Fire Research Abstracts and Reviews, 1958-1959

ISBN
978-0-309-30900-4

294 pages
6 x 9
1958

Committee on Fire Research and the Fire Research Conference of the National Academy of Sciences; National Research Council

Volume I September 1958 Number 1

Fire Research Abstracts and Reviews

Committee on Fire Research
and
Fire Research Conference

Division of Engineering and Industrial Research
NATIONAL ACADEMY OF SCIENCES—NATIONAL RESEARCH COUNCIL
Washington, D. C.

FIRE RESEARCH ABSTRACTS AND REVIEWS is published three times a year by the Committee on Fire Research and the Fire Research Conference of the National Academy of Sciences—National Research Council, 2101 Constitution Avenue, Washington 25, D. C. It is supported by the Office of Civil and Defense Mobilization, the U. S. Department of Agriculture through the Forest Service, and the Department of Defense under Contract CD-SR-58-45. The opinions expressed by contributors are their own and are not necessarily those of the Committee on Fire Research and the Fire Research Conference.

Fire research abstracts and reviews. v. 1–
Sept. 1958–
Washington, Division of Engineering and Industrial Research, National Academy of Sciences, National Research Council.

v. 26 cm.

Issued by the Committee on Fire Research and the Fire Research Conference.

1. Fire extinction—Abstracts. 2. Fire prevention—Abstracts. 3. Combustion—Abstracts. I. National Research Council. Committee on Fire Research. II. National Research Council. Fire Research Conference.

TH9111.F77　　614.84082　　58–60075

Library of Congress

Errata - Volume I Number 1

page 15 line 1 for HH_2 read H_2
line 6 for vertical read horizontal
line 12 for -25 read $\angle 25$

page 16 line 4 from bottom of page
delete entire line
insert - the fire, the flames moved upwards against the spray. With a spray of high entrained

page 24 equation 14 for fr read f_r
line 5 from bottom of page for 0.23° read 0.23

page 25 equation 32 for C_i read C_t

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FOREWORD

This publication will bring together the widely scattered scientific studies out of which will develop a better understanding of the many factors involved in fires. Its aim is to stimulate new investigations by presenting, through abstracts and reviews, the state of the art from which further advances will result.

Fires are considered to be special cases of combustion where the addition of fuel and oxidizer to a flame is not under human control. In their grandest and most fearsome form, fire storms become natural disasters. Yet, little is known about their origin, their propagation, or their ending. The less destructive but more numerous conflagrations that destroy forests, factories, or homes pose equally profound questions to the thoughtful investigator.

While progress in fire prevention based on public education and fire-fighting organization has undoubtedly been considerable, the understanding of the basic causes and relationships in fires has lagged. Compared to the large and impressive research and development effort in the field of combustion that is inspired by its application to engines and heating devices, research in the area of natural fires is relatively small and neglected. This is perhaps understandable since the events are not only unplanned and unexpected but also present numerous complications in view of the complex situations in which fires occur.

Despite these difficulties, it is now realized that the serious challenge can only be met by marshalling a greater effort of probing into the basic relationships. Without this, the other attacks on this ancient problem will be without the powerful assistance of deeper understanding. In furtherance of this, a concerted effort is under way in the United States to formulate a stimulating fire research program addressed toward the broad problem of the nature of fires and their control. It is hoped, in this effort to encourage work both in theory and experiment that will shed new light and aid in the struggle against this scourge.

Walter G. Berl

A PROPOSED FIRE RESEARCH PROGRAM

by

The Committee on Fire Research

Introduction

The magnitude of present civil losses from large fires and the potential fire destruction consequent on nuclear bomb attack need no emphasis. The explosive growth of science and engineering has multiplied our fundamental scientific knowledge, the complexity of our material goods and services, and the hazards from fire; growth in our knowledge of how to cope with fire has not kept pace with these other growths.

The Committee on Fire Research of the National Academy of Sciences—National Research Council has studied the present status of fire-fighting techniques and strategies, and believes that our only hope for being able ultimately to cope with large fires lies in a major expansion of our fundamental research on fires. The large volume of research on combustion properties of building and other materials, on fire-fighting equipment, and on fire prevention has produced significant advances in fire control. But such studies have left untouched several of the fundamental factors associated in a controlling way with the city conflagration or the forest fire. To point out how these deficiencies may be remedied, the Committee on Fire Research recommends a national program emphasizing those areas not already adequately covered by current efforts of military and civil agencies.

