-alcohol extract. The peaks attributed to lignin are shifted in the thermogram for separated lignin, perhaps because lignin is altered in its extraction. A close similarity of the curves for lignin and benzene-alcohol extract suggests the presence of "native" lignin in the extract. The sharply exothermic peak for cellulose at 330°C corresponds to an endothermic nadir reported by other workers for heating in nitrogen instead of air. The thermogram for extract-free wood lacks the peaks attributed to the extracts and that for "bone-dry" wood unaccountably lacks the peaks observed at 145, 163, 210, 265, and 300°C for air-dry wood.

Subject Headings: ***Wood, differential analysis; Differential analysis, of wood.***

F. L. Browne

III. Heat and Material Transfer

Murgai, M. P. (Harvard University, Cambridge, Massachusetts) "Radiative Transfer Effects in Natural Convection Above Fires," *Journal of Fluid Mechanics* **12**, 441–448 (1962)

A theoretical investigation of the effects of radiative heat transfer on the convection plume over a fire requires a solution of the three conservation equations of fluid mechanics coupled with the integro-differential equation of radiative transfer. It is assumed that (1) the flow in the convection plume is turbulent, (2) the atmosphere is calm, isentropic, and emits black body radiation, (3) the radiating material in the plume consists of a single component whose emission and absorption properties remain constant with height, and (4) emissivity and absorptivity are the same.

The general method of analysis follows that given in an earlier paper by Murgai and Emmons.[1] The equations of conservation of mass, momentum, and energy are the same as before except that a term has been included in the energy equation to represent the heating rate H per unit volume due to radiation flux. Solutions to the radiative transfer equation give H for two limiting cases, designated as the "transparent" and "opaque" approximations. In the opaque approximation, it is assumed that the mean free path of the radiation $1/k^*$ is very small compared to the plume width. Murgai's analysis indicates that the opaque approximation reduces to the case of no radiative transfer. In the transparent approximation, it is assumed that $1/k^*$ is large compared to the plume width. In this case the final forms of the conservation equations are

$$\frac{d}{dx}(b^2u)=bu$$

$$\frac{d}{dx}(b^2u^2)=b^2\lambda$$

$$\frac{d}{dx}(b^2u\lambda)=-b^2\phi\{(1+\lambda\delta)^4-1\}$$

All variables are dimensionless and are defined in the same way as in the earlier paper[1] except for δ and ϕ. δ is

$$\delta=\left(\frac{T-T_\infty}{T}\right)_{x=0}$$

where T is the mean plume temperature and T_∞ the temperature of the surrounding atmosphere. The dimensionless radiation number ϕ is

$$\phi=\frac{4k^*\sigma T_{\infty 0}^{3} p_0^{(3k-4)/k} b_0^{1/2}}{\rho_0 c_p g^{1/2} \alpha^{1/2} I^* (\Delta\gamma_0/\gamma_0)_0^{3/2}}$$

where

k^* = radiation absorption factor
σ = Stefan constant
p_0 = ratio of the pressure to some standard pressure
b_0 = source width
ρ_0 = potential density in the plume
$T_{\infty 0}$ = potential temperature of the ambient atmosphere
c_p = specific heat at constant pressure
g = acceleration due to gravity
α = a constant
I^* = a shape factor
γ_0 = potential specific weight in the plume

The boundary conditions are

$$b=1,\ \lambda=1,\ u=u_0=1,\ \text{for } x=0$$

Solutions to the equations are illustrated by a set of curves in which b, u, and λ are shown as functions of x for $\delta=2.0$ and for values of ϕ ranging from 0 (no radiation) to 0.5. An accompanying table shows the heights at which buoyancy and momentum are reduced to ½ their initial values.

Possibly the most striking and puzzling feature of Murgai's results is the marked loss of buoyancy with height. For a convection plume in an isentropic atmosphere, the upward flow of either buoyancy or heat through any horizontal cross section of the plume should be the same for all heights if there is no radiation loss. Also, the upward flux of either quantity should be proportional to the product $b^2\lambda u$. Murgai's curves show that this product is unity at all heights when $\phi=0$ as one would expect. However, for a value of $\delta=2.0$, $\phi=0.02$, and $x=4$, the product $b^2\lambda u$ is only 0.16. This would mean that 84 per cent of the initial heat is radiated from the column in a vertical distance that is only a few times the flame height. Values of radiation from Murgai's theory thus appear to be considerably greater than given by measurements of radiation from flames.

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Subject Headings: ***Fires, radiative transfer; Convection, radiative transfer effects.***

G. M. Byram

IV. Diffusion Flames

Thomas, P. H., Webster, C. T., and Raftery, M. M. (Joint Fire Research Organization, Boreham Wood, England) "Some Experiments on Buoyant Diffusion Flames," *Combustion and Flame* 5, 359–367 (1961)

Dimensional analysis leads to a simple relationship between flame height, burning rate, and orifice size for buoyant diffusion flames; namely

$$\frac{L}{D} \propto \left[\frac{Q^2}{g\,D^5}\right]^n$$

where

L = flame height
D = burner orifice diameter
Q = rate of fuel supply
g = gravitational acceleration

The exponent n is shown to vary from an approximate value of unity to 0.2 as L/D increases; until at high values of Q^2/D^5 when orifice momentum becomes significant, it tends to zero and L/D becomes constant. This upper limit of L/D is typical of a turbulent jet where buoyancy is of minor importance. The authors have assumed, on the basis of the work of Hottel and Hawthorne on laminar flames, that

$$\frac{D^2}{D_v} \propto t_f$$

where

D_v = diffusion coefficient
t_f = time required for fuel to reach the flame tip from burner

Additionally, in writing a functional relationship involving the Grashof and Reynolds numbers, the ratio of the kinematic viscosity of the fuel to that of the air and the ratio of the absolute mean flame temperature to ambient temperature are assumed constant for a given fuel/air system. A functional representation of the concentration of the fuel along the axis of the fuel stream was also assumed. An alternative derivation of the generalized correlation is given and the general equation is discussed.

Experimental results are presented for cribs of spruce on square horizontal bases, cribs in an enclosure and strips of hanging fabrics. By varying the amount of wood in the crib various mass rates of weight loss, ρQ, could be obtained for a given base size (D) by direct weighing, where ρ is the density of the cold fuel gas. The height of the flame, in each case, was measured from the base of the crib. The burning rates reached a maximum value which remained steady for a period of time and this rate of burning as well as a time-averaged flame height were recorded. The experimental results for cribs on square horizontal bases were correlated by

$$\frac{L}{D}=4.4\left[\frac{\rho^2 Q^2}{D^5}\right]^{0.30}$$

where Re>2000. An assumed value of 10^{-4} cgs units were used for the viscosity. For a given burning rate per unit area, the above expression reduces to

$$\frac{L}{D}\propto D^{-0.3}$$

It is noted that when buoyancy is important the mean velocity of the gases increases rapidly with height, and turbulence may be induced at a height which is a small fraction of the total flame height even if the Reynolds number based on the conditions of the emerging fuel shows this flow to be laminar.

National Bureau of Standards data on Douglas fir and U.S. Forest Service data on white fir were plotted and found to be in substantial agreement with the author's results.

The data for cribs in an enclosure were also correlated by plotting L/D versus $(\rho Q)^2/D^5$; Reynolds numbers being varied from 2300 to 5400. This correlation is relatively less established than that on open cribs in view of the limited data obtained. As a first approximation the following correlation is proposed

$$\frac{L}{D}\propto\left[\frac{R'^2}{D^3}\right]^n$$

where R′ is the mass burning rate per unit width in a rectilinear enclosure of which the height is equal to the dimension perpendicular to the opening. For the experiment performed, $o/n \approx 1/3$ and L is only weakly dependent on D.

Subject Headings: ***Flame, buoyant diffusion; Diffusion flame, buoyant.***

L. A. Povinelli

Essenhigh, R. H. and Csaba, J. (University of Sheffield, Sheffield, England) "The Thermal-Radiation Theory for Plane-Flame Propagation in Coal-Dust Clouds," *Paper presented at Ninth Symposium (International) on Combustion, Cornell University, August 27–September 1, 1962.* (To be published in the Proceedings)

The Nusselt radiation theory of steady-state propagation of a plane-flame through a dust cloud has been extended to take into account: a finite temperature difference between the particles and air; and, a finite pre-ignition zone (implying finite ignition time or distance).

The dust cloud is assumed to be monodisperse, formed by the suspension of finely ground coal in air. As the ignition temperature of coal dust is believed to be the coal decomposition temperature, this is a constant, independent of the ambient conditions, and it therefore effectively decouples the pre-ignition and flame zones; this means that the pre-ignition zone can be treated independently of the flame. The dust in the pre-ignition zone is assumed to be heated by radiation from the flame alone; conduction is neglected. Part of the radiant heat absorbed by the particles is then lost by conduction to the surrounding gas. The gas temperature therefore lags that of the particles. Because of this heating, however, the gas expands with the consequence that the gas density and the dust concentration (and therefore the radiation-attenuation coefficient) all drop.

The system as specified is governed by two simultaneous ordinary differential equations; and analytical solutions for the respective rise of the particles and gas temperatures have been found. In the limiting case, when the particle temperature reaches ignition, the solution for the particle temperature provides an expression for the flame speed.

The main conclusions of the analysis are that

1) Flame speed can be defined as the *cold* cloud speed required to hold the flame stationary at some suitable plane; the *hot* cloud speed at the flame front is then the burning velocity.

2) A "fundamental" flame speed, s_o, exists which is obtained when the ignition time or distance is infinite; it is determined solely by combustion conditions and behaviour.

3) The infinite ignition distance can be approximated experimentally; in practice it is achieved approximately if the ignition distance is about 1 meter when the flame speed is also about 1 m/sec. This has been achieved experimentally, in a system mentioned in the paper (though not described in detail).

4) The fundamental flame speed is given by a general equation that may be written

$$s_o = I_f/(T_i - T_o)(D_o c_d + \beta p_o c_p)$$

where I_f is the radiation intensity crossing the flame front (assumed to be derived from a black body at 1500°C); T_i and T_o are the ignition and input temperatures, respectively, of the dust particles; D_o and p_o are the input densities, respectively, of the dust and air; and, c_d and c_p are their specific heats; β is a thermal capacity factor, that appears as a consequence of the particle/gas temperature differential; its value is generally about 0.8 or 0.9.

5) The fundamental flame speed has a normal value of about 1 m/sec., and is expected to peak at the stoichiometric concentration. The flame speed rises with a rising input temperature or preheat; in the fuel rich region, it drops with increasing dust concentration.

6) With reduced input velocity of the dust cloud, the flame speed drops and is then controllable by adjustment of the cloud input velocity. The flame front then adjusts to a position from the burners such that the ignition time or distance is finite. Ignition time and distance are therefore dependent parameters, being related to the independently-controllable flame speed by the equations

$$s = s_o(1 - e^{m t_i})$$
$$\cong s_o(1 - e^{k_o L_i})$$

(t_i and L_i are inherently negative by the mathematical formulation of the analysis, so the equations represent rising flame speed with increasing t_i or L_i). t_i and L_i are ignition time and distance; m and k_o are radiation attenuation coefficients.

7) As the ignition time or distance is allowed to drop, so also does the flame speed; and the position of the flame speed peak (optimum concentration) moves progressively fuel rich.

8) Flame speed in enclosed jet flames is increased by the recirculation of combustion products that, in effect, provides "preheat." Calculations based on the effect of preheating indicate that, at permissible levels of recirculation, this can increase the flame speed by at least an order of magnitude (factor of 10 or more). Recirculation then supplies 90 to 95% of the heat required for ignition. The function of "ignition" refractory round the burners in industrial systems, where this is necessary, is therefore believed to be required to maintain the temperature of the recirculating flow, rather than to increase the radiant flux to the dust cloud.

9. Peak flame speeds in jet flames are usually believed to occur at high fuel-rich concentrations. If this is true (as has yet to be confirmed experimentally), it is probably a consequence of fuel injection speeds, or recirculation preheats, being such as to create low ignition times. The consequence then would be that the peak flame speed would migrate into the fuel-rich region.

Subject Headings: ***Coal dust, flame propagation in; Flame, propagation, in coal dust.***

Authors' Abstract

Fons, W. L. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service, Berkeley, California) "Rate of Combustion from Free Surfaces of Liquid Hydrocarbons," *Combustion and Flame* 5, 283–287 (1961)

This paper reports the results of tests intended to measure the burning rates of liquid n-hexane and cyclohexane as a function of the area of the burning fuel surface. The work was undertaken to help design a model combustion system to represent the fuel and weather conditions in forest fires.

Tests were carried out in open pans ranging from 0.22 to 11.94 inches in diameter. The apparatus was such as to permit a constant surface area to be maintained throughout the twelve to fifteen minutes of burning. Care was taken to ensure that burning took place without rippling or bubbling at the surface of the fuel. With the four largest pans—the three, six, eight, and twelve inch burners—fuel temperature was measured at points 0.625 inches and 0.687 inches below the burning surface.

The burning velocity was found to decrease with pan size when the pans were small and to increase with size for large diameter pans. The minimum occurred at about a five inch diameter as the laminar flow regime entered the transition regime.

For the system studied, the mass transfer-heat transfer analogy assuming natural convection results in

$$\frac{Md}{\nu_\infty \rho_\infty g} \propto \left(\frac{gd^3}{\nu^2_\infty}\right)^n$$

where

M = combustion rate
d = diameter of the burning surface
g = gravitational acceleration
ν_∞ = kinematic viscosity of air
ρ_∞ = mass density of air.

A plot of the data based on average burning rates over the period tested yields values of *n* varying from 0.25 for small pans to 1.0 for the largest pans.

Previous workers have reported values of 0.25 for n for various fuels burning from small spherical surfaces and for alcohol burning from an 11.8 inch diameter pan. Since neither rippling nor boiling of the surface was observed during the test, the author refuses to attribute the increase in n to a change in total surface area. Rather, since the above proportionality is based on heat transfer by convection only, he concludes that n is increasing due to a greater contribution from radiation. As the pan size increases the height of the flame and the emissivity increase, especially for fuels that are likely to burn with sooty flames. Under such conditions the surface temperature is increased due to the radiation and results in the observed increase in n.

Based on the above findings the author suggests it will be necessary to determine the importance of the area of the fuel bed in the burning of solid fuels before designing a model for a forest-fire combustion system.

Subject Headings: ***Combustion rate, from free surfaces; Surfaces, combustion rate from; Hydrocarbons, combustion rate, from free surfaces.***

F. Falk

Hirst, R. and Sutton, D. (Rocket Propulsion Establishment, Westcott, Aylesbury, Bucks, England) "The Effect of Reduced Pressure and Airflow on Liquid Surface Diffusion Flames," *Combustion and Flame* 5, 319–330 (1961)

The experiments reported in this paper were carried out to obtain information on the stability of flames at high altitudes under conditions similar to those existing in airplane engine nacelles. While other types of fires are possible, this work is concerned only with puddle burning, which the authors consider the most difficult to extinguish. The first portion of the paper deals with temperature measurements in the carbon-free part of the flame, temperatures in the liquid, the rate of fuel consumption, and flame dimensions as they are influenced by pressure, burning diameter, air flow around the burner and vitiation. The second part of the paper is concerned with the determination of the air velocity required to extinguish the flame both with and without simple flameholders.

To carry out the first portion of the work burners varying in diameter from 1.1 to 3.8 inches were installed in a 200 cubic foot capacity cylindrical decompression chamber which could be pumped out to a minimum pressure of 0.04 atm, a simulation of 70,000 ft altitude. The apparatus was arranged so as to maintain a constant fuel level in the burner throughout the test. A laminar airflow was supplied to the burner from a 6.3 inch tube. Both isodecane and kerosene were used as fuels.

For very small air flows the flame was extinguished after some finite burning time. This was apparently due to an insufficient oxygen supply and general vitiation of the chamber atmosphere. Higher airflows, used for subsequent experiments, were found to have essentially no effect on fuel consumption.

The rate of fuel consumption was found to be quite dependent on pressure, burner radius, and vitiation. Results with all burners indicated the rate of consumption to be proportional to the 0.46 power of the pressure and the 1.5 power of the burner radius. Fuel consumption fell off rapidly with vitiation (air with added nitrogen) until a limiting oxygen concentration extinguished the flame.

In the second part of the work reported in this paper, the effect of airflow on low pressure liquid surface diffusion flames was studied in a small variable density wind tunnel. An airfoil section containing a five inch long tray of fuel provided the surface for burning. Fuel was supplied through support tubes to maintain the surface at a constant level. The airflow profile was examined and shown to be substantially laminar.

Tests were carried out to determine the velocity of air which caused flame-out under the various pressure conditions. Variations in the length of the nose section of the model from 6 to 26 inches failed to change the extinction velocities indicating that within the accuracy of the method and over the range studied the boundary layer thickness is not important. Extinction velocities varied from about 2 ft/sec at 0.1 atm to 14 ft/sec at 1.0 atm.

When obstructions were placed just upstream of the fuel tray on the model surface, marked increases in extinction velocity were noted. For the particular configuration used, a ⅜ inch high plate provided the greatest increase, resulting in a stable flame up to 160 ft/sec at 0.4 atm pressure.

Fuel temperature was found to have no effect on extinction velocity at pressures above 0.4 atm. At 0.2 atm, however, a decrease from 40 to about 5°C resulted in a decrease from 12 to 8 ft/sec with no obstruction on the model.

Based on the work reported, the authors conclude the following:

1) At altitudes up to 40,000 ft (0.19 atm) the probability of a stable flame in an undamaged engine nacelle is high. At 50,000 ft (0.11 atm) the probability is much less and at 60,000 ft (0.07 atm) the probability is almost negligible.
2) In a damaged nacelle it may be possible to maintain a stable flame even above 60,000 ft due to the obstructions which will provide additional stability.

Subject Headings: ***Diffusion flames, liquid surface; Flame, diffusion, effect of pressure and airflow.***

F. Falk

V. Combustion Principles

Chen, T. N. and Toong, T. Y. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "Structure and Propagation of Laminar Flames near a Heat Sink," *Combustion and Flame* 4, 313–323 (1960)

A theoretical analysis is presented of the structure and burning velocity of a laminar, one-dimensional flame in the presence of heat sinks. Arbitrary functions are chosen to describe the rate of heat loss inside the flame and at the hot boundary. The reaction kinetics are assumed to be of first order and are represented by an overall Arrhenius equation. At the cold boundary the reaction rate is made equal to zero. First, the heat loss rate per unit flow area is made to be a function of the fraction of material reacted. In the presence of such a heat loss term, a very pronounced effect on the burning velocity is computed; namely $S_u \propto \exp(-T_b^o/T_b)$ where T_b^o is the adiabatic flame temperature in the absence of a heat sink inside the flame in a direction normal to the gas velocity. Next, the heat sink is chosen at the hot boundary parallel to the gas flow. The results indicate that a steady-state solution for the burning velocity does not exist below a lower limit for the temperature of the combustion products. This limit in the rate of heat loss per unit area at the hot boundary differs from that deduced on the basis of stability considerations.[1, 2]

The authors extend their calculations to an examination of the effect of the temperature of the unburnt mixture on burning velocity. In spite of the questionable assumptions made in the description of the reaction kinetics the theoretical curve appears to fit well the experimental measurements on methane-air flames.[3] Such an agreement should not be taken as a measure of the degree of realism of the model.

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Subject Heading: ***Flame, laminar, propagation near heat sink.***

H. Wise

Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "Effect of Reactant Consumption on the Induction Period and Critical Condition for a Thermal Explosion," *Proceedings of the Royal Society* **A262,** 192–206 (1961)

In the thermal theory of ignition or explosion by self heating, explosion will occur for given conditions of external heat exchange if a parameter δ exceeds a critical value δ_c. The nondimensional parameter δ is a measure of the magnitude of the thermochemical heat release rate per unit volume relative to the rate of heat dissipation by internal conduction. For $\delta > \delta_c$ the induction time before the explosion, being dependent on the value of $\exp[E/(RT_o)]$,[1] has been used experimentally to infer activation energies. However, as shown by the numerical solutions of Rice, Allen, and Campbell,[2] Todes and Melentiev[3] and the analysis of Frank-Kamenetskii,[4] both the magnitude of δ_c and the dimensionless induction time τ_e are affected by reactant depletion for finite values of the group

$$\left(\frac{E}{RT_o}\right)\left(\frac{Q}{cT_o}\right)\left(\frac{1}{n}\right)$$

where

E = activation energy
R = universal gas constant
T_o = initial temperature of sample
Q = heat release per unit mass of reactant
c = specific heat of material
n = true reaction order

In the present paper the author re-examines this problem analytically, assuming $[E/(RT_o)][Q/(cT_o)][1/n]$ is large but finite. By invoking assumptions similar to those used in previous treatments of the transient state * the behavior of the

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* Namely, the use of (i) an effective mean temperature and effective transfer coefficient to the surroundings, and (ii) a quadratic approximation[5] for $\exp[-E/(RT)]$.

system is shown to be related to properties of the well tabulated Airy functions[6] Ai(x), Bi(x). This leads to the following asymptotic relation between δ_c in the absence (∞) and presence of reactant depletion

$$\delta_c \sim \delta_c(\infty)\left\{1+2.85\left[\left(\frac{E}{RT_o}\right)\left(\frac{Q}{cT_o}\right)\left(\frac{1}{n}\right)\right]^{-2/3} - \ldots\right\}$$

a relation which is consistent with the numerical results of Rice, *et al.*[2] and Todes and Melentiev.[3] This relation is also of the same form as that obtained earlier by Frank-Kamenetskii,[4] however, the numerical constant (2.85) is more than twice that given in reference 4. It is further shown that the sensitivity of the non-dimensional induction period τ_e to reactant loss depends only on

$$\left[\left(\frac{E}{RT_o}\right)\left(\frac{Q}{cT_o}\right)\left(\frac{1}{n}\right)\right]^{2/3}\left[1-\frac{\delta_c(\infty)}{\delta_c}\right]$$

and numerical limits are given outside of which activation energy experiments will be free of the complications associated with reactant loss for reactions with $n \neq 0$. Thus, in the self heating and ignition of wood and similar low heat-of-reaction materials, experiments in which induction times are proportional to $\exp[E/(RT_o)]$ may nevertheless be performed near the critical condition.

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Subject Headings: ***Explosion, thermal, induction period; Induction period, of thermal explosion.***

D. W. Rosner

Applied Physics Laboratory, The Johns Hopkins University "Flame Inhibition Research," *Quarterly Progress Report (1 May 1961–31 July 1961) (TG 376–3) ERDL Project No. 8M76–05–001–03*

This report represents the third quarterly progress report on a program of basic research on the mechanism of inhibition of hydrocarbon-air flames by halogenated compounds. The system being studied is the methane-oxygen flame ($CH_4-0.078$, $O_2-0.92$ $P=0.05$ atm) with and without the addition of hydrogen bromide inhibitor. The investigators plan to study the effect of the inhibitor on the flame structure by determining temperature and composition profiles by thermocouple and micro-probe sampling techniques. The composition profile studies are designed to include the determination of radical concentrations by "scavenging" techniques, i.e., by the reaction of radicals within the probe with some appropriate chemical species, with the formation of a stable product whose analysis will permit the calculation of the precursor radical concentration.

The program to date has proceeded along three lines. In one phase methane-oxygen flames with and without added hydrogen bromide have been burned on a flat flame burner at 0.05 atmosphere. Further experiments along these lines were performed in the present quarter but difficulties engendered by the attack of hydrogen bromide and bromine atoms on the metal apparatus were so great that the investigators have redesigned the burner using glass, ceramic, and teflon as building materials. No results have yet been obtained with this burner.

In another phase of the work, the experimental evaluation of the high temperature diffusion coefficients required for the interpretation of the probe studies is being pursued. Binary diffusion coefficients for the relevant flame species are to be measured at 300 and 500°K using the point-source method developed in this laboratory. In the present quarter the apparatus was calibrated with the He-N_2 system. Plans call for studies of the binary systems, argon-flame species, with hydrogen being the first such species studied.

In the third phase of the work the experiments on the effectiveness of selected "scavengers" are being performed. Chlorinated hydrocarbons had been proposed as "scavengers" for hydrogen atoms, i.e., $H+CCl_4 \rightarrow HCl+CCl_3$ but it was found in the present quarter that the reaction above could not compete effectively with atom recombination. Nitrogen dioxide on the other hand was found, in initial experiments, to be a suitable O atom "scavenger" via $O+NO_2=NO+O_2$. Here the difficulties are due, not to insufficiently rapid reaction, but to the corrosive properties of nitrogen dioxide. Further work with nitrogen dioxide is indicated.

Subject Headings: ***Flame, inhibition; Inhibition, of flame; Hydrogen bromide, as flame inhibitor; Methane, flame, HBr inhibitor.***

J. B. Levy

Applied Physics Laboratory, The Johns Hopkins University "Flame Inhibition Research," *Quarterly Progress Report* (*1 August 1960–31 October 1960*) *and Yearly Summary* (*1 November 1960–31 October 1961*) (*TG 376–4*) *ERDL Project No. 8M76–05–001–3*

This report combines the fourth quarterly progress report on this program with the first annual report. The program is directed at the study of the effect of halogen-containing inhibitors on hydrocarbon-air flames. The system chosen for initial study is the methane-oxygen flame. The inhibitor being studied first is hydrogen bromide. The general plan of the program is the study of the effect of the inhibitor on the flame structure by the determination of temperature and composition profiles by thermocouple and microprobe sampling techniques which have been developed in this laboratory.

In order to interpret any probe results, data on the high temperature diffusion coefficients of the gaseous species are required. Measurements of binary diffusion coefficients by the point-source method are being made. The measuring system was calibrated with helium-nitrogen mixtures at 300 and 500°K. Most recently, measurements on argon-hydrogen mixtures have been made at atmospheric pressure from 300 to 1070°K.

Another feature of this program is the attempt to sample atoms and radical species by the probe technique as well as stable molecules. This is being done by allowing the sampled gases to mix, in the probe, with molecules that will "scavenge" the atoms or radicals and convert them unambiguously to stable species whose concentration then allows a calculation of the atom concentration. "Scavenger" species must of course be able to react with the atom before other reactions intervene. To date NO_2 appears to be satisfactory for the determination of O atoms via the reactions $O+NO_2 \rightarrow O_2+NO$ but the reaction which was designed for H atom analyses, i.e., $H+CCl_4 \rightarrow HCl+CCl_3$, apparently cannot compete effectively with recombination.

Initial flame-probing experiments were performed on the flat flame burner with methane-oxygen ($CH_4-0.078$, $O_2-0.92$) flames inhibited by up to 0.035 mole fraction hydrogen bromide. Here difficulties arising from attack of hydrogen bromide on the metal apparatus were so great that it was necessary to design a new burner made of glass, ceramic, and Teflon. This is under construction.

Further experiments have been performed using a spherical flame apparatus with the system $CH_4-0.09$, $O_2-0.179$, $A-0.72$, $P=0.05$ atm. Composition profiles were measured for the uninhibited flame and for the flame inhibited by hydrogen bromide. Temperature profiles were also measured for these systems and it was found that the rate of reaction of the major species, i.e., CH_4, O_2 and CO, was lowered by the inhibitor. The apparent hydrogen atom concentration was measured by the "scavenging" technique and was strongly depressed by the inhibitor; the "scavenging" technique for hydrogen atoms is, as discussed above, not very reliable, however.

The results also indicated that a significant part of the reaction occurred at the surface of the ceramic sphere so that the extent of the contribution of heterogenous processes is uncertain.

Subject Headings: ***Flame, inhibition; Inhibition, by hydrogen bromide; Hydrogen bromide, as flame inhibitor.***

J. B. Levy

Laderman, A. J., Urtiew, P. A., and Oppenheim, A. K. (University of California, Berkeley, California) "On the Generation of a Shock Wave by Flame in an Explosive Gas," *Paper presented at Ninth Symposium (International) on Combustion, Cornell University, August 27–September 1, 1962.* (To be published in the Proceedings)

The fact that the transition from slow buring to detonation is, to a large extent, governed by the action of shock waves, is today well known. The most intricate problem in this respect is posed by the question: How do the shock waves originate?

The belief most prevalent in the literature is that, in order to generate detonation, the combustion zone has to become first distributed in space either by the action of turbulence or by breaking down into separate combustion pockets, providing thus a sufficiently large increase in flame front area to render the combustion process an "explosive" character. Basically such a property of a combustible mixture should be exhibited most unequivocally by the facility it has in generating shock waves. However, except for the analytical inquiries of Boa-Teh Chu, who investigated the mechanism of pressure wave generation by the flame, and of Jones, who demonstrated under what circumstances shocks are formed in a compression wave preceding a highly idealized piston model of a flame, very little has been done so far to explore this phenomenon.

It is for the purpose of elucidating upon this question that the present paper is offered. Experimental observations demonstrate that at the initial stage of the development of the process, shock waves are formed by laminar flames which exhibit a certain amount of cellular structure but are still far from breaking down into a turbulent brush. Furthermore, analysis of the process reveals that acceleration of the flame is usually sufficiently intense (its value increasing with time) to promote the formation of the shock inside the simple wave generated by the flame, rather than at its leading edge. Both the experimental evidence and the theory indicate that shock waves are fully formed quite early and surprisingly close to the front of the accelerating flame.

Subject Headings: *Flame, generation of shock waves; Detonation, transition, of flames into.*

Authors' Abstract

VI. Radiation

Oppenheim, U. P. (Israel Institute of Technology, Haifa, Israel) "Spectral Emissivity of the 4.3 μ CO_2 Band at 1200°K," *Paper presented at Ninth Symposium (International) on Combustion, Cornell University, August 27–September 1, 1962.* (To be published in the Proceedings)

Recently a number of studies have been made of the radiant infrared power emitted by molecules present in the exhaust plumes of rockets and jet engines. The interest in quantitative infrared emission data is based on the information which such data can give about the composition and temperature of the emitting gases. Basic information about the chemical and physical processes occurring in flames may thus be obtained.

The difficulties in studying infrared emission from flames are mostly due to inhomogeneities in concentration and to temperature gradients. In order to obtain the fundamental radiation properties of the constituent gases of the flames it is advisable, therefore, to study the gases statically in a closed vessel, which is raised to the desired temperature. Conditions in the flame (apart from those of flow) may then be simulated by changing the composition, temperature, pressure, and optical depth of the gas in the vessel. Low resolution studies of CO_2 heated in closed vessels up to about 1200°K have been reported by various authors.

Theoretical calculations of infrared emission (or absorption) have been carried out by Plass.[1] These calculations were of two types: one type gave a prediction of the band absorption as a function of various parameters of the gas (pressure, optical depth, etc.) in the form of universal absorption curves; another produced the spectral emissivity of CO_2 in the 4.3 μ band as a function of temperature.[2] The latter was intended as an illustration of the theoretical predictions of the former. However, large discrepancies were discovered between these results for CO_2 and the experimentally obtained emissivities. The agreement between results from different laboratories was also unsatisfactory. It is the intention of the present paper to show how agreement may be found between the various experimental results, and how the theoretical work of Plass[1] can be used to extrapolate these results to arbitrary values of the parameters of the emitting gas.

Plass has given an exhaustive treatment of the various models which may be used in calculating band emission. We shall assume here that at a temperature of 1200°K the statistical model with Lorentz line shape and equally intense lines is valid for the 4.3 μ band of CO_2. Plass has calculated curves which give the percent absorption A of such a band, or of a small wavelength interval in the band, as a function of the parameters x and β. These are actually generalized curves of growth for large assemblies of spectral lines of known shape and spacing. x is the parameter of Ladenburg and Reich defined by

$$x=\frac{Spl}{2\pi\alpha}$$

where S is the integrated intensity of a single line, p the partial pressure of the emitting gas, l the length of the emitting column of gas and α the half-width of a line. The parameter β is given by

$$\beta=\frac{2\pi\alpha}{d}$$

where d is the average spacing between spectral lines, Since α is proportional to the total pressure P it may be written

$$\alpha=\alpha_0 P$$

It is seen that β is proportional to P.

If β is kept constant and the parameter x is increased the curve giving the percent absorption A as a function of $\beta^2 x$ at first rises linearly, then levels off and finally reaches 100% absorption. In its linear part the curve is given by

$$A=\beta x$$

As x increases it is given by $A=1-e^{-\beta x}$, the so-called weak-line approximation. In its uppermost part it is represented by the strong-line approximation defined by

$$A=1-e^{-\beta}\left(\frac{2}{\pi}x\right)^{\frac{1}{2}}$$

There are intermediate regions where the functional form of A is more complicated. However, the dependence of A on total pressure always follows an exponential law of the type $A=1-\exp(-k\beta)$, which may be mistaken for the simple Lambert-Beer law $A=1-\exp(-k_\upsilon pl)$. It is evident that k assumes different values in the different regions of the A-curve, and is therefore not a constant, such as the spectral absorption coefficient k_υ appearing in Lambert-Beer's law. It is also seen that the dependence on x, and therefore on the length l, is at first linear and later becomes "square root" as the absorption saturates.

Since in most experiments l is not varied, many investigators have successfully fitted their results to some form of Beer's law. However, large discrepancies were found between results taken with different lengths l. As an example we quote $k_\upsilon=1.0$ obtained by Tourin[3] for CO_2 at 4.4μ, at a temperature of 1273°K, while Steinberg and Davies[4] obtained $k_\upsilon=2.9$. A detailed analysis of existing experimental data will be presented, in which agreement between different laboratories is obtained only after a Plass-type dependence of the absorption on β and x is assumed. It will be shown, also, that the calculated values of Plass for the 4.3μ CO_2 band at a temperature of 1200°K do not agree with experimental results, but that they may be applied after certain corrections are carried out.

The experimental spectroscopic data needed for a Plass-type representation of laboratory absorption data for the CO_2 fundamental at 4.3μ have so far not been available for elevated temperatures. We have therefore measured this band at a temperature of 1200°K as a function of pressure and optical depth. In order to settle the dependence of the absorption A on l, it was decided to use pure CO_2 and to vary the length of the absorption cells. The gas was introduced, therefore, in metal vessels varying in length between 5 mm and 250 mm, with sapphire windows permitting optical observations. A Perkin-Elmer Model 12G grating spectrometer was used for absorption measurements. The entire optical system could be flushed with inert gases and atmospheric absorption could be eliminated. Data were obtained both for the total band absorption and for the spectral absorption over a wide range of pressures and optical depths. The data were fitted to a set of Plass-type curves of growth and satisfactory agreement was found when a statistical band model was used. It is believed that with the help of these curves reliable values of the absorption may be obtained for any desired value of the parameters of the gas.

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Subject Headings: ***Emissivity, of carbon dioxide; Carbon dioxide, emissivity.***

Author's Abstract

Siddall, R. G. and McGrath, I. A. (University of Sheffield, Sheffield, England) "The Emissivity of Luminous Flames," *Paper presented at Ninth Symposium (International) on Combustion, Cornell University, August 27–September 1, 1962.* (To be published in the Proceedings)

The solid carbon particles which are formed in a flame as a result of the incomplete combustion of hydrocarbons are extremely desirable because they increase flame emissivity. However, the exact prediction of the emissivity resulting from the presence of a cloud of solid particles has proved extremely difficult. Experimental investigations carried out by various workers in an attempt to elucidate this problem have led to values for the extinction coefficient of a cloud or soot layer. Their work suggested that a satisfactory form for the variation of the extinction coefficient ($K\lambda$) with the wavelength (λ) of the incident radiation is $K\lambda = k\lambda^{-\alpha}$, where k is independent of wavelength. The four most important previous conclusions regarding α are:

1. α is independent of wavelength in the visible spectrum.[1, 2, 3, 4]
2. $\alpha = a - b\ln \lambda$ in the infra-red region, where 'a' and b are independent of wavelength.[3, 4]
3. α depends upon the fuel from which the soot is formed.[1, 3, 4]
4. One author [2] suggests that conclusion 3 should be that α depends not only upon the fuel from which the soot is formed but also upon the size of the soot particles which are formed.