The solution of most problems involving the laws of nature may in general be made in one of two ways. The empirical approach is to try one idea after another to see which works best. Many of man's problems have been solved satisfactorily this way—sometimes quickly, and often without much understanding. The scientific approach is to build up knowledge of the problem from fundamentals, describing the situation so adequately in terms of the fundamental laws—for example, in fire problems, the laws of thermodynamics, fluid mechanics, and chemical kinetics—that the complete description of the problem itself leads to its solution. The method often seems very slow, but no other would have yielded some of the results to its credit. The scientific method lags the empirical one today in fire research. But there have been phenomenal advances in fluid mechanics in the last two decades and equally impressive growth in fundamental combustion studies stimulated by the interest in high-output power plants for propulsion devices. These provide the research worker with the necessary tools for a more scientific approach to the fire problems, and now offer the promise of good progress in describing fire—and then of controlling it.

The Need for Research on Fire Persistence and Spread

At the present time it is impossible to predict the course a fire would take if a match were dropped into a pile of dry leaves in the middle of a brush area. While many factors like wind, humidity, type and condition of fuel, topography, etc., have been recognized as important, no quantitative estimates can be made of such effects as, for example, the height to which the flames will rise, the magnitude and direction of local fire-induced wind velocity, the radiative energy loss and its effect on the rising convection column and the drying and gasification of the fuel.

Until a quantitative prediction of the persistence and spread of a fire under given conditions is possible, we cannot pretend to understand the process of fire-front propagation in a sufficiently exact way to provide much assistance in directing our efforts to extinguish it. So long as we understand fire behavior only qualitatively, our extinguishment efforts must be based wholly on experience and cannot profit by the large increase of scientific knowledge of the past few decades.

To make clear the parameters of physics, chemistry, and environment which the Committee on Fire Research believes are of fundamental importance in fire persistence and spread and are capable of rapid scientific development at the present time, consider the following qualitative description of the fire-spread phenomena:

> A forest fire has burned for some hours. There is a growing perimeter of active combustion. Flames and smoke cover the luminous solid remains of grass, brush, and trees. Radiation from the luminous flames heats the fuel in and ahead of the fire front. The amount of heat thus received, together with convected heat by the rising convection column, gasifies additional fuel. The non-uniform fuel distribution and details of the topography cause convection columns and flames which are here violent, there gentle. By interaction with the general wind, these irregular columns help produce eddies, small whirlpools of gases and firebrands which help propagate the fire front. The rising convection column alters the local wind pattern and thus alters the manner in which air is brought into the fire for its maintenance and the manner in which hot gases and brands are moved for its spread.

Developments in the sciences of aerodynamics, heat transfer, and applied mathematics aided by experimental techniques and large-scale computing machines, make timely (and the Committee believes fruitful) a quantitative scientific treatment of all of the phenomena suggested by the above qualitative description.

Quite independent of the need for an organized attack on the problem of understanding the physics of fire spread and its prevention is the need for optimum use of accumulated experience with fires as encountered in cities and forests. This is the function of *Operations Research.*

This new method for coping with large-scale complex operations involving men and natural phenomena was developed during and subsequent to World War II. Operations research has had extraordinary success in application to some highly complex problems of military tactics, business and industrial operations. The method uses data from actual operational experience and deduces quantitative relationships which become available for use in a mathematical model of the over-all operation. The mathematical model then becomes capable of predicting effects of changes in tactics. It is to be noted that, in contrast to the physical fire model described previously, a useful mathematical model can be set up without actually understanding the physical mechanisms involved in fire; but the validity of the conclusions is dependent on the availability of a sufficient mass of good data on past experience with fire fighting. The use in addition of data from the physical fire-model studies will improve the validity of the mathematical model. In a very real sense, then, the two kinds of models are complementary.