This paper provides further experimental evidence as a test of the above conclusions. α values were found from measurements on soot layers produced by holding an optically ground rock salt disc in a small laminar diffusion flame. The fuels used in the flames included amyl acetate, gas oil, petrotherm, town's gas and some hydrocarbon gases. Extinction curves were obtained for each soot layer by means of an infra-red spectrometer. Particle sizes for the various soot layers were measured by means of electron microscopy. The results are:

1. The variation of α with λ may be approximated by $a + b\ln\lambda$ in some cases, and by a parabola in λ in others.
2. The 'mean' α for any soot (obtained as the slope of the best-fit straight line to the results plotted in the form of graphs of $\ln\ln(I_O/I_L)$ against $\ln\lambda$) appears to be independent of the mean soot particle size, in contrast with conclusion 4 above.
3. The mean α appears to be definitely correlated with the carbon to hydrogen ratio of the soot.

As neither previous nor the present experimental evidence was sufficiently conclusive to permit the accurate prediction of the extinction coefficient (and hence the emissivity) of a cloud of particles a theoretical treatment of the problem, based upon the Mie theory, was undertaken and is presented in the paper. The resulting equations for α and k are:

$$\alpha = 1 + \frac{\ln\left[\dfrac{F(1)}{F(\lambda)}\right]}{\ln\lambda} \tag{1}$$

and

$$k = 36\pi c F(1) \tag{2}$$

where c is the average volume of particles per unit volume of cloud and $F(\lambda)$ is a function depending solely on the refractive index of the material of the soot. α is thus shown to be independent of the soot particle size. An illustrative calculation is carried out for baked electrode carbon at 2250°K. For this case:

1. α is approximately constant for wavelengths in the visible spectrum
2. α is given within 5 per cent by the equation $\alpha = 0.906 + 0.283 \ln\lambda$ for the range $1\mu < \lambda < 10\mu$.
3. As $\lambda \rightarrow \infty$, α tends to an absolute maximum of 2.
4. $k = 5.688c$

The method is extended to give a single curve from which the monochromatic emissivity of a cloud of particles of the specified material may be found for any wavelength and concentration of material. From this curve the variation of total emissivity with particle concentration may be found by numerical integration. The method may be used to draw up similar results for any material under any conditions provided that sufficient is known about the material under the given conditions.

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Subject Headings: ***Flame, emissivity; Emissivity, of flame.***

Authors' Abstract

Millikan, R. E. (General Electric Research Laboratory, Schenectady, New York) "Measurement of Particle and Gas Temperatures in a Slightly Luminous Premixed Flame," *Journal of the Optical Society of America* **51,** 535–542 (1961)

A direct experimental comparison of particle temperature and gas temperature in a rich ethylene-air flame is described in this paper. Theoretically, these temperatures should be nearly the same. Only a few experimental measurements bearing on this problem have been made, and they tend to support the theoretical conclusion. The flame chosen for this work is such that the carbon particles are formed in it far from equilibrium; hence, any deviation between the two temperatures should be maximized.

A water-cooled flat flame burner 7 cm in diameter was used. The ethylene-air ratio was 0.144 (2.07 times stoichiometric). A Perkin-Elmer 12G spectrometer equipped with a quartz fore prism and a 75 line/mm grating was used for the spectrophotometric measurements. The detectors used were RCA 1P28 or 1P21 or Du Mont 6911 photomultipliers. A multiple path mirror system was used for the soot extinction measurements. The uniformity of temperature across the burner was determined by a thermocouple traverse across a similar lean ethylene-air flame on the same burner.

Sodium line reversal, soot emission, and soot extinction measurements were made 6, 9, and 12 mm above the burner. A quartz probe was used to collect samples of the soot onto electron microscope screens. The particle sizes were found to be about 50 Å at the 6 mm level and about 200 Å at the 12 mm level.

The soot extinction data were used to evaluate their emissivity, which, in turn, was used to find the particle temperature from the soot emission data. Only the soot emission values obtained at the 12 mm height were used. The emission at 6 mm and 9 mm was too faint for accurate measurement. The temperature so obtained was $1714 \pm 60°K$. The sodium line reversal temperature found at this level was $1775 \pm 20°K$. At the 6 mm level, the sodium line reversal temperature was 1826°K; and at the 9 mm level it was 1795°K. The observed decrease in temperature can largely be accounted for as radiative loss. This suggests that the sodium line reversal temperature is the gas temperature.

After a consideration of the errors the conclusion is that the particle and gas temperatures agree to within the accuracy of the measurements. The article ends with a brief discussion of the effects of heat addition to the particles as a consequence of growth by chemical reaction.

Subject Headings: ***Flame, premixed, particle and gas temperature; Temperature, measurement, in luminous premixed flame.***

P. R. Ryason

VII. Suppression of Combustion

Friedman, R. and Levy, J. B. (Atlantic Research Corporation, Alexandria, Virginia) "Mechanism of Fire Extinguishment by Alkali Metal Salts," *Technical Report No. 1 (Final Report) ONR Contract NAopr 24–60 and OCDM Contract CDM–SR–60–22* (July 31, 1961)

The report describes the first year of research into the mechanism of the inhibition of hydrocarbon-air flames by alkali metal salts. This type of inhibition is well known, and finds practical application in, for example, the prevention of mine gas ignition by blasting charges, or in the suppression of gun muzzle flash, or the afterburning of rocket exhausts. However, experiments designed to elucidate the mechanism of inhibition by particulate clouds do not easily permit clear interpretation. First, there are experimental difficulties associated with the production of uniform dispersions of powder and with accurate control of particle size. Second, the physical state of the particles at the high flame temperature is not known so that the relative contributions of chemical effects and physical surface effects are indeterminate. Nevertheless, the indication from work reviewed early in the paper is that salts of the alkali metals (sodium, potassium, rubidium and cesium) might be particularly effective chemical inhibitors. The authors of the paper have therefore attempted to single out the chemical effects by introducing the salts, or the metals themselves, in the vapor state, thus giving a homogeneous system.

High preheat temperatures are necessary in order to allow the introduction of significant amounts of the salt or metal vapors. Hence methane was used as the principal test gas, since its burning properties are similar to most hydrocarbons, while it is more resistant to thermal cracking. For premixed flames with air, inhibition would be shown by the effect of the additive on the burning velocity. In diffusion flames, which were more frequently used, inhibiting effects were evaluated by a method similar to that described by Potter *et al.*[1] The diffusion flame is maintained between co-axial opposed laminar jets of methane (+ additive) on the one hand and air (or oxygen) on the other. If both flows are about the same the flame can be maintained midway between the jets while both flow rates are gradually increased simultaneously. However, when a critical flow is reached, a small dark spot or hole appears in the center of the flame, and further increases in flow rate cause the hole to become larger. The appearance of the hole has been interpreted to be a measure of the flame reactivity in the diffusion flame, so that the effect of an inhibitor should become apparent.

Controlled amounts of the inhibitors were added by bubbling the methane through the molten additive (at temperatures up to 500°C) in a bubbling device constructed of nickel. Nickel is reported to be resistant to corrosion by the alkali metals and their compounds. Such corrosion resistance was not completely confirmed by Friedman and Levy's experience here. They suggest that their own findings could be due to reduction (under the conditions of their experiments) of an oxide layer normally present on the nickel.

Early attempted experiments using sodium amide as the additive were discontinued due to decomposition of the amide at those temperatures where its vapor pressure was adequate. One premixed flame with sodium amide additive (very small amounts only) showed no effect on the flame, though an experimental problem at that time rendered the result somewhat inconclusive.

Sodium and potassium metals were later used as additives, and diffusion flames were studied. Again, due to experimental problems, few conclusive experiments were carried out, but the result was obtained that 0.26 atoms per cent sodium in methane had no detectable effect on the diffusion flame. It is pointed out, however, that the effectiveness of the test needs further evaluation using a standard inhibitor such as bromide.

In certain of the early experiments another phenomenon was noted when there was no flame. When the sodium containing methane jet was observed in a darkened room, without any ignition source, a sharply defined surface emitting an orange glow was clearly observed. No light was emitted except at the interface itself. The glow disappeared when the methane was replaced by nitrogen, but reappeared when hydrogen was used. There was no general ignition of the hydrogen or the methane. The glow was tentatively assumed to be associated with air oxidation of the sodium. However, the authors were unable to reproduce the phenomenon at a later date, and felt that further investigation was necessary.

Finally, an attempt to study the effect of potassium (which has a higher vapor pressure than sodium) on the diffusion flame again met with experimental difficulty and no definite result is described. The authors consider that the many experimental problems encountered in the work as a whole could be overcome, so that more definite results should be obtainable in the future.

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Subject Headings: ***Fires, extinguishment, by alkali metal salts; Extinguishment, of fires, by alkali metal salts; Alkali metal salts, fire extinguishment.***

G. Dixon-Lewis

Joint Fire Research Organization, Boreham Wood, England "Extinguishing Room Fires with High and Low Pressure Water Sprays: JFRO Tests," *Fire Protection Review* (May 1960)

In Great Britain, the experience of the British Fire Brigade has been that 75 per cent of the fires in which water has been used for fire fighting have been extinguished using hand-line nozzles. Three factors may influence the efficiency of hand-line nozzles, namely: (1) rate of water application; (2) form of application, i.e., spray or solid stream; (3) nozzle pressure. This article describes the tests conducted by the Joint Fire Research Organization to determine the effects of these factors on nozzle performance.

In these tests, two well-ventilated, isolated chambers each having a volume of 1750 ft^3 and wooden floors 14 foot square were used individually. These chambers contained mock-up furniture. The fire load for each chamber was 52,000 Btu. per square foot. The fire was ignited by using two small pans of burning gasoline motor fuel. About 3½ minutes were required for the room to be completely involved (flashover of flames to all surfaces). Application of water from the test nozzle was commenced two minutes later. A hand-operated nozzle equipped with a trigger control was used, which allowed the operator to control individual spray and stream periods of application. Application of water was continued without interruption until control was reached; then application was made to cover pockets of fire improved with ventilation.

The nozzles were impinging-jet-type. Nozzle orifices varied so that application rate ranged from 6 to 30 U. S. gpm in five steps at four discrete nozzle pressures, 80 to 500 psig. The orifices were $\frac{1}{16}$ in and the mass median drop size varied with conditions of spray application from about ⅓ to nearly 1 mm. Solid stream nozzles were used having the same rates as the spray nozzles, but only at 80 psig pressure.

Two fires were conducted for each water rate and nozzle pressure combination. The results showed that in this range nozzle flow rate and pressure did not alter the quantity of water required to control or completely extinguish the test fire. About 8½ U.S. gals of water were required for control and 20½ U.S. gals for complete extinguishment.

The authors do not specify rates of fuel consumption in the test model. This would allow comparison of apparent rate of heat release and rates of heat "absorption" afforded by the water applied. The authors point out that use of sprays offer protection to the operator not given by a solid stream, and that in practical fire fighting, a rapid extinguishment corresponding to higher rates of application might be desirable. The test operator reported that the solid stream of application was more suited for extinguishment of deep-seated fire pockets than the spray application.

Subject Headings: *Extinguishment, room fires, with water sprays; Water sprays, fire extinguishment; Fires, extinguishment, with water sprays.*

J. E. Malcolm

Dumont, J. C., Combourieu, J., Delbourgo, R., and Laffitte, P. Laboratoire de Chimie Generale, Sorbonne, Paris, France) "Effect of Dispersion on the Suppression of Detonation of Stoichiometric Methane-Oxygen by Finely Powdered Potassium Bitartrate," *Comptes Rendus* **252,** 3806–3808 (1961)

Previous work[1] has shown that potassium bitartrate is a good inhibitor both of combustion waves and detonations. The present note summarizes a systematic study of the effect of dispersion of the cloud of inhibitor (particle size α 10μ) on the detonation at atmospheric pressure of the stoichiometric mixture CH_4+2O_2 whose velocity is known to be of the order of 2300 m/s.

It is found that a minimum of dispersion is necessary to obtain suppression of a detonation with a minimum amount of substance. Above this dispersion the density of the suppressing cloud decreases and the necessary amounts are greater. The mean density at suppression, expressed as surface of powder per unit volume of suppressing cloud (cm^2/ml), tends towards a limit. The suppression is always accompanied by a reduction in speed coincident with a cooling of the gases and a reduction in luminosity of the recorded phenomenon.

Dispersion favors the inhibition provided the density of the suppressing cloud is sufficient. The mechanism can be considered to be a thermal phenomenon as well as a deactivation of active centers.

Reference

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Subject Headings: *Detonation, suppression of; Potassium bitartrate, use in detonation suppression; Dispersion, effect of, on suppression of detonation.*

R. Long

Hardy, C. E., and Rothermel, R. C. (Northern Forest Fire Laboratory, Intermountain Forest and Range Experiment Station, U.S. Forest Service, Missoula, Montana) and **Davis, J. B.** (Pacific Southwest Forest and Range Experiment Station, U.S. Forest Service, Berkeley, California) "Evaluation of Forest Fire Retardants—A Test of Chemicals on Laboratory Fires," *Intermountain Forest and Range Experiment Station Research Paper 64* (1962)

A laboratory evaluation of the effectiveness of seven forest fire retardants in slowing down or stopping the advance of fire in beds of ponderosa pine needles is presented. The fire retardants tested had previously shown promise in other laboratory and field tests and further tests under more uniform controlled conditions were considered appropriate. The results are presented in this paper.

The characteristic and cost of each of the chemicals is briefly described. Those tested included: algin-diammonium phosphate (algin-DAP), algin-calcium chloride (algin-gel), bentonite, sodium calcium borate (Firebrake), sodium calcium borate (Borate XPI-113), ammonium sulphate-attapulgite clay (Fire-Trol), and pectin-diammonium phosphate (pectin-DAP). All chemicals were mixed in accord with manufacturers' recommendations and applied to the fuel bed at a rate of 2 gallons per 100 square feet.

The retarding ability of each chemical was determined by three measurements: (1) rate of fire spread, (2) radiation, and (3) convection column temperature. The percentage reduction of each of these measurements from that registered on similar untreated fuel-bed sections was the basis of evaluating the effectiveness of the retardant. Each chemical was tested after two periods of drying, 1 hour and 3 hours, following application, and under two wind conditions, 0 mph and 3 mph. Trays of conditioned fuel (ponderosa pine needles) were used in all tests, both in the laboratory and in the wind tunnel. Ambient conditions for the tests were 90 to 95°F. and 14 per cent relative humidity.

Results of the tests are presented in a series of photographs showing the flame characteristics during the tests and the postburn condition of the fuel bed. Graphs are also presented showing the percentage reduction of radiation in comparison to the percentage reduction of rate of spread. The relative effectiveness of each retardant under each of the test conditions of drying time and wind is shown by means of per cent reduction bar graphs for rate of spread, radiation, and convection column temperature.

Pectin-DAP, algin-DAP, and Fire-Trol effected the best reduction in rate of spread under no wind conditions and after 1 hour drying time. After 3 hours of drying, however, Firebrake gave better results than Fire-Trol with pectin-DAP and algin-DAP maintaining their superior position. In the presence of wind, Fire-Trol gave the best results after both 1 hour and 3 hours' drying. Bentonite was found to be less effective than Firebrake with increasing drying time in wind and no wind. Borate XPI-113 usually ranked between bentonite and Firebrake while algin-gel was least effective in most tests.

The greatest reduction in radiant energy in all tests was caused by Fire-Trol and the diammonium phosphates. The effectiveness of bentonite in reducing radiation under no wind conditions decreased with an increase in drying time while Firebrake improved with a certain amount of drying. Again, Borate XPI-113 usually ranked between bentonite and Firebrake while algin-gel exhibited the least effectiveness.

The convection column temperature was less significant in demonstrating the effectiveness of the retardants; however, this means of evaluation gave the same general relation between chemicals as was found for rate of spread and radiation.

The paper concludes with a brief discussion on field testing as a next step in the evaluation of the most promising retardants. A specific program of field evaluation is described.

Subject Headings: *Forest fire, retardants; Fires, forest, retardants; Retardants, of forest fires.*

W. Y. Pong

Nash, P. and French, R. J. (Joint Fire Research Organization, Boreham Wood, England) "Foam Compounds for Use Against Fires in Water Miscible Solvents" *Journal of the Institute of Petroleum* 47, 219–222 (1961)

Normal protein-based foam compounds can be rendered "all-purpose" and suitable for use on fires in water miscible solvents (hereafter called solvents) by additives which the author describes as either "raft-forming" or "bubble-wall stabilizers." The performance of three of the former and two of the latter were compared with all-purpose foam on fires in petrol, methylated spirit, methanol, (i)propyl alcohol, acetone, and methyl ethyl ketone.

The laboratory scale apparatus (details not given) is stated to permit applying gently to the fuel surface at controlled rates foams of the same physical properties as would be produced with a standard branchpipe.

A reduction in radiation intensity to ⅓ of the initial value was considered to constitute fire control. The minimum application rate and the quantity of foam solution to effect control were measured.

Normal foam and two all-purpose foams were tested on petrol. Eleven tests with all-purpose foam were made on selected solvents. Methanol fires were easiest to control, MEK fires were most difficult, and gentle application was particularly important.

Conclusions

1) On petrol fires all-purpose foam is less effective than normal foam, requiring 1.5 to 10 times as much foam and usually a higher application rate.
2) On solvent fires all-purpose compounds "are likely to be fairly economical . . . with consumption ranging from one to five times and minimum effective application rates of one to four times that of a normal protein compound on a petrol fire." Gentle application is important.