Fundamental Research Problems

Fire research is distinguished from *combustion research* in that it applies to situations in which the rate of production of heat controls the rate at which fuel becomes available to the fire and is consumed, whereas in ordinary combustion the fuel rate is held constant or varied in an independent manner. Fire research, therefore, emphasizes many fundamental aspects of physical sciences which have been neglected in combustion work. These are primarily aerodynamic phenomena associated with heat release at atmospheric pressure; for example, convection currents and induced turbulence, and ignition and pyrolysis phenomena, in which elucidation of the mechanism of energy transport is of primary importance. Finally, fire research is concerned in a major way with the basic factors involved in inhibition of fire propagation.

In the following paragraphs, the areas in which basic studies would contribute most significantly to understanding of fires are elaborated.

A. The convection of air and hot gases associated with a liberation of heat has two aspects: the general rising air currents and the local gas movements in and near the heat source. The general motions are gravity currents modified by interaction with winds, topography, density gradients, and turbulence. The local motions are driven by the general motion but are modified by gravity and gas expansion associated with combustion. The quantitative and in most cases even the qualitative features of these convection currents and their interaction with the burning processes are unknown.

B. Inadequate information is available on gas and flame emissivities as a function of frequency at high temperatures. Mathematical techniques also must be developed for prediction of the radiation emitted by distributed sources and transmitted through absorbing gases. These data and techniques are necessary in order quantitatively to determine the radiant heat transfer which has a large influence on the rate at which fuel becomes available to the fire.

C. Many fundamental questions are raised by the addition of suppressants to fires. The thermochemistry of suppressants in solid matter combustion has up to now been only superficially examined. Cooling, smothering, and direct chemical kinetic action (particularly in the case of water suppressant) should be critically examined in order to define and understand their actual roles; the ways in which the fundamental physical and chemical phenomena of fires are altered.

D. Fundamental information on the aerodynamic properties of burning bodies in motion is needed. Available scanty information indicates that burning decreases drag. The magnitude of this effect and its connection with the aerodynamic pickup and transport of embers is unknown.

E. The mechanism and thermochemistry of pyrolysis and oxidation of solid combustibles should be studied. The process involves heat and mass transfer coupled with endothermic and exothermic reactions within the solid phase. Gas evolution and transport away from the surface, and heat transfer to the surface from the burning gases, are also involved.

F. The model laws for aerothermodynamic systems in which the fuel consumption rate is dependent on and is controlled by the heat evolution rate should be determined. This is a large and important field, essential for an understanding of fire phenomena. Parameters to be studied include effects of geometry, fuel type, radiation, and heating rates. Types of fire-front propagation should also be studied, e.g., continuous flame fronts or discontinuous sources of ignition distributed by aerodynamic forces.

G. Fundamental studies of sprays should be extended to yield further quantitative data on the behavior in environments typical of fire situations. Studies should include evaporation rates, distribution of droplet sizes, jet characteristics, entrained air. Also included are the factors influencing stability and effects of sprays on aerodynamic and physical properties of the medium into which the spray is injected.

OUTLINE OF PROPOSED FIRE RESEARCH PROGRAM

In this outline that portion of the program directed toward understanding the physics and chemistry of fire and fire spread has been divided into two categories, *Laboratory Studies* and *Field Studies*. Each of these must be accompanied by theoretical studies to give guidance and meaning to the experimental work. The third section covers *Operations Research* and the fourth section deals with *Ad Hoc Developments*.

I. Laboratory Studies

A. Ignition and Combustion Properties of Fuels

1. Gas evolution from heated solids—rate as affected by mode and rate of heat application. Inflammability limits of evolved gases
2. Effect of fuel geometry on ignition and early stage combustion characteristics of fuels
3. Rating of various fuel types, solid or liquid, by ignition temperature, heating cycle to produce ignition, energy absorption to ignition
4. Effects of fuel- and air-moisture
5. Heat and material transport and reaction phenomena inside the surface of heated combustibles
6. Convection *vs.* radiation as an ignition means
7. Gas-phase reaction kinetics in relation to flame suppression

B. Model Studies for Quantitative Prediction of Convection

1. Using flameless heat source
   - a-e) Effects of wind, topography, lapse rate, energy liberation rate and its distribution in space
2. Using fire as the heat source
   - a-e) Study of effects under B1 above
   - f) Convection pattern in and near the fire

C. Model Studies of the Factors Determining Radiation

1. Effect of fuel type, condition, and geometry on total emission rate and its spatial distribution
2. Evaluation of view-factors (factors permitting estimation of radiation received by surfaces) of gaseous emitters as seen by fuel in various orientations, and of surface-to-surface view-factors

D. Determination of the Model Laws for Fire Development and Spread

1. Measurements to be made include such items as
   - a) Fuel-system properties and air properties (including temperature, wind velocity, humidity, lapse rate)
   - b) Total rate of energy release *vs.* time
   - c) Space-distribution of energy release rate
   - d) Temperature, convection and radiation pattern around fire
2. Problems to be studied
   - a) Mechanism of fire development and fire-front propagation
     - (1) Interaction of fuel properties, fuel-bed geometry, convection, and radiation
     - (2) Propagation by firebrands
       - (a) Classification of firebrand types from urban and forest fires (by heating value, burning rate, contact area, etc.)
       - (b) Flight characteristics of firebrands in relation to natural and convection winds

    - b) Delineation of range of importance of various model groups (identification of the many factors of micro- and macro-environment and their expression in quantitative form)
    - c) Testing of scaling laws by comparison of model and field results

E. Development of Quantitative Fire-fighting Relationships

1. The use of water on reproducible fires
    - a) Effects of rate, distribution, degree of dispersion
    - b) Determination of minimum water requirements for control under model conditions
    - c) Consideration of possible need for modifying water properties, especially surface tension, for model use
2. The modification of water as a fire-fighting agent
3. The use of other extinguishing agents
4. Fuel geometry changes to stop fire—before and during involvement
5. Modeling backfires—assessment of merits of different backfiring techniques
6. Testing of effectiveness of miscellaneous procedures

F. Developmental Program on Instruments for Laboratory and Field Use

(See, e.g., II A2)

II. Field Studies

A. On Naturally Occurring Fires

1. Types
    - a) Forest fires
    - b) Building fires
    - c) Other—lumber, oil, storage, etc.
2. Measurements on forest fires
    - a) Rate of area involvement
        - (1) By advancing flame front. Such measurements as
            - (a) Expendable radio broadcasters placed in depth along fire front, with tape-recording reception
            - (b) Ground photo studies of local effects
            - (c) Time-lapse photography from the air
        - (2) By spotting. Measurements generally by reliance on visual or photographic evidence, plus some data from instruments used in A2a) (1) (a)
    - b) Vertical involvement. Rate of area involvement at various elevations. Measurements as under A1, at
        - (1) Ground
        - (2) Surface
        - (3) Crown
    - c) Fuel amounts and conditions in the fire area
        - (1) Before fire
            - (a) Qualitative identifying description
            - (b) Distribution curve of surface per unit mass *vs.* cumulative fractional mass
            - (c) Variation of above distribution with height above mineral soil
            - (d) Moisture content
        - (2) After fire—appropriate portions of above
        - (3) Rate of conversion from (1) to (2) at different times, for different fuel components. Rate obtained by timing each at selected intervals by actual on-ground observations

d) Ambient atmosphere at all significant elevations
    (1) Wind speed and direction
    (2) Turbulence
    (3) Vertical motion
    (4) Temperature
        (a) Lapse rate
        (b) Dew point temperatures
    (5) Air moisture
    (6) Cloud activity
e) Topography of fire area, obtained from maps
f) Fire convection column
    (1) Measurements to be made
        (a) Speed
        (b) Height
        (c) Direction
        (d) Turbulence
        (e) Shape of column
        (f) Indraft pattern
        (g) Other phenomena—whirlwind, explosion, flash-over, etc.
    (2) Possible methods of measurement
        (a) Time-lapse photography from fixed points on ground several miles from fire
        (b) Time-lapse photography from aircraft
        (c) Use of artificial vertical smoke trails to mark indraft and other air movement

(Measurements of these convection properties possibly by time-lapse photography, supplemented by close-up visual and photographic on-ground observations. Time-lapse motion picture photography provides an excellent continuous record of convection column behavior. Provision should be made for keying the film to a time scale. Film should be exposed from one or more fixed points several miles from the fire, and cameras should be capable of wide angle to telephoto operation. Pocket-size wire recorders are available for use in recording running account.)

g) Micro-weather around fire perimeter
    (1) Air and fuel temperatures
    (2) Surface air speed and direction
    (3) Radiation intensity along fire front (4 π pickup)

(All these measurements would profit by development of expendable transmitters)

h) Control status
    (1) Portions of fire perimeter limited by control lines
    (2) Backfires
    (3) Water or chemical applications

(Control operations will be progressing during the period of investigation in most instances. Continuous record of control work influencing the observed fire behavior is necessary in order to evaluate properly the observations. The fire control organization can provide some of the information currently, but must be supplemented by on-ground observations by a study task force.)