Subject Headings: *Foam, use in water-miscible solvents; Fire fighting, use of foam.*

O. W. Johnson

Brown, K. C. (H. M. Factory Inspectorate, Ministry of Labour), **Cook, R.** (British Shipbuilding Research Association), **James, G. J.** (Formerly Safety in Mines Research Establishment, Ministry of Power), and **Palmer, K. N.** (Joint Fire Research Organization, Boreham Wood, England) "Crankcase Explosions in Marine Oil Engines, The Efficacy of Gauze and Crimped-Ribbon Flame Traps," *Paper presented at The Institute of Marine Engineers, February 27, 1962*

An experimental investigation of the use of flame traps is reported. The tests were conducted in explosion vessels of 200 cu ft and 66 cu ft capacity, fitted with oil-wetted flame traps. Two kinds of traps were used; one composed of layers of metal gauze and the other a crimped ribbon trap about 2 inches deep. Both weak pentane-air mixtures (2 per cent pentane by volume) and oil mists were used as explosive mixtures. The explosion vessel was filled with the mixture and ignited and observations were made on the temperature of the gases issuing from the trap. The pressures in the vessels were followed by a piezo-electric transducer. The point of ignition was varied to change the severity of conditions on the trap. Generally, no flame could be seen. The crimped ribbon trap seemed to be more effective than the layers of gauze in reducing the temperature of the effluent gas. Both kinds of traps were damaged by the explosion. In a number of instances, the gauzes became red hot and continued to glow for a time after the explosion. Replacing steel with Monel for the gauze material was found to have no significant advantage.

Experiments were made with the two vessels separated by a gauze flame trap. Both vessels were filled with an explosive mixture of oil mist. The mixture was ignited in one of the vessels, and the other observed. In no case was a flame transmitted. However, the vent ratios (area of trap/volume of vessel) employed were large, 6.85 sq in/cu ft and 13.7 sq in/cu ft. The minimum standard vent ratio, and the practical ratio are both 0.5 sq in/cu ft.

In the theoretical section of the paper, the effectiveness of a trap, based on its heat capacity, is calculated and predictions are made of the effectiveness of various combinations of gauzes. These are in reasonable agreement with the experimental results.

The possible application of these traps to existing marine engines is discussed in some detail. It is concluded the weight of the gauzes and mechanical difficulties combine to make venting impractical as a means of protection. Currently, explosion relief valves are used on marine diesel engines for this protection. It is concluded that to avert an explosion oil mist dectectors and carbon dioxide injectors are more practical than venting the crankcases.

The data on flame traps should be useful in other systems in which explosion hazards arise, and such traps are mechanically feasible.

Subject Headings: ***Flame, traps, in marine engines; Engines, flame traps in.***

P. R. Ryason

VIII. Model Studies and Scaling Laws

Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "Size of Flames from Natural Fires," *Paper presented at Ninth Symposium (International) on Combustion, Cornell University, August 27–September 1, 1962.* (To be published in the Proceedings)

Uncontrolled fires produce flames where the initial momentum of the fuel is low compared with the momentum produced by buoyancy. The heights of such flames with wood as the fuel have been examined and are discussed in terms of both a dimensional analysis and the entrainment of air into the turbulent flame and are compared with other experiments on the flow of hot gases.

Some recent experiments on the effects of wind on such flames are also reported.

Author's Summary

Bruce, H. D., Pong, W. Y., and Fons, W. L. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service, Berkeley, California) "The Effect of Density and Thermal Diffusivity of Wood on the Rate of Burning of Wood Cribs," *Pacific Southwest Forest and Range Experiment Station Technical Paper No. 63* (1961)

This report is a continuation of PROJECT FIRE MODEL—a research project designed to study the basic physical phenomena and fundamental laws of fire. Started in cooperation with the Office of Civil and Defense Mobilization, the work is now being continued under contract with the National Bureau of Standards. The project has been transferred from California to Macon, Georgia at the Southern Forest Fire Laboratory.

Five species of wood were selected for this study of burning rates in relation to density and thermal diffusivity, (white fir, southern magnolia, sugar maple, basswood, and longleaf pine). Cribs were constructed from stock having nearly the same density although there was some variation in average density between cribs of the same species. In preparation for burning, the cribs were conditioned to 10.5 per cent moisture and burned on the fire table, using the steady-state technique described in previous reports on PROJECT FIRE MODEL.

As in the past, the experimental fires demonstrated a curvilinear relationship between rate of spread and density. As wood density increased, fire spread decreased. There were also differences observed in the rate of spread for different species of wood having the same density. Although reliable values of specific heat were missing for the species of wood tested, there was a linear relation between the rate of spread and thermal diffusivity. One significant finding indicated that the chemical nature and amount of extractives in wood may produce different burning rates without a corresponding influence on the thermal diffusivity.

Subject Headings: ***Wood, effect of density and thermal diffusivity on burning; Burning rates, of wood cribs.***

J. H. Dieterich

Fons, W. L., Clements, H. B., and George, P. M. (Southern Forest Fire Laboratory, U.S. Forest Service, Macon, Georgia) "Scale Effects on Propagation Rate of Laboratory Crib Fires," *Paper presented at Ninth Symposium (International) on Combustion, Cornell University, August 27–September 1, 1962.* (To be published in the Proceedings)

This paper presents results of a laboratory-scale propagating flame model in which crib fires are used. The model permits establishment of a steady-state condition for the free burning of solid fuels in the form of wood cribs. The principal objectives are to evaluate quantitatively the effects of the properties of fuel and fuel bed on the many attributes of fire behavior and to establish relationships of the variables in terms of several dimensionless groups.

A dimensionless relationship of flame dimensions and modified Groude number is presented for data from a propagating flame model and is in close agreement with findings of other investigators using stationary flame models. Scale effects are also given for the fuel and fuel bed variables on burning time, propagating rate, and burning rate of laboratory crib fires.

Conclusions of work led to the following:

1. Laboratory crib fires may be used to represent line fires.
2. Scaling of fuel size to the 1.5 power for burning time is valid for loosely packed fuel beds.

3. Same dimensionless groups may be used for correlation of data from propagating flame models and stationary flame models.

Plans for future investigation include the use of crib fires to determine the effects of fuel spacing, wind, and slope on the burning characteristics.

Authors' Summary

Putnam, A. A. and Speich, C. F. (Battelle Memorial Institute, Columbus, Ohio) "A Model Study of the Interacting Effects of Mass Fires," Paper presented at *Ninth Symposium (International) on Combustion, Cornell University, August 27–September 1, 1962.* (To be published in the Proceedings)

This research program has shown that a valid model for studies of mass fires can be produced using multiple jets of gaseous fuels. The basic requirement is that the fuel jets produce turbulent diffusion flames which are buoyancy controlled. A specific operating range where this requirement is believed to be met was found for this model.

A number of flame arrays have been studied in which the dimensionless groups of array flame height/single flame height, number of jets, array factor, and flame spacing/(fuel-flow) 2/5 were the important variables. Assuming the flame to be a series of point sources, only array flame height/single flame height and flame spacing/(fuel-flow rate) 2/5 showed a strong correlation. This correlation is shown to exist both theoretically and experimentally but not to the same extent. The experimental data showed no consistent effect of jet number or flame array. The difference between the theoretical and experimental trends is accredited to an aspiratory effect of one flame upon another which decreases the effective spacing between the jets. A good correlation was also obtained, considering the flame as an area fire, between the dimensionless flame height and the total fuel flow rate. By accounting for the differences in heat release, induced air, and density differences, good comparison can be made between data for solid and gaseous flames.

Authors' Summary

IX. Atomization of Liquids

Eisenklam, P. (Imperial College, London, England) "Atomisation of Liquid Fuel for Combustion," *Journal of Institute of Fuel* 34, 130–143 (1961)

This comprehensive compendium of information on the atomization and vaporization of liquid fuels in a combustor effectively updates similar reviews which abounded in the literature of the 1950's.[1] Except for a number of notable omissions, referred to in subsequent paragraphs, subject report provides the combustion engineer with a ready reference on the pertinent physical properties of fuel sprays.

Mass transfer from sprays is analyzed by consideration of Fick's Law for Diffusion:

$$\dot{m}' = -S_0 \triangle Ch \tag{1}$$

where

$\dot{m}'$ = rate of mass transfer per unit volume
S_0 = specific surface area of the liquid
$\triangle C$ = concentration gradient
h = mass transfer coefficient

Since S_0 varies inversely as the droplet diameter (exactly, for a monodisperse spray), $\triangle C$ is independent of diameter, and h varies inversely with d, equation (1) indicates the direct variation of total mass evaporation rate $\dot{m}$ with d, as observed experimentally. The resultant linear variation of droplet surface area with time is defined, and the effect of relative velocity is expressed by Frossling's equation. Entrainment of drops in a moving air stream is analyzed in terms of Ingebo's report,[2] although it is noted that the direct variation of droplet acceleration with its relative velocity (cf. Figure 10, reference 2) indicates a simple inverse variation of drag coefficient with Reynolds number. Application of the foregoing concepts to practical combustion systems indicates (1) a decrease in predicted vaporization rates due to the increase in ambient vapor pressure; (2) a variation of minimum combustor length with the product of droplet area and velocity; and (3) an inverse variation of heat release rate with droplet surface area.

The physical factors, originally identified by Rayleigh,[3] which affect the formation of sprays are listed as the density (ρ), surface tension (γ), viscosity (μ), and velocity (U) of the injected liquid and its surrounding environment. Three types of liquid sheet instability are noted, and the importance of the Weber number:

$$We=\frac{\rho g U^2 d}{\gamma} \qquad (2)$$

(where ρg is the air density and d is the droplet diameter) in droplet shattering is stressed. Viscosity effects are represented by the "viscosity number," previously used by Ohnesorge[4] in the correlation of his experimental data.

$$Vi=\frac{\mu}{\sqrt{\rho\gamma d}}$$

The phenomenon of droplet coalescence is considered briefly, and the relative velocity regimes of elastic rebound, coalescence, and droplet shatter are noted.

The standard types of atomizing devices—pressure, rotary, and twin fluid atomizers—are described and photographs of representative resultant spray patterns are presented. Despite the exotic configurations displayed by the several nozzles considered by the author, the conspicuous absence of both "shower-head" and flat spray pressure injectors is regrettable, since both types have been used extensively in liquid propellant rockets. Atomizer performance is expressed in terms of nozzle flow number, spray spatial distribution, and drop size. Although flow rate is found to vary with the 0.4 rather than the theoretical 0.5 power of pressure drop, the flow number (FN) is found to be fairly constant for each orifice area (A) and liquid:

$$FN=\frac{\text{flow rate}}{\sqrt{\text{pressure drop}}}=293\,\frac{C_q A}{\sqrt{\rho}} \qquad (3)$$

where C_q is the discharge coefficient. The complicated variation of discharge coefficient with viscosity is presented graphically. Although the spray angles for fan spray nozzles cannot be reliably predicted by theory, the cone angle for swirl spray nozzles is determined as the arctangent of the ratio of tangential to axial velocity at the nozzle exit.

Of primary importance in assessing the combustion potential of a given spray is its average drop size. Size distributions are determined experimentally by the wax "substitute method," the frozen drop technique, or impingement collection; each of which has definite limitations. It is noted that a fluorescent technique developed recently by Benson, El-Wakil, Myers, and Uyehara[5] has succeeded in circumventing most of the objectionable features (no evaporation, selective impingement) of the foregoing methods. Size distributions are characterized chiefly by their mean or median diameters, plus the 95 and 5 per cent diameters. Of greatest use are the surface medium diameter (SMD) and mean evaporation diameter (MED), defined by:

$$\mathrm{SMD}=\frac{1}{\sum\frac{\Delta\bar{v}}{d}} \tag{4}$$

and

$$\mathrm{MED}=\sqrt{\frac{1}{\sum\frac{\Delta\bar{v}}{d^2}}} \tag{5}$$

Variation of mean drop diameter with liquid properties and nozzle geometry can be determined from established equations based primarily on empirical data. However a quasi-theoretical derivation, confirmed by experimental data for pressure jets of the cylindrical,[6] flat,[7] and conical[8] configuration, yields the following equation:

$$\frac{d}{L}=f(R)(We)^{-\frac{1}{3}} \tag{6}$$

where L is a characteristic orifice dimension and f(R) is a function of the Reynolds number of flow, which allows for viscosity effects. Inadvertently omitted in the author's discussion was the experimental results of Hinze and Milborn[9] for rotary atomizers:

$$\frac{d}{\Delta}\propto\Big[(We)(Vi)^n\Big]^{2/(4+n)} \tag{7}$$

where Δ is the cup diameter and n is an empirical constant.

In summary, subject paper presents a commendable review of the status of spray technology, as related to the combustion process and aids in posting the reader on pertinent publications within the past several years.

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Subject Headings: *Atomization, of fuels; Vaporization, of fuels.*

C. C. Miesse

Eisner, H. S., Quince, B. W., and Slack, C. (Safety in Mines Research Establishment, Buxton, England) "The Stabilization of Water Mists by Insoluble Monolayers," *Discussions of the Faraday Society No. 30 The Physical Chemistry of Aerosols,* 86–95 (1960)

An experimental study of prolonging the life of water mists by reducing the evaporation rate of individual droplets was made. Such stabilization of mists was achieved by dispersing small amounts (0.05–0.2 per cent) of a fatty alcohol in the water. As the water evaporates the alcohol forms an insoluble monolayer at the droplet surface.

Droplets in the size range of 2–20μ were considered. For this range diffusive mass transport predominates and the Fuchs equation for droplet evaporation in still air can be used:

$$\frac{dm}{dt}=\frac{4\pi MD}{RT}(fp_T-p_\theta)\frac{a}{(D/a\nu\alpha+1)} \tag{1}$$

where

$\frac{dm}{dt}$ = rate of evaporation of a droplet of a radius a
M = molecular weight of the liquid
D = diffusion coefficient for the vapor into the air
f = relative humidity expressed as a fraction
p_T = vapor pressure of the liquid at the ambient absolute temperature T
p_θ = vapor pressure of the liquid at the droplet temperature θ
R = gas constant
$\nu = (RT/2\pi M)^{\frac{1}{2}}$
α = coefficient of evaporation (or condensation)

The retardation of the evaporation of droplets is accomplished by reducing the value of α from its value of 0.04 for pure water to the value $(2.90\pm0.26)\times10^{-5}$ for the fatty alcohol dispersion (0.2 per cent by weight of fatty acid and 0.2 per cent dispersing agent).

The principal experiment involved the measurement of the "cut-off" radius, i.e., the initial radius of a droplet that falls an arbitrary distance through quiescent air before completely evaporating. The measurement of the "cut-off" radius under carefully controlled conditions of air temperature and humidity permitted comparison of experiment with theory. Confidence in the theory was thus satisfactorily established and consequently the integrated form of the Fuchs equation is recommended for estimating the lifetime t of both water and dispersion droplets of initial radius a_0:

$$t=\frac{RT\rho}{MD(p_\theta-fp_T)}\left[\frac{a_0^2}{2}+\frac{Da_0}{\nu\alpha}\right] \tag{2}$$

where ρ is the density of the liquid. The equilibrium temperature θ of the drop may be determined from:

$$\theta=\frac{LMD}{kRT}\frac{(fp_T-p_\theta)}{(D/a\nu\alpha+1)}+T \tag{3}$$

where L is the latent heat of vaporization of the liquid and k is the thermal conductivity of the ambient air. For dispersion droplets where α is less than 10^{-4} and a is less than 40μ, the difference between θ and T is negligible and p_θ may be taken equal to p_T.

Some calculated lifetimes are tabulated for both water and dispersion droplets at different combinations of ambient air temperature and humidity. An example of the stabilization which can be produced: at 20°C and a relative humidity of 80 per cent the life of a dispersion droplet of 40μ initial radius is 81 times that of a pure water droplet; the ratio increases to 530 when the initial radius is 5μ.

When a certain minimum concentration of fatty alcohol is exceeded, the stabilization action evidently no longer improves. For example, in tests with air at 28.3°C and 52 per cent r.h. the retardation of evaporation was constant for dispersions ranging from 0.05 to 0.4 per cent. For 0.025 per cent the retardation was somewhat diminished. The authors cite a previously measured value of $\alpha = 2.2 \times 10^{-5}$ obtained with a film of pure undispersed fatty alcohol on a water surface. Since this value is only slightly less than that observed with their dispersions, they doubt whether droplet life can be increased still further by this method.

Subject Headings: *Fog, water, stabilization of; Water fog, stabilization of.*

G. A. Agoston

Derjaguin, B. V., Bakanov, S. P., and Kurghin, I. S. (Institute of Physical Chemistry of Academy of Science of U.S.S.R.) "The Influence of a Foreign Film on Evaporation of Liquid Drops," *Faraday Society Discussions No. 30 The Physical Chemistry of Aerosols* 96–99 (1960)

In an effort to provide theoretical confirmation of the experimental results reported by Tovbin and Savinova[1] the authors derived equations for the stationary and nonstationary evaporation rates of liquid drops and flat surfaces covered with an insoluble film. By assuming that the substance of the drop diffuses through the liquid film and applying the diffusion (Laplace) equation with appropriate boundary conditions, the following equation is derived for stationary evaporation from a film-covered drop:

$$-\frac{dM}{dt}\frac{1}{4\pi a^2} = \frac{m(C_0 - C_\infty)}{\frac{C_0}{C_p}\frac{\delta}{D_1} + \frac{1}{D_2}\frac{a^2}{a+\lambda} + \frac{1}{\alpha v/4}} \tag{1}$$

where

M = mass of drop
m = molecular mass of droplet liquid
a = radius of drop
t = time
C_0 = equilibrium concentration of droplet liquid vapor in its saturated solution in vapor of the liquid film
C_p = equilibrium concentration of droplet liquid in its solution in the liquid film
C = ambient gas concentration at infinity
D_1 = diffusion coefficient of droplet in the liquid film
D_2 = diffusion coefficient of droplet liquid in the ambient gas

v = mean velocity of gas molecules at given temperature
α = evaporation accommodation coefficient
δ = thickness of insoluble liquid film
λ = thickness of adjoining gas layer (of the order of mean free path of gas molecules)

Comparison of equation (1) with the corresponding equation for evaporation rate of the droplet without the insoluble film yields the following criterion for an increase in evaporation rate caused by the surface-active insoluble film:

$$\alpha > \frac{\alpha_0}{1 - \frac{C_o}{C_p}\frac{\delta}{D_1}\frac{\alpha_0 v}{4}} \qquad (2)$$

where α_0 is the accommodation coefficient of an uncovered liquid.