3. Measurements on other fires—generally parallel to those on forest fires, with some obvious modifications

4. Objectives
    a) Formulation of conclusions which can affect present fire-fighting practice, equipment, and preventive measures
    b) Providing of an adequate quantitative description for use in planning model experiments. Determination of range of model-law parameters
    c) Use of results for comparison with prediction from a simplified mathematical model; and determination of numerical values of coefficients appearing in the model

B. On Planned Fires

1. Types
    a) Crib fires
    b) Area fires using naturally occurring fuels—forest, brush, cane, grass, etc.
    c) Area fires using multiple fabricated fuel units—packing cases, cribs, pans of oil, gas jets, etc.
    d) Structure fires—including available abandoned buildings

2. Measurements (in general, similar to A2 with possibility of more adequate instrumentation)

3. Objectives
    a) Formulation of conclusions which can affect present fire-fighting practice, equipment, and preventive measures
    b) Providing of an adequate quantitative description for use in planning model experiments. Determination of range of model-law parameters
    c) Use of results for comparison with prediction from a simplified mathematical model and determination of numerical values of coefficients appearing in the model
    d) Testing validity of developed model laws based on laboratory studies, including the modeling of firefighting
    e) Inclusion of factors difficult or impossible to simulate properly on a laboratory scale, such as lapse rate and radiation

III. Operations Research *

A. Operations Analysis. Rational planning of a fire control system requires recognition of and action on the following generalizations:

1. A fire control system should be planned to meet a clearly formulated protection objective

2. Preventing fires and putting out fires are the functions of fire control and should be balanced for maximum benefits

3. Putting out fires requires facilities and activities

4. The principal activities include measures undertaken before fires to make them manageable, to find out where and when fire does occur, and to put into effect measures to extinguish or limit the spread of fire

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* This heading presents an unavoidable problem in semantics. "Operations Analysis" and "Operations Research" are terms widely used to refer to statistical studies of past patterns of action to establish the best one; it will be called "Operations Analysis" here, Section A. In addition, there is need for experimental field studies of competitive approaches to fire control. This is Section B.

Each of these and its sub-parts presents a host of problems concerned with the selection of alternatives the best choice of which depends on decisions best made by application of operations analysis. Examples of these problems follow.

5. Urban fire control problems
    a) Evaluation of a municipal fire control system through construction, on a computer, of the simulation of a fire and its response to the measures put into operation to deal with it
    b) Optimum distribution of funds and effort between prevention measures and preparedness for fire fighting for a variety of conditions. Prevention studies would include, for example, an examination to determine the optimum interval between fire-prevention inspection of buildings; preparedness studies would include placement of fire companies, effect of running distance for fire companies, and traffic conditions on the amount of destruction which occurs before fire-fighting measures can be effective

6. Forest fire control problems
    a) The evaluation of a forest fire control system through the simulation on a computer of a forest fire—its growth, the attack, and the decay of the fire
    b) Evaluation and merits of different tactics including manpower distribution, equipment available, use of backfiring, evaluation of limits
    c) Optimum fire crew spacing
    d) Value of proposed new access roads (probably keyed to progress under a) above)
    e) Optimum standards and frequency of firebreaks
    f) Optimum distribution of funds and effort between prevention measures and preparedness for fire fighting, for a variety of conditions

7. Systematizing of fire reporting—the need for a common basis of reporting by fire departments in different cities. Possible desirability of central collecting agency

B. Experimental Field Research on Operations

Comparative studies of relative effectiveness of different fire-fighting techniques, strategies, tactics, and equipment

IV. Ad Hoc Developments

The existence and importance of a large amount of effort on fire control of a character dependent to a very minor degree on an understanding of the fundamentals of fire growth is recognized. Because the deficiency of effort here is so markedly less than in those fields more dependent on the scientific approach, this category will not be elaborated here. It is realized, however, that ideas may sometimes be presented which hold sufficient promise of quick development without research on fundamentals as to justify support of direct developmental effort.