A similar criterion is derived for a flat surface in a gas stream, which forms a boundary diffusion layer. Corresponding analyses of the nonstationary liquid drop and flat surface result in expressions for the initial evaporation rate which are proportional to the stationary solutions, so that the same criteria apply.

The derived expressions for stationary and initial nonstationary evaporation rates provide a ready means for experimental determination of the parameters α and δ/C_pD_1 for a given film.

Reference

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Subject Headings: ***Evaporation, effect of film; Film, effect on evaporation of drops; Drops, evaporation, effect of film.***

C. C. Miesse

X. Meteorological Interactions

Hoffman, T. W. (McMaster University, Hamilton, Canada) and **Gauvin, W. H.** (McGill University and Pulp and Paper Research Institute of Canada, Montreal, Canada) "Evaporation of Stationary Droplets in High Temperature Surroundings," *The Canadian Journal of Chemical Engineering* 38, 129–137 (1960)

The effect of ambient temperature on droplet evaporation was investigated extensively by the authors, under very carefully-controlled conditions and with precision instrumentation. Droplets of water, methanol, cumene, pentane, and benzene (ranging in diameter from 0.4 to 1.4 mm), were suspended in an electrically-heated 9-inch stainless steel sphere in which the gaseous environment consisted of superheated vapors of the respective liquids at temperatures from 100 to 550°C. Droplets were suspended from a 70 micron glass filament which terminated in a small 200μ ball of 0.0005 in. platinum-10% rhodium wire. Heating was provided by nichrome wire heaters installed inside a 16 x 16 x 12 in. housing, and uniform temperature was ensured by preheating the apparatus for two hours prior to each test. Air was purged from the sphere by injection of 75 cc of the appropriate vapor approximately one-half hour prior to test.

After detailed consideration of the various theories of mass transfer under free convection conditions, the authors noted a linear variation of droplet surface with time, but were unable to achieve a single correlation of evaporation rate versus temperature data by consideration of convection effects. However, an excellent correlation of data, including those of Kobayasi,[1] was achieved by use of Godsave's [2] theoretical parameters:

$$\frac{\dot{m}C_p}{\pi Dk}(Pr)^{-\frac{1}{3}}=3.2\left(\frac{C_p\Delta T}{\lambda}\right)^{0.97} \qquad (1)$$

The apparently negligible effects of radiation and convective flow on the evaporation rate is demonstrated by Equation (1), which provides confirmation of the direct variation of evaporation rate with temperature difference, as reported by Nishiwaki [3] and Kumagai and Isoda.[4]

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Subject Headings: ***Droplets, evaporation in high-temperature surroundings; Evaporation, of droplets.***

C. C. Miesse

Lee, S. (North Carolina State College, Raleigh, North Carolina) **and Emmons, H. W.** (Harvard University, Cambridge, Massachusetts) "A Study of Natural Convection above a Line Fire," *Journal of Fluid Mechanics* **11,** 353–368 (1961)

In this paper the natural convection plume above a line heat source is studied both theoretically and experimentally. Using standard methods for turbulent convection the dependence of the buoyancy and plume width on height are obtained. The theory is found to correlate with measurements made above a slot burner.

In the theoretical analysis the fully developed turbulent flow above a finite source of buoyancy and momentum is assumed to be incompressible and in uniform surroundings. The boundary layer approximation is applied, and following other authors, the rate at which fluid is entrained into the plume is taken to be proportional to the vertical velocity on the axis of the plume. Gaussian velocity and buoyancy profiles are assumed with different scale widths. The appropriate integral equations for conservation of mass, momentum, and buoyancy are written. It is shown that the significant dimensionless parameter is a modified Froude number of the form

$$F=(2/\pi)^{\frac{1}{4}}u_o(\alpha\gamma_1/gb_o\Delta\gamma_o)^{\frac{1}{3}}$$

where

b_o = the source width
u_o = the source velocity
$\Delta\gamma_o$ = the source buoyancy
γ_1 = the weight density of the ambient fluid
g = the acceleration of gravity
α = the entrainment constant ($v=\alpha u$)
λ = the ratio of the buoyancy scale width

Particularly simple results are obtained if $F=1$. In this case a finite source can be represented by a line source at a virtual origin. The velocity along the center line of the plume is constant and the plume width is proportional to the height. Numerical solutions are obtained for the two cases $F>1$ and $F<1$. The case $F=1$ corresponds to a balance between the entrained mass and buoyancy. If the plume velocity is too small, $F<1$, the plume expands slowly, or even contracts if $F<2^{-\frac{1}{2}}$, to increase the local Froude number. If the plume velocity is too high, $F>1$, the plume grows more rapidly and the velocity is decreased.

Measurements of the plume width and centerline buoyancy above a slot burner are given. Acetone and methyl alcohol were used as fuels in order to determine the effect of radiation. Radiation losses were in agreement with previous measurements. Excellent correlation of the experimental results with theory was obtained in the following manner. The measured asymptotic dependence of the plume width and buoyancy on height was used to determine the constants α and λ. The values obtained agreed with previous measurements. The values of F and b_0 were then determined by a best fit for each set of data. Using these values of the parameters α, λ, F, and b_0, universal plots of buoyancy and plume width against height were obtained using the theory developed. A simplified flame model yielded values for F which were in good agreement with the values obtained by curve fitting.

The work presented in this paper should be encouraging to fire research. The authors have been able to obtain a significant correlation between theory and experiment in one of the most difficult of all scientific fields, turbulent combustion. The method of separating the basic mechanisms in a fire problem and then studying the more restrictive problem on a laboratory basis would seem to offer considerable promise.

Subject Headings: ***Convection, natural, above line fire; Fires, natural convection above line.***

D. L. Turcotte

Morton, B. R. (University of Manchester, Manchester, England) "Forced Plumes," *Journal of Fluid Mechanics* 5, 151–153 (1959)

This paper describes a theoretical investigation of incompressible turbulent forced plumes generated by the steady release of mass, momentum, and buoyancy from a source in a semi-infinite, uniform or stably stratified, region. A forced plume is a combination of a jet from a source of momentum and a plume from a source of buoyancy. For well-developed turbulent flow the profiles of velocity and buoyancy in a vertical plume are assumed to be similar. As a result the profiles and rate of entrainment can only depend on the differences in mean density and velocity between the plume axis and the ambient fluid.

The author first considers forced plumes in uniform surroundings. A point source of buoyancy and momentum is considered and it is shown that the mass flux must be zero. The similar profiles of velocity and buoyancy are both assumed to be Gaussian functions of the radius, but with different widths. Total differential equations are written for the conservation of mass, momentum, and density deficiency. Solutions are obtained and are compared with results for the jet and for the plume. It is shown that a forced plume from a finite source is equivalent to a forced plume from a point source at a virtual origin. The equivalent plume has the same buoyancy but a different momentum flux.

Forced plumes in a stably stratified region are also considered. The author is required to assume square profiles for velocity and buoyancy in this case. It is found that increasing the momentum from a given source of buoyancy has the effect, first of reducing the total height of the plume, and only for a large flux of momentum does the height increase.

Subject Heading: ***Plumes, forced.***

D. L. Turcotte

Morton, B. R. (University of Manchester, Manchester, England) "The Ascent of Turbulent Forced Plumes in a Calm Atmosphere," *International Journal of Air Pollution* 1, 184–197 (1959)

An analysis is developed which gives the height to which thermal plumes will rise in a calm atmosphere which is uniformly and stably stratified. The heat sources are orifices, such as chimney tops, which release streams of hot gas with an appreciable flow of mass and momentum. The resulting plumes are designated as *forced plumes.*

To make the problem mathematically tractable, it is assumed that (1) profiles of mean vertical velocity and excess temperature (or buoyancy) are each of similar form at all heights in the plume and (2) the entrainment rate at the edge of the plume is proportional to the mean velocity on the plume axis. For simplicity, "top-hat" profiles are assumed instead of Gaussian. A finite source discharging buoyancy, mass, and momentum has an equivalent point source of buoyancy and momentum only, so the simpler point source equivalent is used.

After some simplification the equations expressing the conservation of mass, momentum, and heat are written as

$$\frac{d}{dz}(R^2w)=2\alpha Rw$$

$$\frac{d}{dz}(R^4w^4)=2\lambda^2(R^2w)\left(R^2wg\,\frac{\rho_a-\rho}{\rho_{a0}}\right)$$

$$\frac{d}{dz}\left(R^2wg\,\frac{\rho_a-\rho}{\rho_{a0}}\right)=R^2w\,\frac{g}{\rho_{a0}}\,\frac{d\rho_a}{dz}$$

in which R, w, ρ, and ρ_a are respectively the mean radius of the top-hat profile, mean vertical velocity, mean plume potential density, and ambient air potential density—all at height z. ρ_{a0} is the ambient air potential density at the point source ($z=0$). Values of 0.116 and 1.08 were assigned to the entrainment constant α and the spreading ratio λ.

The height H to which a plume will rise above the point source is given by the solutions to the conservation equations and the boundary conditions at the finite source orifice. The equation for H is

$$H=2^{-\frac{5}{8}}\alpha^{-\frac{1}{2}}\lambda^{-\frac{1}{4}}\left[R_0{}^2w_0g\,\frac{\rho_{a0}-\rho_0}{\rho_{a0}}\right]^{\frac{1}{4}}\left(-\frac{g}{\rho_{a0}}\,\frac{d\rho_a}{dz}\right)^{-\frac{3}{8}}H_1(\tau)$$

where R_0 is the radius of the circular source; w_0 and ρ_0 are the mean velocity of flow and gas density respectively at the source. The function $H_1(\tau)$ is the dimensionless plume height and τ the dimensionless parameter

$$\tau=\frac{w_0{}^2g\rho_{a0}(d\rho_a/dz)}{w_0{}^2g\rho_{a0}(d\rho_a/dz)-\lambda^2g^2(\rho_{a0}-\rho_0)^2}$$

Curves are presented with $H_1(\tau)$ plotted against τ for three different combinations of momentum and buoyancy flux.

The height of the plume top above the finite source will be $H-h$ where h is the distance between the virtual point source and the finite source. Because stratification has a negligible effect on the behavior of the lower part of a forced plume, it was assumed in the analysis for h that the atmosphere is isentropic. In such an atmosphere, both ρ_a and the upward flux of buoyancy are constant for all values of z. Hence only two conservation equations are required. The distance h can be expressed in terms of an appropriate scale factor and a function $h_1(\gamma)$ which is the dimensionless distance between the finite source and the equivalent point source. The parameter γ is written as

$$\gamma^5 = 1 - \frac{5\lambda^2 g(\rho_a - \rho_0)R_0}{8\alpha\rho_a w_0^2}$$

Several combinations of buoyancy (plus and minus) and momentum (plus, minus, and zero) from the point source are considered.

For a given heat source strength and stratification of the atmosphere, increasing the momentum flux is not an effective way of increasing $H-h$. Small reductions in heat source strength result in relatively small plume height losses but substantial reductions produce large losses. Stratification of the atmosphere has a marked effect on plume height.

Subject Headings: *Plumes, turbulent forced.*

G. M. Byram

Fultz, D. (University of Chicago, Chicago, Illinois) "An Experimental View of Some Atmospheric and Oceanic Behavioral Problems," *Transactions of the New York Academy of Sciences* **24**, 421–446 (1962)

The sample problems discussed in this paper illustrate a growing trend in the geophysical sciences toward the use of the methods of modeling in studying phenomena associated with the large-scale motions of the atmosphere and oceans. The problems are all related to the effects of the rotation of the earth system as a whole on the relative motions in a fluid medium, such as the oceans or atmosphere. Under most circumstances the effects of rotation are stabilizing and modes of oscillation of the system are possible which could not exist in the absence of rotation. However, this stabilizing tendency does not always exist. One group of experiments involving thermal convection involves strong effects of instability away from certain otherwise possible configurations.

A rotating vertical cylindrical tank of homogeneous liquid constitutes a simple system in which the effects of rotation are stabilizing. If the tank is not rotating, the only free modes of oscillation in the fluid are gravity waves. If the cylinder and liquid are rotating rigidly but at a slow rate, a class of internal oscillations becomes possible which depends on the stability of the vortex tubes associated with the absolute rotation of frequency Ω. These oscillations do not depend on gravity but are associated with the conservation of angular momentum in the rotating fluid. Fluid rings displaced outwards slow down in absolute motion and those displaced inwards are speeded up. Both are accelerated back toward their equilibrium position. The standing oscillations have eigenfrequencies that are always less than $2\,\Omega$ and depend only on the ratio of liquid depth to cylinder radius. As this ratio approaches zero, the eigenfrequencies approach $2\,\Omega$.

Three other experiments of increasing complexity are discussed. The first of these concerns the oscillatory modes for a fluid between two concentric cylinders when the inner cylinder rotates more rapidly than the outer cylinder. If the speed of rotation of the inner cylinder is above a certain critical value, a self-sustaining cellular motion of a definite scale develops in consequence of instability of the original pure azimuthal motion. Another experiment involves free oscillations of an inviscid liquid which are of a mixed rotational-gravitational type.

The most complex experiment is one in which thermal convection is introduced by supplying heat to specific locations in the rotating fluid. Experiments of this type may have considerable significance for understanding the general circulation of the atmosphere.

Subject Headings: ***Motion, large scale, in atmosphere; Atmosphere, models of large-scale motion; Models, large-scale motion in atmosphere.***

G. M. Byram

Webb, E. K. (Commonwealth Scientific and Industrial Organization, Aspendale, Victoria, Australia) "Thermal Convection with Wind Shear," *Nature* **193**, 840–842 (1962)

This note outlines a theoretical approach to thermal convection with wind shear. The theory is principally concerned with the intermediate region where both forced convection and free convection must be accounted for.

The principal difference between the method presented here and that of Priestley[1] is the way in which the wind-shear turbulence is taken to provide the initial properties of the buoyant elements. The results obtained are in agreement with experiment although as in all turbulent transport theories several free parameters are included. Reasonable values of the free parameters show that the forced convection region where mechanical turbulence dominates ends at $z/L=0.03$ where z is the height and L is Obukhov's stability parameter. It is also shown that $\partial\theta/\partial z$ where θ is the mean potential temperature diminishes sharply above $z/L=1$ which is the region of free convection and buoyancy dominates. In the intermediate region, $0.03<z/L<1$, approximate solutions of the derived nonlinear differential equation indicate that a nondimensional heat flux is constant.

$$H^*=H/c_p\rho(g/\theta)^{\frac{1}{2}}z^2|\partial\theta/\partial z|^{3/2}$$

Reference

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Subject Headings: ***Convection, thermal, with wind shear; Wind shear, of thermal convection.***

D. L. Turcotte

Cramer, O. P. and Lynott, R. E. (Pacific Northwest Forest and Range Experiment Station, U.S. Forest Service, Portland, Oregon) "Cross-Section Analysis in the Study of Windflow over Mountainous Terrain," *Bulletin American Meteorological Society* 42, 693–702 (1961)

Patterns of fire-weather variation in the Oregon Coast Range are complicated by (1) cold air in the lower layers offshore; (2) dry, subsiding air sometimes descending below 3000 feet; (3) warm, dry winds from east of the Cascade Range; (4) a thermal trough dominating southwestern Oregon; (5) the physical effects of mountainous terrain. Under these conditions predicting wind has proven very difficult. Cross-section analysis of potential temperature, based on the Salem radiosonde observations and five surface stations at various elevations, was attempted as a means of obtaining a clear, simplified representation of factors affecting windflow in an area 30-mile square.

The publication consists almost exclusively of explained model cross sections corresponding with the following common synoptic situations:

1) Marked stability and stratification of moisture,
2) Instability and convergent lifting,
3) Local heating in mountain areas in subsiding air,
4) The heat trough and an invasion of maritime air,
5) The breakup of a hot spell,
6) A shallow, pronounced sea breeze.

The cross section graphically supplies the vertical element of the weather pattern which otherwise is only surmised. Types of wind action and levels to be affected are readily apparent. Likelihood of local convective circulation can be detected more readily than from soundings at valley stations alone. A series of cross sections can show the progressive effects of sustained lifting or subsidence. Potential temperature and mixing ratio are especially well adapted to tracing flow patterns in situations of strong, stratified flow.

Although developed for meteorologists, the model potential-temperature cross sections appear sufficiently distinctive to permit the layman to recognize certain common fire-weather situations.

Subject Headings: ***Wind, flow across mountains; Mountains, flow of wind.***

G. R. Fahnestock

Crapper, G. D. (University of Leeds, Leeds, England) "Waves in the Lee of a Mountain with Elliptical Contours," *Philosophical Transactions of the Royal Society of London* **A254,** 601–623 (1962)

This paper is concerned with the mathematical solution of the equations of air motion over a mountain with elliptical contours for two types of undisturbed air stream. In the first case, the static stability parameter (proportional to $(g/V^2)\left(\frac{dT}{dz}\frac{1}{T}\right)$ where T is the potential temperature, z the altitude, g the acceleration of gravity and V the undisturbed main stream velocity) is assumed to be constant throughout the atmosphere and in the second, this parameter is assumed to fall exponentially with the altitude. Since this paper is primarily concerned with a rigorous solution of the differential equations of motion, and since the analytical expressions obtained are rather complex, no attempt will be made in this abstract to present in any part the mathematical steps involved. Let it suffice to say that this paper extends the work of a previous paper by the same author in which similar solutions are obtained for a mountain with circular contour. Since the exact differential equations of motion are nonlinear, these equations were first linearized by the usual perturbation techniques before any attempt at the solution was made. Consequently, the results apply only to air flow over a mountain whose height is small compared with its width. These linear differential equations were reduced by the double Fourier-transform technique to a single ordinary differential equation with the transformed vertical air velocity as the dependent variable and the altitude as the independent variable. Integration of the resulting transformed equation is straightforward and results in a closed analytical expression. The double inverse transform of this expression back to the original variable constitutes the major part of this paper. In the author's previous paper dealing with circular mountain contours, this integration was accomplished, after making suitable approximations, by use of the calculus of residues; in the present paper the author uses the same technique for the first integration and follows this with the method of steepest descents for the final integration. Although both wave-like and nonwave-like solutions are found, only analytical expressions for the former were obtained. The latter solutions were considered to be at the present uninteresting.

The results of this investigation show that when the static stability parameter is constant the form of the lee waves is determined by the quantity $\frac{1}{V}\frac{d^2V}{dz^2}$ (another parameter of the system usually assigned the value zero in previous papers). When this latter quantity is zero the waves lie in a strip in the lee of the highest part of the mountain, but when the quantity is large enough the waves are contained in a wedge, resembling ship waves. When the static stability factor falls off exponentially with altitude, the waves closely resemble ships waves for all values of the above-mentioned parameter. Clearly some physical explanation of these results for the strip type flow is desirable; however, at present no such explanation is offered by the authors. An interesting feature of these solutions is that the waves in the lee of the mountain seem to experience a "resonance" when their wave length is in the correct relationship with the mountain width; that is to say that the wave amplitude experiences a maximum for this correct relationship. The amplitude of the waves also increases with increasing altitude to a maximum value and then decreases in amplitude with further increase in altitude. Since a good deal of approximating had to be made to arrive at these results, there appears to be considerable work still necessary on this problem to arrive at an exact solution of the linearized differential equation.

Subject Heading: *Air flow, over mountains.*

H. E. Perlee

Vonnegut, B. and Moore, C. B. (Arthur D. Little, Inc., Cambridge, Massachusetts) **Stout, G. E., Staggs, D. W., Bullock, J. W., and Bradley, W. E.** (Illinois State Water Survey, Champaign, Illinois) "Artificial Modification of Atmospheric Space Charge," *Journal of Geophysical Research* 67, 1073–1083 (1962)

This paper describes the apparatus used and the electrical perturbations produced when natural atmospheric space charge was modified by artificial means. A 14 km long, 0.04 cm diameter stainless steel wire, supported horizontally about 9 m above the ground, was energized at potentials up to 50 kv by an unfiltered half-wave rectifier power supply. The effect of wind direction on charge output was minimized by using two wires at right angles so that the length of wire normal to the wind varied only slightly with wind direction. Potential drop along the wire was less than 1 per cent of applied voltage because the operating current was typically less than 5 ma. Current to the wire varied with wind speed but no current flowed until the potential of the wire was greater than that required for corona, approximately 5 kv. Total current flowing to the wire is the sum of two components, a current flowing to ground which varies as the square of the potential and the current into the air which depends linearly on potential and wind speed.

Effects of the introduction of charge were observed both from the ground and from a low-flying airplane. From the ground it was observed that in a wind of several meters per second the potential gradient was significantly changed for 5 or 10 km downwind and for about 100 m upwind. The normal fair weather gradient of about 1 volt/cm was changed by 10–20 volts/cm immediately downwind, the sign of the change depending on polarity of the charge.

Observations made from the airplane showed that the plume of electric charge released by the wire behaved like the visible plume of smoke from a chimney. In a thermally stable atmosphere effects of the wire were difficult to detect from above but when the atmosphere was convectively unstable the wire caused potential-gradient and space-charge perturbation of considerable vertical extent, with vertical transport of charge being limited by the height of the atmospheric inversion.

At fixed observation stations several km downwind of the wire, gradient perturbations were of the order of 5 volts/cm when the wind was about 5 m/sec. This gradient perturbation corresponds to a space-charge concentration of about 2×10^3 elementary charges/cm^3 in a 9 m thick layer. Both ground and aerial measurements, however, indicate a space-charge concentration of about 100 elementary charges per cm^3. Since the horizontal dispersal of space charge is small, it is concluded that the observed 10– or 20–fold decrease in space charge is caused by vertical mixing. Observations also indicate that the space charge emitted by the wire is diluted by a factor of 100 by the time it goes very far either vertically or horizontally.

The work reported here was done in central Illinois where low natural space-charge concentrations prevail, so that even though the space charge produced at the ground is rapidly diluted by mixing to 1/100 of its original density, the effects are still important. Obviously, where the natural concentrations are much higher, the additional effect of the wire is proportionately less. Moreover, during electrical storm conditions, any effects produced by the wire will be totally swamped.

Finally, the authors conclude that the clear-air atmospheric electrical conditions under which cumulus clouds originate and develop can be significantly modified by artificial means. Furthermore, it is suggested that the artificial space-charge technique is well suited to tracer experiments.

Subject Headings: *Space Charge, modification of; Atmosphere, modification of space charge.*

A. Strasser

Dessens, J. (Observatoire du Puy de Dome, Université de Clermont, Clermont, France) "Man-Made Tornadoes," *Nature* **193**, 13–14 (1962)

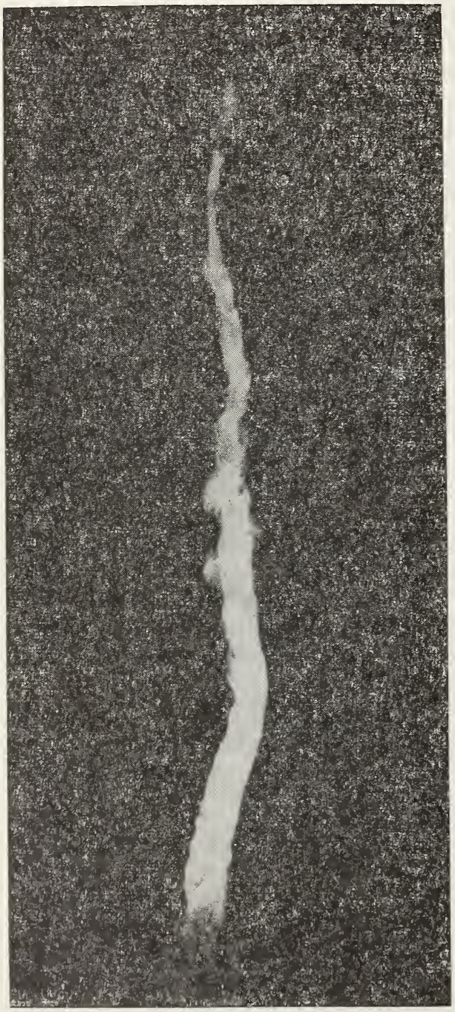
An experiment initially designed to produce a cumulus cloud over a strong convection column resulted in a small tornado on the leeward side of the column. One hundred burners regularly spaced over a 125 by 125 meter area constituted the heat source which could burn fuel (presumably oil) at a rate of one ton per minute.

Photographs show the tornado as a dark tube about 10 meters in diameter and 200 meters long suspended from the black and tilted convection column. The foot of the tornado was from 400 to 500 meters from the fire.

On another test, a strong whirl developed near the fire and three of the burners were blown out.

Subject Headings: ***Fires, laboratory, tornado; Fires, laboratory, whirlwind; Whirlwind, laboratory fire; Tornado, laboratory fire.***

G. M. Byram



(*Editor's Note:* With his review of the paper by J. Dessens, Mr. G. W. Byram enclosed a photograph and brief comments.

"You may be interested in having a photograph of a model fire whirlwind resembling in some respects that described by Dessens. The photograph shows one of the fire whirlwind models with which we have been working at the Southern Forest Fire Laboratory. This particular whirl is about 10 or 11 feet high and is burning in the open air over a pool of denatured alcohol about 14 inches in diameter."

Byram, G. M. and Martin, R. E. (Southeastern Forest Experiment Station, U.S. Forest Service, Asheville, North Carolina) "Fire Whirlwinds in the Laboratory," *Fire Control Notes* **23,** 13–17 (1962)

Model fire whirlwinds were produced by burning alcohol in a small pool within a cylindrical chamber which permitted tangential entrance of air. Approximate values of rotation velocity and updraft were calculated to be 6000 to 7000 revolutions per minute and 40 to 50 miles per hour, respectively. No details are given of the calculations, which were based on energy equations, temperatures, and dimensions of the whirl. The values have not yet been verified by direct measurement.

A threefold increase in burning rate of the alcohol which occurs when the whirl forms is probably due to turbulent premixing of fuel and air.

Subject Headings: ***Fires, laboratory, tornado; Fires, laboratory, whirlwind; Whirlwind, laboratory fire; Tornado, laboratory fire.***

A. Strasser

XI. Operational Research Principles Applied to Fire Research

Earp, K. F. (Scientific Advisers' Branch of the Home Office, London, England) "Deaths from Fire in Large Scale Air Attack—with special reference to the Hamburg Fire Storm," *Home Office Report CD-SA 28* (April 1953)

This study was made to provide a better understanding of the underlying causes of human death in wartime shelters in fire-storm areas particularly in Hamburg, Germany during World War II. These data were drawn and rationalized from 21 sources and are based on some 39 nonfire-storm and 5 fire-storm air raids.

The objective of the study is to reduce the casualties from atomic, incendiary, high-explosive, chemical-warfare, and biological-warfare raids.

Investigation of the air raids in Germany revealed that the average death rate per short ton of bombs dropped on target was 9.0 in fire-storm raids and in other raids the average rate was 1.3. In fire-storm raids, a combination of similar circumstances prevailed: the weather beforehand was warm and dry, the areas were heavily built-up and highly susceptible to fire, and the bomb density was high (about 200 t/sq mi). For purposes of congruity in thought in this review, the effects of only one such fire storm in Hamburg on July 27–28, 1943 is considered. It was estimated that 1 in 3 to 1 in 2 buildings were set afire during the main 30-minute raid of the city. (In nonfire-storm raids, the maximum house-burning density was 1 in 6).

This rate of fire build-up was sufficient to overcome normal turbulence and gave rise to the formation of one massive column of hot gases and flames over area of 5 square miles. The air, which fed this fire from all sides, was drawn in at "hurricane force." This particular fire reached its peak in about 2 to 3 hours and raged at "full force" for 3 hours prior to subsiding.

The types of shelters used by the people in this fire area were as follows:

Public Bunkers—Partially or completely underground, reinforced concrete structures designed to (1) withstand direct hits of 500 to 2000 lb high-explosive bombs and (2) permit high-capacity occupancy for extended periods. The units were gasproof, and equipped with utilities and facilities for air treatment and control.

Public Splinterproof Surface Shelters—Surface, reinforced concrete structures with walls and ceiling about 32 inches thick with an occupancy capacity of 500. The units were gasproof and had provisions for ventilation.

Public Cellars—Converted large cellars in business districts. The ceilings were reinforced concrete generally 2 to 5 feet thick. The units were also strengthened by the addition of beams and columns, and by reinforcing the walls. The units were equipped with utilities and ventilation was provided.

Private Cellars—In city areas, the cellars were under 4 or 5 storied brick houses. The ceilings were generally a brick arch. These apparently crude units had an average capacity of 10 persons. There were at least two exits, one of them leading to an adjacent building.

The estimate of the distribution of the approximate 280,000 people in the area of the fire storm was:

	Percent
Public Bunkers	10
Public Splinterproof Surface Shelters	9
Public Cellars	16
Private Cellars	65

Comments regarding the conditions and fire-storm fatalities in the above shelters were:

1) Virtually no fatalities were indicated for occupants of the bunkers and splinterproof surface shelters. Further, none of the occupants were *forced* to leave the shelters during the fire storm, although the air was described generally as almost unbearable due primarily to the entry of hot air and smoke into the units before the ventilating systems were shut off.
2) Virtually all fatalities occurred in the public and private cellars (14 per cent of the total population and 20 per cent of the population in cellars). As for the 80 per cent of the cellar survivals, about 75 per cent either survived in the shelters or escaped by their own initiative and the other 25 per cent were rescued by various organized groups (Police, Medical Teams, Rescue and Armed Forces, Fire and Decontamination Services). Those who escaped on their own from the cellars risked an early escape and managed to find protection in canals, waterways, and large gardens or lawns (larger than 300 meters in diameter). In addition, escape by own initiative also occurred around the perimeter of the fire, coincidentally, this was the prime rescue area also.

Accumulation of data from a variety of sources indicated that the causes of death in the public and private cellars were most frequently due to carbon monoxide or heat exhaustion, or a combination of both. Death caused by the seepage of carbon monoxide into these inadequate shelters appeared to predominate, even though investigators reported that the heat was unbearable in some of these shelters for over a week. It was noted, in addition, that death in streets appeared to be due predominantly to heat exhaustion.

Suggestions were made (1) regarding methods of reducing the risk of fire-storm occurrence and (2) for providing adequate shelters. Particular emphasis was placed upon carbon monoxide detection at sublethal levels to provide an improved probability of surviving fire storms in shelters.

Subject Headings: ***Fire storm, Hamburg; Fires, death in Hamburg fire storm.***

R. A. Gorski

Joint Fire Research Organization, Boreham Wood, England "United Kingdom Fire Statistics, 1960" *London: Her Majesty's Stationery Office*

This is a comprehensive statistical analysis of fires involving fire brigades in the United Kingdom during 1960. It covers 133,484 fires of which 62,460 were fires in buildings. The study indicates a general upward trend in the number of fires in buildings since 1946.

An interesting comparison of fires by months is shown which indicates a peak for fires in buildings in January and December which corresponds to the maximum use of heating equipment and a corresponding decrease in indoor humidity. In this regard, a definite trend in recent years is shown in which fires attributable to open fireplaces, have been declining and those originating as chimney and flue fires have been increasing. This would indicate the transition to central heating equipment and an eventual trend to fewer fires due to space heating equipment. Fires associated with the use of electricity show an upward trend over the past few years. The major part of the increase is attributed to fires in cookers, heaters, wireless and television sets and a wide variety of other electrical equipment. This must be evaluated against the tremendous increase in the use of such equipment in recent years.

The number of fires attributed to matches and smoking materials has increased for several years and makes an appreciable contribution to the total fire incidence. Both, in 1959 and 1960, approximately 23 per cent of the fires in buildings were attributed to the misuse or careless disposal of these materials.

A study of sprinkler performance in England and Wales during 1960 is presented which closely parallels their excellent performance in this country. Unfortunately (for statistical purposes) only 136 incidents are reported which would indicate a relatively small number of sprinkler-protected properties in comparison with those in this country; however, in these incidents, 120 or 89 per cent were controlled or extinguished with either no sprinklers operating or less than five. If a criterion of less than 10 sprinklers is used, the satisfactory number of incidents handled rises to 130 or approximately 96 percent of all reported incidents in sprinklered properties. This is almost identical with the experience in the United States.

Another interesting tabulation to those interested in fire alarms is presented. This is an analysis of the methods used in calling fire brigades in England and Wales during 1960. It points up the increasing use of public telephone systems as opposed to special fire service methods in calling fire departments. Unfortunately, data for preceding years is not presented which might indicate a trend. The figures indicate that 63.9 per cent of all alarms were received over public telephone facilities as compared to 0.4 per cent by fire and police alarm services. This is in line with similar experience in the United States and deserves serious study by municipal officials and underwriting authorities.

Subject Heading: ***Fire statistics, United Kingdom.***

J. J. Ahern

Cramer, O. P. (Pacific Northwest Forest and Range Experiment Station, U. S. Forest Service, Portland, Oregon) "The 1961 Fire Season in the Pacific Northwest," *Pacific Northwest Forest and Range Experiment Station Publication* (December 1961)

This is the tenth annual publication of fire-season descriptions by the same author. As the title suggests, the descriptions themselves are of interest primarily to forest protection agencies of the five sections of the Pacific Northwest for whom they were written. Wider attention is warranted, however, by the method used for comparing severity among fire seasons and relating fire experience to severity rating by means of indexes based on total days without rain, average days between rains of ¼ inch or more, and burning index (an expression of the combined effects of fuel moisture content and wind speed). Each annual rating for Oregon and Washington contains an example of this system and should be read in conjunction with author's 1959 publication, "Relation of Number and Size of Fires to Fire-Season Weather Indexes in Western Washington and Western Oregon" (*Pacific Northwest Forest and Range Experiment Station Research Note 175*).

Tables compare the three variables for spring, summer, fall, and the whole season with corresponding values for the preceding year, the 10-year average, and the highest and lowest of record. Additional tabulations give numbers of days with relative humidity $\leqq$ 30 per cent, with burning index above specified levels, and with lightning storms, and compare actual with computed fire occurrence. Unfortunately the masses of data, although probably necessary for detailed study, tend to hinder comparisons. Simplified, preferably graphic presentation would be a welcome addition to make essential relations stand out clearly.

Two of the strongest indications from the 1961 seasonal rating were that more man-caused fires occurred than the weather seemed to warrant and that the number of lightning fires increased far more than did days with thunderstorms. More exhaustive interpretation of such findings by the author would make future issuances in this series more helpful and more interesting.

Subject Heading: ***Fire season, Pacific Northwest 1961.***

G. R. Fahestock

King, A. R. (Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia) "The Efficiency of Rural Firefighters," *Chemical Research Laboratories Technical Paper No. 4* (1962)

Grass, brush and forest fires are discussed. The physical capability of fire fighters is limited by the rate at which the body can reject heat, including that generated within the body by physical work plus that received by radiation from the sun and particularly from the fire itself.

Maximum heat rejection for the average man is about 290 cal/sec corresponding to the evaporation of 0.5 gms/sec of water (3½ pts/hr).

When working actively, with maximum internal heat generation of 150 cal/sec, there is a margin of only about 140 cal/sec that the body can receive from all external sources without rise in body temperature and impairment of functions.

Author's tests show that with ⅓ of the body exposed to radiant heat of the fire under five described sets of fire conditions, the heat received by the body may range from 50 to over 500 cal/sec. At the higher rates pain and inability to continue work will result. Clothing to reduce the exposed body area to a minimum is deemed essential.