ABSTRACTS

I. Ignition Phenomena

Fons, W. L. (California Forest and Range Experiment Station, Berkeley, California) "Heating and Ignition of Small Wood Cylinders," *Industrial and Engineering Chemistry*, **42**, 2130–2133 (1950)

Studies of forest fire control require information about ignition time and temperature under conditions of rapid heating. Ponderosa pine cylinders $5\frac{1}{8}$ in. long, in six size classes from $\frac{3}{32}$- to $\frac{3}{8}$-in. diameter within ±0.003 in., uniform in density and structure, were sandpapered to remove rough spots and preconditioned to desired moisture content, usually 1.5 per cent. Extra contemporaneous specimens were analyzed for moisture by xylene reflux distillation.

By a mechanical device and one at a time, specimen at desired initial temperature were inserted within a small fraction of a second in an electric furnace held within 3°F. of the required temperature. Strip chart recorders were automatically started by insertion of the specimen and stopped at the moment of ignition when light from the flames impinged on a photoelectric cell placed outside an opening in the furnace wall. Charted record was made of ignition time and, when desired, of the temperature at a thermocouple within the specimen.

From 30 to 40 specimens of one size and condition constituted a run. The coefficient of variation was 6–9 per cent, being nearer the lower limit for the smaller specimens.

Ignition time increased with moisture content. For $\frac{1}{4}$-in. specimens exposed to 1150°F., the average time was 6.83, 7.21, 8.90, 10.51, and 15.47 secs. at 2.2, 3.6, 7.8, 11.3, and 19.3 per cent moisture, respectively. The increase exceeded that attributable to increased specific heat due to moisture. Perhaps pyrolytic gases cannot attain their lower flammability limit in air until the moisture has been dissipated.

Between 50° and 150°F. the initial temperature of the specimens did not affect the ignition temperature.

At 1300°F. furnace temperature, specimens of all sizes ignited in 3 secs. At lower temperatures, the larger the specimen the longer the ignition time, according to a relation that indicated a maximum ignition time for specimens slightly larger than $\frac{3}{8}$ in. At 865°F. with $\frac{1}{8}$-in. specimens the ignition time was 27 secs.; at 830°F. with $\frac{3}{8}$ in. specimens the ignition time was 90 secs. Below those temperatures the wood was reduced to charcoal without flame, but the charcoal soon began to glow at temperatures down to 450°F.

To determine the surface ignition temperature, 17 specimens of $\frac{3}{8}$-in. diameter were made with a No. 30 Chromel-Alumel thermocouple embedded $\frac{3}{32}$ in. from the center and at the midpoint of the specimen, and 17 specimens with the thermocouple $\frac{1}{8}$ in. from the center. They were made by drilling $\frac{3}{16}$- and $\frac{1}{4}$-in. holes, respectively, in one end of the specimens to a distance of 3 in. and then plugging the holes with snugly fitting cylinders with the thermocouples looped over the ends of the plugs. With the furnace at 1150°F., the temperature $\frac{3}{32}$ in. from the center was 129°F. and $\frac{1}{8}$ in. from the center 210°F. at the moment of ignition. With these data and a simplified equation for thermal conduction as developed by Boelter, Cherry, and Johnson ("Heat Transfer Notes", 2nd ed., chap. v, pp. 13-15, Univ. of Cal. Syllabus Ser. 1942) the surface ignition temperature was found to be 650°F., which is somewhat higher than reported for wood by other investigators.

The results provide information for predicting critical sectors where forest fires will spread rapidly on a fire perimeter. Normally fire spreads rapidly through the finer fuel and only singes larger fuel. But under conditions of high wind, steep slopes, and loosely arranged fuel, heating at the fire front may reach the equivalent of 1300°F. furnace temperature, after which size of material no longer governs the rate of spread. In studies of fire spread, particular attention must be paid to the character of the flame front.