Discussed are some characteristics of protective clothing, reflective face creams, water and salt intake, diet, smoke protection, eye protection, and the effects of nervous tension. Ten references are given.

Subject Headings: *Fire fighting, efficiency of rural; Heat rejection, by human body.*

O. W. Johnson

National Board of Fire Underwriters (New York, New York) "The Bel-Air-Brentwood Conflagration, Los Angeles, California, November 6–7, 1961)" **and Wilson, R.** (National Fire Protection Association, Boston, Massachusetts) "The Los Angeles Conflagration of 1961—The Devil Wind and Wood Shingles," *Quarterly of the National Fire Protection Association* **55**, 241–288 (1962)

The principal contributing factors for this fire may be classified as follows:

a) The severe three-year drought preceding the fire date when only 4.5 inches of rain was deposited during the last half of this period, April 1960 until November 1961.
b) The onset of "Santa Ana" weather patterns reduced the average relative humidity to extremely low values of around 4–10 per cent. This condition was present for several days prior to the fire date. Accelerated further dehydration occurred during this period.
c) The topography is hilly and quite difficult to traverse. Non-built-up areas are covered with heavy brush which is very fast-burning.
d) The majority of the dwellings are inherently poor fire risks. Most of them are of wood frame and have wood shake or shingle roofs.

The fire erupted in a relatively inaccessible non-built-up area and spread quickly through the canyons toward the southwest. Fire lines were quickly broken as flying debris such as roofing brands carried the flames to areas ahead of the main burning path. Wind speeds were high during the initial hours of the disaster.

Recommendations for future prevention of this type of blaze include the total banning of wooden roofing materials, the widening of roadways to improve maneuverability, the enlargement of the minimum lot size to further separate individual structures, the removal of all brush surrounding built-up areas or regular watering of it by the State or private individuals. Also a water supply system must be designed to deliver a larger volume flow at high pressures adequate for and reaching all areas.

Subject Heading: *Conflagration, Bel-Air-Brentwood.*

P. Breisacher

XII. Instrumentation

Martin, S. B. and Ramstad, R. W. (U. S. Naval Radiological Defense Laboratory, San Francisco, California) "Compact Two-Stage Gas Chromatograph for Flash Pyrolysis Studies," *Analytical Chemistry* **33**, 982–985 (1961)

A gas chromatographic analytical system has been designed for the study of the rapid degradation of relatively nonvolatile solids and liquids when subjected to high intensity, short duration flash heating. The flash pyrolysis is carried out within the carrier gas stream just prior to entering the liquid partition column of the first stage and the coupled absorption column of the second stage.

Each stage was placed inside a small Dewar flask. A solid brass block was machined to contain the detectors and the preheater elements necessary to get the carrier gas temperature up to the column temperature. Column selection is accomplished by a specially constructed valving system. The pressure pulses incurred in such switching systems are eliminated to a large extent by electrically controlled variable flow resistances. These are made of stainless steel needles embedded in asbestos. The flow is varied by heating the needle directly.

The reaction being studied is initiated by a carbon arc source or xenon flash tube. The time span varies from one second to one millisecond. The products are formed immediately and swept down to the gas-liquid partition column (GLPC). The fixed gases are not retained in the latter and proceed to the gas-solid absorption column (GSAC) where they are resolved. The columns are connected with the previously described variable flow resistances. Collection of the eluting fractions from both columns is accomplished by diverting the GLPC eluents from the GSAC to a collection manifold before the first fraction has a chance to emerge.

To prevent blockage of the narrow (⅛" O.D.) tubing by tarry reaction products it was necessary to insert a short stripping column between the reactor and the top of the GLPC. This section is exposed to carrier gas flow for only a few minutes before being switched out of the system. Analysis of compounds trapped in this column is done later. Sample sizes down to 10^{-8} mole can be used. Some examples are given of the pyrolysis of cellulose. Performance data for a large number of ethers, aldehydes, ketones, esters, and alcohols are tabulated. Data includes sensitivities, retention volumes and peak widths at various temperatures for two columns of equal length.

The apparatus here described is quite ingenious and will prove very useful for analyzing products of both fast and slow reaction systems.

Subject Headings: ***Pyrolysis, chromatograph for study; Chromatograph, in pyrolysis study.***

P. Breisacher

Lindemuth, A. W., Jr. (Rocky Mountain Forest and Range Experiment Station, U. S. Forest Service, Fort Collins, Colorado) "Development of the 2-Index System of Rating Forest Fire Danger," *Journal of Forestry* **59**, 504–509 (1961) and "How to Use the 2-Index System for Rating Forest Fire Danger," *Rocky Mountain Forest and Range Experiment Station Paper No. 63* (August 1961)

In these two papers the writer introduces another system of measuring and evaluating forest fire danger. The 2-index system, as described in these articles, is designed specifically for the ponderosa pine timber type in the Southwest but has been used in the Black Hills of South Dakota as well.

The paper in the *Journal of Forestry* discusses the principles behind the development of the 2-index system, presents an adequate description of the two independent indexes (drought index and rate-of-spread index), and summarizes performance under actual operating conditions. The *Station Paper* has been prepared as an instructional handbook covering calculation of the indexes, proper recording procedures, interpretation, and how to apply the indexes. There is also a section on the location and care of the meteorological instruments used to sample fire weather.

A system was needed that would rate cumulative drying throughout the year as the basis for an index of fire potential, and use current weather as a basis for determining when a fire will develop its full potential. The primary consideration was to find a way to consistently and accurately identify bad burning conditions.

Fuel moisture estimates are the foundation upon which both indexes are based. Fuel moisture during wetting periods and during drying periods is used to relate a buildup of critical burning conditions, or an easy situation that generally results from frequent rainfall.

Winter precipitation is an important factor in determining soil moisture and moisture content of large fuels from year to year. For this reason, the drought index is based on the moisture depletion or accretion in the upper foot of bare soil. A series of tables are used to compute drought index on the basis of the winter's total precipitation and current precipitation during a 48-hour period preceding observation.

The rate-of-spread index is based on three factors: (1) litter moisture, (2) air temperature, and (3) wind velocity. These factors are integrated in a slide-rule type meter to produce a numerical index that represents the relative rate at which a surface fire burning in litter fuels may be expected to spread along its forward axis. The numerical scale progresses by 5-point jumps from 0 to 100 and is divided into four classes or adjective ratings, low 0 to 15, moderate 20 to 35, high 40 to 65, and extreme 70 to 100.

Paired indexes, that is both drought index and rate-of-spread index, may be used to estimate or describe expected fire behavior. At this point, however, the 2-index system resembles many other systems that have been developed in that only *relative* descriptions are possible. For instance, a spread index of 49 with this system falls within the "high" class, but a similar reading on the Intermountain Model 8 meter would mean "average" conditions; while on the Lake States meter, a rating of "very high" would be indicated. None of these indexes produce an actual rate-of-spread value in terms of any specific unit.

There is an excellent section in the Station Paper on application of the two indexes. Examples are included on how to use the drought index and rate-of-spread index individually and in combination to more effectively handle peak fire loads through fire prevention and suppression activities.

Subject Headings: ***Fire danger rating; Forest fire, 2-index system rating.***

J. H. Dieterich

Hirsch, S. N. (Intermountain Forest and Range Experiment Station, U. S. Forest Service, Ogden, Utah) "Possible Application of Electronic Devices to Forest Fire Detection," *Intermountain Forest and Range Experiment Station Research Note No. 91* (1962)

This paper, which is introductory and descriptive, provides fascinating reading. Forest fires result mainly from man's activities or lighting. The detection of fires involves several physical problems identified as the need for continuous search, detection through smoke and haze, and the fact that fires are widely scattered. The first problem is eased somewhat since there are peak fire hours that occur in the late afternoon. The phenomena for use in fire detection are infrared, radar, and sferics.

Infrared scanners can be based on a mountain top or aboard aircraft. A signal indicating a fire may come from a direct view of the fire or from the hot gas column. A wave-length response from 1 to 10 microns (5000 to 80°F source temperatures) seems desirable although this is not specifically stated in the paper. The radiation is attenuated by certain molecular species and by particles.

Radar is of help to locate cloud formations, e.g., cumulo nimbus, associated with lighting. Areas with clouds may have lightning, which may initiate fires.

Sferics designates a method of detecting and locating lightning by observing its electromagnetic radiation. There is considerable energy in the VLF region of the spectrum. By using two sferics listening stations and by careful analysis of the signals, it may be possible to determine the location of the lightning and to know whether it is of cloud-to-ground or cloud-to-cloud origin.

The extent to which electronic devices will be used in the future depends on research presently being conducted.

Subject Heading: ***Forest fire, detection.***

A. E. Fuhs

Nash, P., Pickard, R. W., and Hird, D. (Joint Fire Research Organization, Boreham Wood, England) "Automatic Heat Sensitive Fire Detection Systems," *Fire Protection Review* (May-June 1961)

The role of automatic fire-detection systems in reducing fire losses in buildings and the main features affecting their performance and reliability are discussed.

Three stages of delay are recognized from the time a fire starts to the time the fire department arrives on the scene. These are (1) time from fire initiation to detection, (2) time from detection to alarm at the fire house, and (3) time for arrival of the fire-fighting apparatus. Automatic fire detection systems minimize the first delay and also the second, if automatic relaying of the alarm to the fire department forms a part of the systems.

There are two types of heat-sensitive detectors, as distinguished from smoke-sensitive detectors: (1) point or spot detectors using bimetallic strips, fusible links, or electrical resistance changes to detect sudden temperature increases; and (2) strip or line detectors using the expansion of fluid in a long metal tube, or electrical resistance changes of long lengths of wire to monitor the cumulative effect of temperature changes over a large ceiling area.

Detector reliability must be such as to insure satisfactory operation for several years in dirty, corrosive atmospheres. Point detectors should be small but robust, corrosion-resistant, vibration-resistant, omnidirectional, and capable of being monitored to guard againt circuit defects.

Detector sensitivity should be the maximum possible within the limitation that no false alarms be given under non-fire conditions. Factors affecting the sensitivity to which point detectors should be adjusted are: local temperature conditions, building geometry, location and spacing of sensors, flammability of building and contents, and location of the building with respect to available fire department protection. Specifications for line detectors are not yet available, but are expected to be similar to these point detector specifications.

Automatic fire detection may be expected to decrease fire losses considerably both in urban communities and rural areas.

Subject Headings: ***Fires, heat-sensitive detection systems; Detection, system for fires.***

B. Greifer

XIII. Fire-Fighting Techniques, Equipment Design, Materials of Construction

Ashton, L. A. (Joint Fire Research Organization, Boreham Wood, England) **and Bate, S. C. C.** (Building Research Station, England) "The Fire-Resistance of Prestressed Concrete Beams," *Proceedings Institution Civil Engineers* **17**, 15–38 (1960) and Discussions on this Paper, *Proceedings of Institution of Civil Engineers* **20**, 305–320 (1961)

The main results of an investigation of the fire resistance of simply supported composite prestressed concrete beams with post-tensioned steel cables carrying heavy floor loads are presented. The main object of this investigation was to obtain information on the design of beams for buildings of high fire risks, such as warehouses, where a fire resistance of up to four hours is required for structural elements by local authority bylaws.

The technique was to establish a relation between fire resistance and scale of beams which would permit extrapolation for larger beams. The investigation was divided into three phases due to the fact that the equipments used at various times limited the sizes of the beams or the scale of test specimens. The provision of a new furnace during phase 3, however, covered scales up to 6/5 full-size.

The design of the test specimens was based on a nominal full-sized beam with a clear span of 20 ft. which consisted of a prestressed concrete rib with a reinforced concrete flange cast later. The thickness of the flange for the full-sized beam was 6 inches, corresponding to a fire resistance of 4 hours.

Five different types of beam sections were tested but four of them were variants of the one just described, the composite T-section with a single cable. First variation was of similar size but stressed with two cables providing similar prestressed conditions with a reduced cover of concrete to the prestressing steel. Second variation was to introduce a relatively thin portion of the web in the section. In the third variation, the concrete cover to the prestressing steel was increased. The last variation consisted of the prestressed rib only.

The preparation of test specimens, such as the selection of type of cement, aggregate, and cables; stressing and fixing the cables; the provision of vermiculite encasement at sides and suffit of the beam; the introduction of secondary mild steel reinforcement; the positioning of thermocouples; the aging of the specimens; etc. were fully described in the text. The beams were structurally tested before going through fire tests.

The conditions for fire test were specified as (1) the procedure of test and a standard rate of heating defined as a temperature-time curve were given by British Standard 476; (2) test load was made up by a dead load plus 1.5 live load, and was equally applied at 4 points, ⅛, ⅜, ⅝, and ⅞ of the span; (3) the furnace was open at the top, hence the sides and suffit of the beam were exposed to the furnace, a case representing a fire on the underside of a floor.

The grade of fire resistance attributed to a specimen is that period of the following, which is nearest to but lower than ½, 1, 2, 4, and 6 hours.

A typical result obtained in the fire tests was described as follows: On a loaded beam a relatively rapid increase in deflection was observed with little apparent damage to the concrete. At this stage, a quantity of water sometimes issued from the beam and ceased before the cable temperature reached 100°C, a phenomenon not found in structural tests. Deflection remained unchanged when the average temperature of the steel rose to 100°C but considerably visible damage of the concrete developed. At the time the temperature reached 100°C and remained for a period during which the concrete and grout dried out completely. When the average temperature was between 200 and 300°C, deflection rose again and more superficial damage to concrete by cracking and spalling occurred. When the average temperature of steel reached 400°C, the beam collapsed.

Factors expected to influence the fire-resistance of structural elements were (1) size of beam; (2) form of section of beam; (3) condition of end-restraint; (4) conditions of loading; (5) type of aggregate; (6) properties of concrete; (7) thickness of concrete cover to the prestressing steel; (8) initial stress in the prestressing steel; (9) type of steel in the tendon; (10) provision of secondary mild-steel reinforcement; and (11) use of additional protection. All these factors, except (5) (6) and (8), were treated as variables, and their influences on the behaviour of beams in the fire tests were discussed in great detail in the light of test results, from which the following conclusions were deduced:

1) The mode of failure changed with size of beams. This result limits the scaling technique and uses of full size models are advised.
2) Failure will occur when the mean temperature of the prestressing steel reaches about 400°C.
3) Fire resistance depends on the protection given to the steel, and periods of 4 hours were obtained provided a concrete cover of 4″ thickness is retained in position with secondary reinforcement.
4) The adhesion of an insulation layer on to the exposed surface will increase substantially the fire resistance of the beam. A layer of reinforced vermiculite encasement is equivalent to twice its thickness of concrete in insulation. Other fire tests suggested that a layer of vermiculite/gypsum plaster or sprayed asbestos is equivalent to three times the thickness of concrete.
5) The failure of prestressed concrete beams with secondary reinforcement is gradual and is accompanied by large deflections which gives ample warning.
6) If the temperature of the steel in a prestressed concrete beam exposed to fire has exceeded about 180°C, the reduction in the stiffness of the beam necessitates the replacement of the structural member.

Subject Headings: ***Concrete, fire resistance; Beams, concrete, fire resistance of; Fire resistance, of concrete beams.***

A. S. C. Ma

Cary, H., Easterday, J. L., Farrar, D. L., Weller, A. E., and Stember, L. H., Jr. (Battelle Memorial Institute, Columbus, Ohio) "A Study of Reliability of Flight-Vehicle Fire-Protective Equipment," *Aeronautical Systems Division, Air Force Systems Command Contract No. AF 33(616)–7306. ASD Technical Report 61–65* (September 1961)

The objective of this study is the development of procedures for determining design criteria in order to attain a higher reliability for fire-protective equipment in future flight vehicles. Since extensive data collected in an earlier study indicated that reliability could not be attributed to any single factor, an attempt was made to study the problems of justification of flight vehicle fire-protective equipment from the viewpoint of the overall weapon system.

The study is presented in four sections which outline the decision-making process involved in the selection of reliable equipment: design studies to identify hazards; problems in fire-protection and in determining performance specifications; preliminary studies on system and components; a study of design development and fabrication problems.

In the first section the design requirements of the flight vehicle are analyzed to identify potential hazards and quantify potential risks resulting from the presence or absence of protective devices. Hazards are identified in terms of the fire characteristics of the materials involved. A hazard index is introduced to identify and measure the fire threat for sets of isolated compartments within the flight vehicle. In order to establish a basis for justifying the use of fire-protective devices, a procedure is presented for measuring equipment characteristics and the risk or potential costs inherent in various fire situations. Based on the relationship between the potential savings gained from fire-protection equipment and the cost of the equipment plus the cost of equipment error, an equation is derived for a maximum acceptable probability of fire. Equipment is justified if actual experience in similar situations indicates a higher probability of fire than that indicated as allowable by the equation.

The second section outlines procedures for establishing performance specifications for the fire-protective equipment. The specifications are obtained from three sources: the risk study discussed in the first section; a fire-detection study to investigate appropriate detection principles and requirements; the characteristics of the extinguishment system chosen and the probability that it will actually extinguish the fire.

The third section discusses a preliminary study of equipment problems taking into account the specifications produced in the second section. Various approaches are presented which depend on whether or not the specifications require additional development or research work. Procedures are outlined for considering the recommendations and proposals of outside vendors.

The fourth section discusses the letting of the production contract. The mock-up program, qualification testing, system integration and other start-up problems are also studied.

Recommendations are presented which suggest further effort to test and improve techniques in design review and in the areas of hazard and risk definition and fire detection. It is recognized that many of the techniques presented in the study are conceptual and have not had the benefit of laboratory or field verification. They are not intended to be rigorously applied in the form presented.

Subject Heading: *Fire protection, reliability of.*

A. L. Goldstein

Langdon-Thomas, G. (Joint Fire Research Organization, Boreham Wood, England) "Fire and Board," *Board* 3, 61–65 (1960)

The author presents a discussion of lining materials and their role in providing fire resistance in construction, test methods, and treatments for improving the fire resistance of lining materials.

Fire resistance cannot be defined for a material except in terms of the performance of that material as an element of construction. That is, fire resistance can be defined in terms of the time during which structural members under normal structural load resist the effects of fire exposure. Although this discussion concerns primarily lining materials and their resistance to flame spread, other construction features are also considered, such as the effectiveness of seam closures, resistance of ceiling lining supports, resistance of unexposed surfaces, and the use of draft stops in hollow wall construction, all of which affect the fire resistance of lined structural elements.

The classification of fire hazard under British Standard 476 is outlined in "The Science of Fire Protection—Structures, Materials and Their Resistance" by G. Langdon-Thomas published in *The Times Review of Industry*, October 1960 (See *Fire Research Abstracts and Reviews* 4, 128, 1962). In addition to the Standard Test procedure, a reduced scale test, and an alternate test procedure called the "Fire Propagation Test" are discussed. At the time of writing, the Fire Propagation Test was still under development, using a 9 by 9 inch test specimen. The specimen constitutes one side of an otherwise noncombustible chamber, which is heated by gas jets and electrical heating elements. The gas jets are lighted and electric heating is initiated after the first three minutes of gas heating. A blank time-temperature profile is determined using no combustible (test) specimen in the chamber; then from a time-temperature profile with a test specimen, the specimen classification can be made, using a schedule as follows: where e equals the temperature in degrees centigrade obtained in the blank run after t time in minutes—

Class A	Test chamber reaches e plus 50°C in more than three minutes and remains at e plus 50°C for less than three minutes.
Class B	Test chamber reaches e plus 50°C in more than five minutes and remains at e plus 50°C for more than three minutes.
Class C	Test chamber reaches e plus 50°C between three and five minutes and remains at e plus 50°C for more than three minutes.
Class D	Test chamber reaches e plus 50°C in less than three minutes.

This classification schedule would relate to the classification resulting from the British Standard Tests approximately as follows: Class A would comprise noncombustible Class 1 materials; Class B would comprise other Class 1 materials; Class C would comprise Class 2 and Class 3 materials; and Class D would comprise Class 4 materials.

The reduced scale tests, patterned on the British Standard tests have enabled product developers to conveniently screen their experimental materials, but the Standard Test is required for official rating. The Fire Propagation Test, on the other hand, has been proposed to enable differentiation between materials which currently are placed in the Class 1 standard category (i.e., combustibles vs. noncombustibles).

The author divides surface treatments into two broad types, coatings and impregnations. The intumescent phosphate resin is cited as an example of one of the most effective coatings, and monammonium phosphate was noted as an example of an effective impregnating agent. Practically speaking, treatments must also be considered, such as covering power, adhesion, durability, washability, and thermal stability (resistance to flaking or cracking under heat). Impregnation is favored over coating as a treatment since (a) cut edges of impregnated materials display essentially the same resistance to flame spread as the undisturbed surfaces, and (b) abrasion damage does not reduce the treatment protection.

Subject Headings: *Fire resistance, of structural materials; Structures, fire resistance.*

J. E. Malcolm

Kingman, F. E. T. (Joint Fire Research Organization, Boreham Wood, England) "New Techniques for Fighting Factory Fires," *Manufacturing Chemist* 33, 56–59 and 76 (1962)

This article is a follow-up to an earlier article outlining the general principles of fire protection in the chemical industry in the United Kingdom. The author describes some of the latest developments and presents some statistics on the incidence of fires in the chemical industry.

The fire record in the chemical industry was comparatively good in 1960 accounting for only 544 fires out of 10,741 fires in British Industry. In view of the rather severe hazards presented by the chemical industry, this is a creditable showing.

Recent developments include a measure of exposure hazard based upon the radiation from building fires and a determination of threshold values of radiation required for ignition making it theoretically possible to calculate the separation required to prevent a fully-developed fire in one fire division from spreading to an adjoining building. Attention is also given to the variation in fire resistance requirements in buildings according to size and nature of the industrial occupancy. This will correspond to the combustible fire-load theory used in this country and presents the same difficulties encountered here when a change of occupancy occurs. Under structural features, a review is made of roof venting and its relationship to draft curtains and spread of interior fires. This information parallels the work which has been done on these features in this country.

A review is also presented of detection and extinguishing methods which stresses dry powder and foam and discusses the compatibility problems encountered with these materials. The most significant new development is that involving the use of inert gas generators for extinguishing fires in basements and ships' holds. An interesting feature is the use of a jet engine carried on a five-ton truck to provide the inert gas. The exhaust gas from the turbine is cooled by the injection of water which is converted to steam producing a gas output of 40,000 cu ft/min composed mainly of water vapor and nitrogen and containing only 7 per cent oxygen.

In summary, this is a brief review of recent developments in the protection of buildings with emphasis on design principles.

Subject Headings: *Fires, factory, techniques for fighting; Fire fighting, factory.*

J. J. Ahern

Nash, P. (Joint Fire Research Organization, Boreham Wood, England) "Some Factors in the Design of Hose-Reel Equipment," *Institution of Fire Engineers Quarterly*

Hose-reel equipment is defined as the pump, hose, and nozzles used in applying water from hose-reels carrying hose of ¾ inch inside diameter and 1½ inch outside diameter. The author cites British Fire Brigade practice during the five-year period, 1954 through 1958, when 45.5 per cent of all fires extinguished were extinguished using hose-reel jet stream equipment. The usual operating pressures and capacities for the hose-reel nozzles are described as 80 to 120 psig and 8 to 10 gal/min.

Special equipment types are described, which have been used experimentally, operating at 500 psig, using a nozzle with variable pattern control and trigger operation.

Essentially, the effectiveness of the hose-reel equipment is measured in terms of the time and quantity of water required for the extinguishment of fires. The characteristics of the methods of water application upon which the effectiveness depends are the rate of application or flow, the throw or reach, in some instances the cone angle of spray, and the mean water droplet size. These characteristics are in turn dependent on the nozzle design and the water pressure at the nozzle inlet. The author discusses these characteristics and their importance in the extinguishment of solid fuel and liquid fuel fires.[1–3] The author refers to a paper by Rasbash and Stark[4] in which liquid fuels are classified into three groups:

1) High flash point fuels, i.e., those whose liquid surfaces may be cooled by water sprays below the fuel flash point to effect extinction.
2) Water miscible fuels, i.e., those extinguishable by water dilution.
3) Low flash point fuels, i.e., those whose burning vapors must be cooled below the minimum flame temperature to effect extinguishment.

The effect of droplet size in extinguishing fires with fuels in each group is considered, and it is stated that a droplet size less than 0.35 mm is preferable for all three groups. It is pointed out, however, that only fuel fires of the first group could be extinguished reliably with water sprays.

An empirical formula developed by Rashbash is included which relates the nozzle spray reach or throw with other characteristics

$$T=0.68\frac{R^{0.36}P^{0.28}}{\left(\tan\frac{\theta}{4}\right)^{0.57}}$$

where

T = throw in feet
R = rate of flow in gal/min over the range of 10 to 500 gal/min
P = nozzle pressure in lbs force/sq in, psig, over the range of 10 to 150 psig, extrapolated to 1000 psig
θ = cone angle in degrees over the range of 30 to 90

Figure plots are presented relating the throw of straight stream nozzles to nozzle pressure; and power requirements, including those resulting from hose line losses and nozzle power dissipation, are reviewed.

Line pressure drop is related to other parameters by

$$\Delta P = 0.032 \frac{R^2}{D^5} \frac{L}{100}$$

where

P = pressure drop (psig)
R = flow rate (gal/min)
L = hose length (ft)
D = hose internal diameter (in)

A table is included giving power and pressure requirements for 240 ft of ¾ in hose with a swirl chamber spray gun at flow rates from 5 to 25 gal/min. Six figures comparing nozzle and hose characteristics are presented.

Other considerations discussed include nozzle reaction, optimization of the flow rate, and desirability of choice in operation between wide cone angle for personnel protection, a moderate cone angle for residence room coverage, and a jet stream of 35 ft at maximum flow rate to give adequate reach and penetration into solid fuel configurations. A nozzle reaction of 11 lbs force is stated to be "comfortable" for the nozzle man, and 20 lbs force is recommended as a maximum tolerable, corresponding to a nozzle flow rate, for example, of 20 gal/min at 500 psig at the nozzle.

The need for fine droplet size for the extinction of the more volatile flammable liquid fires is stressed, though the practicality of producing this type spray in hose-reel equipment is questioned. In addition, the value in liquid fuel fires of cooling surrounding surfaces with coarse sprays is cited.

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Subject Heading: ***Hose reel, design of.***

J. E. Malcolm

FIRE RESEARCH ABSTRACTS AND REVIEWS, Vol. 4,
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COMMENTS AND DISCUSSIONS

The Burning Rate of Liquid Fuels from Open Trays by Natural Convection

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Several articles[1–3] in the present journal have referred to the fact that, when the tray diameter is large, the linear regression rate v_∞ of a fuel burning from an open tray is independent of size, and obeys the law:[4]

$$\frac{v_\infty\left(\Delta H_{vap}+\int_{t_F}^{t_S} c_F\,dt\right)}{\Delta H_{comb}}=0.0076 \text{ cm/min} \tag{1}$$

where the bracketed term is the enthalpy difference between saturated fuel vapor at the interface temperature and the fuel in the reservoir state, while the denominator is the heat of combustion of the fuel.

Reference 2 contains some discussion of equation (1) in a paragraph headed: "The Dominance of Radiative Heat Transfer." The present contribution questions the appropriateness of this heading by showing that convection theory would predict burning rates of the same order as those found experimentally. This theory, which is well supported by earlier experiments[5] on natural-convection burning of liquids from spherical and flat vertical surfaces, will be applied so as to provide an expression for the right-hand side of equation (1) which depends chiefly on the air requirement of the fuel.

On page 126 of reference 5, it is shown that both the solution of the boundary-layer equations for laminar burning from a vertical flat plate and the experimental data for burning under laminar conditions from a spherical surface can be well represented by:

$$\frac{v_\infty \rho_F d}{k/c}=0.45\,B^{\frac{3}{4}}\left(\frac{g d^3 \rho_G{}^2}{k^2/c^2}\right)^{\frac{1}{4}} \tag{2}$$

where

ρ_F = liquid fuel density
d = linear dimension of fuel surface
k = thermal conductivity of gas
c = constant pressure specific heat of gas
ρ_G = density of atmospheric gas
g = gravitational acceleration
B = "transfer number"

$$\equiv\frac{\left[\frac{m_{ox,G}}{r}\Delta H_{comb}+c(t_G-t_S)\right]}{\left[\Delta H_{vap}+\int_{t_F}^{t_S} c_F\,dt\right]}$$

$m_{ox,G}$ = oxygen mass fraction in atmosphere
r = mass of oxygen combining with unit mass of fuel
t_G = temperature of atmosphere
t_S = temperature of liquid-gas interface

The properties k and c are inserted at their atmospheric values. The group $gd^3\rho_G{}^2/(k/c)^2$ is of course related to the Grashof number which arises in most natural-convection studies.

No experiments were reported in reference 5 for the turbulent-flow regime. It is however well known[6] that, at large Grashof numbers, the exponent of the Grashof number changes to ⅓ and the coefficient multiplying it is reduced in the ratio 0.54 to 0.14. We may therefore expect that, for large dimensions of fuel surface, equation (2) must be similarly altered. When this alteration is made, it is easily seen that d disappears from the equation, which becomes:

$$v_\infty = 0.117\, B^{\frac{3}{4}} g^{\frac{1}{3}} \rho_G{}^{\frac{2}{3}} (k/c)^{\frac{1}{3}} \rho_F{}^{-1} \tag{3}$$

Now the second term in the numerator of B is usually small (except for cryogenic fuels) so that an equation similar to (1) can be derived from (3), namely:

$$\frac{v_\infty\left(\Delta H_{vap} + \int_{t_F}^{t_S} c_F\,dt\right)}{\Delta H_{comb}} = 0.117\, B^{-\frac{1}{4}} (m_{ox,G}/r) g^{\frac{1}{3}} \rho_G{}^{\frac{2}{3}} (k/c)^{\frac{1}{3}} \rho_F{}^{-1} \tag{4}$$

For hydrocarbon fuels burning air, we have

$m_{ox,G} = 0.232$
$r \approx 3.48$
$g = 981$ cm/s^2
$\rho_G = 1.2 \times 10^{-3}$ g/cm^3
$k = 6 \times 10^{-5}$ cal/cm s °C
$c = 0.24$ cal/g °C
$\rho_F \approx 0.8$ g/cm^3

Substitution of these values into equation (4) yields 0.04 $B^{-\frac{1}{4}}$ cm/min as the value of the right-hand side.

Now hydrocarbon fuels burning freely in air have B values in the neighborhood of 5. Inserting this value in equation (4) yields:

$$\frac{v_\infty\left(\Delta H_{vap} + \int_{t_F}^{t_S} c_F\,dt\right)}{\Delta H_{comb}} \approx 0.003 \text{ cm/min} \tag{5}$$

The value on the right-hand side of this equation is of the same order of magnitude as the experimentally determined value of 0.0076 cm/min (equation (1)). In view of the roughness of the calculation, this is perhaps as much as may be expected.

It appears reasonable to draw the following conclusions:

(i) An application of the established theory of natural-convection burning, modified to take account of the transition to turbulence at large Grashof numbers, correctly predicts that the burning rate of liquid-fuel trays will be independent of tray diameter.

(ii) The use of heat-transfer data obtained in turbulent natural convection to supply the numerical constant in the burning-rate equation predicts burning rates of the same order of magnitude as the experimental rates.

(iii) A re-plot of the original experimental data in the terms suggested by equation (3) appears to be well worth while. Only if systematic deviations from that equation are exhibited should new mechanisms for the process be sought.
(iv) The burning rates predicted by equation (5) are about one half the experimental ones. It may be that the difference is caused by the radiative heat flux. However, a more precise estimate of the convection controlled burning rate is needed which does not rely on the crude extrapolation from laminar to turbulent conditions which is used here.

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Comments on "The Burning Rate of Liquid Fuels from Open Trays by Natural Convection" by D. B. Spalding

D. Burgess and J. Grumer

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We appreciate the ingenuity of Professor Spalding's analysis and agree that his convection theory predicts burning rates of the same order as those found experimentally. It seems to us that convection may be important in diffusion flames of slow-burning fuels such as methanol, in wind-driven flames, and in some kinds of decomposition flames.[1] However, with faster-burning diffusion flames such as those supported by liquid hydrocarbons, there are numerous reported observations that are at odds with Spalding's concept.

First it should be pointed out that flames above large liquid pools do not resemble the illustrations of reference 2 but conform to the flame shapes reported by Rasbash,[3] i.e., with a thick vapor zone interposed between luminous zone and liquid surface. The various fuel vapors differ considerably in their absorptions of flame radiation,[4] and the vapors immediately above the liquid are not necessarily very hot. For example, with hydrogen and butane fires we could not monitor the liquid level with a thermocouple; there is no sharp discontinuity of temperature at the interface.

The temperature profiles within the liquid are also informative. Some years ago, Khudiakov[5] assumed that heat is transferred only to the liquid surface, as by conduction or convection or by radiation to a strongly absorbing liquid, and postulated that the elevation of liquid temperature should be

$$\triangle T = (T_S - T_i)\exp(-c\rho vx/k) \qquad (1)$$

TABLE 1

COMPARISON OF EXPERIMENTAL BURNING RATES WITH VALUES PREDICTED FROM SPALDING EQUATIONS

	Predicted burning rates, cm/min			Experimental burning rates, cm/min		
Tray diameter, cm	10	30	∞	10	30	∞
Hexane	0.28	0.21	0.30	0.16	0.32	0.73
Butane	.34	.26	.36	—	.45	.79
Methane	.42	.32	.45	—	.38	.66
Benzene	.21	.16	.22	.21	.29	.60
UDMH	.21	.16	.22	—	.20	.38

where x is distance below the surface and other symbols are as defined by Spalding but referring to the liquid phase. With methanol, which strongly absorbs its own flame radiation, it is well to verify equation (1) experimentally, even in rather large pools.[6] With benzene, which is rather transparent to its own flame radiation,[4] temperatures within the liquid are everywhere higher than given by equation (1); the relatively flat temperature profile with benzene demands the storage of considerable heat in the liquid phase; in reference 4 we attempted to identify this heat storage with the inital "burn-in," i.e., slow-burning, period. The burn-in was almost absent with two fuels, UDMH and methanol, both of which absorb their own radiations almost completely within a 3-mm path length of liquid.

To accept Professor Spalding's analysis we must neglect what seems to us to be the sense of his equation (1),[7] that each of an assortment of fuels (we omit the uncertain data for liquid hydrogen) yields about the same burning rate constant of 0.0076 cm/min. By his equation (4), the rate constant should range from 0.0027 cm/min for benzene to 0.008 cm/min for methanol, a threefold variation. One also loses the trend of experimental burning rates with pool diameter as shown by Table 1; to obtain the values listed we used his equation (2)[7] for the small diameters and his equation (4)[7] for infinite diameter.

In the specific case of methanol, convective transfer seems altogether reasonable, and the trend of experimental burning rates is almost duplicated by equation (2) at small diameters, as shown by Table 2. We have assumed laminar rather than turbulent vapor flow at all pool diameters since the vapor column at the largest diameter was surmounted by a luminous zone comprised of beautiful large cells; the flame fluctuations were exceedingly regular at 70–72 cycles per minute. We are also skeptical of the importance of turbulence in the vapor flow above hydrocarbon pools. With butane and hexane the flame tips were rumpled and luminous and fluctuating, but these were located some distance downstream

TABLE 2

BURNING RATES OF METHANOL AS FUNCTION OF POOL DIAMETER

Pool diameter, cm	2.6	7.6	14.8	30.5	61.0	122.0
v, experimental, cm/min	.13	.090	.082	.095	.11	.13
v, convective contribution, cm/min	.17	.13	.11	.091	.076	.064

from the liquid surface. The sides of the flames in proximity to the fuel surface were smooth, transparent, and remarkably steady. All of our observations, of course, refer to nearly windless conditions.

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