Subject Headings: ***Heating of wood cylinders; Ignition of wood cylinders; Wood cylinders, heating and ignition.***

Frederick L. Browne

II. Thermal Decomposition

Wright, R. H. and Hayward, A. M. (Division of Chemistry, British Columbia Research Council, Vancouver, B. C.) "Kinetics of the Thermal Decomposition of Wood," *Canadian Journal of Technology*, **29**, 503–510 (1951)

As part of a series of experiments performed to study possible methods of producing fuel gas from waste wood, the work recounted in this paper concerns itself with the thermal decomposition of western red cedar and western hemlock woods. The wood was cut into cubes ranging in size from 3 to 19 mm. edge; and was dried in an oven at 105°C. for 24 hrs. or more before being used. Sample weights varied between 1.5 and 3.3 gms. An arbitrary number of the wood cubes was dropped into a retort furnace heated to a predetermined temperature by external resistance elements. The furnace was flushed with bottled nitrogen before each experiment. Automatic temperature regulation enabled the experimenters to focus their attention on the pressure increases due to gas liberated from the cubes. Pressure changes (as indicated by a diaphragm manometer) were recorded by an oscillograph. From these pressure-time traces useful data were deduced. Results were obtained at furnace temperatures of 500°, 700°, and 900°C.

The data of these experiments were treated primarily with the use of a calibration curve constructed by comparing deflections on the oscillograph traces with actual readings from a mercury manometer. Deflections at various times were read to $\frac{1}{10}$ mm. from the oscillograph traces. All pressures (at the various times) were expressed as percentages of the final pressure, *i.e.*, $P/P_f \times 100$. Then a useful parameter, $100 (1 - P/P_f)$, which represented the percentage of undecomposed wood was calculated. The square root of this expression plotted against time fortunately turned out to be a fairly decent straight line. The authors conclude from this that the decomposition of wood cubes is kinetically of order $\frac{1}{2}$. An equation with the form of a straight line whose slope yielded a rate constant was deduced.

A look was taken at the variation of the rate constant with cube size. The constant varied inversely as cube length, but there was a difference in slope of the curves for cedar and hemlock at the same temperature. This difference in the curves was due to the difference in the densities of the two woods. After incorporating the density in a plot of the rate constant against the reciprocal of cube edge length, a single set of equations could be set up which applied to both cedar and hemlock. Two equations are given and are said to enable one to calculate decomposition times for any wood cubes at any temperature covered by experimental data. Good agreement is obtained between computed curves and the experimental data for hemlock using the derived equations to obtain a rate constant. The initial portion of the curves (pressure *vs.* time) appeared to show a slight drop in pressure and then a finite time was required before the reaction really got under way. The authors point out that the cold wood cubes cool the gas in the furnace and thereby initially produce a decrease in pressure. Similar behavior has been observed in spontaneous ignition temperature studies where cold liquid is introduced into a hot chamber. The retardation of the decomposition reaction was estimated to be about 15 to 20 per cent of the total reaction time. The latter was confirmed using an experiment with sawdust.

The discussion of the authors involves hypothesizing two mechanisms by which the thermal decomposition of wood is accomplished. In the first case, wood is considered as a perfect isotrope where the rate of decomposition could conceivably be determined by the rate of propagation of the reaction. Here the decomposition zone is thin and travels inward from the surface. At any given instant (in the case of cubes), the area of the reaction zone would be proportional to the $2/3$ power of the amount of undecomposed wood. This reaction would be of $2/3$ order kinetically. In the second case, wood is assumed to be extremely anisotropic so that the reaction is propagated at a much faster rate parallel to one axis; in that case the area of the reaction zone remains constant and the reaction order is zero.

The kinetic order found experimentally falls between the two extreme postulates. A test of this hypothesis was carried out using very small cedar disks at 600°C. The decomposition rate for disks cut across the grain was nearly twice that for those cut along the grain. A better straight line was obtained when the amount of undecomposed wood was plotted *vs.* time, than when the same parameter to the $1/2$ power was plotted. The latter indicated a kinetic order of zero for disks. The faster reaction occurred with the disks cut across the grain as was shown quite clearly in the figure.

The authors conclude that the reaction takes place in a zone which advances inward from the surface. For a given particle size, the reaction rate was essentially the same for both cedar and hemlock woods used in the experiments. The over-all rate of the decomposition reaction is, therefore, largely determined by a physical factor rather than chemical composition. This might have been expected since most rate constants in combustion reactions of any sort are closely connected with transport phenomena. In fact, the writers choose as the most probable controlling factor the rate of heat transfer from the reaction zone to the undecomposed portion of the wood piece.

Subject Headings: ***Wood, kinetics of thermal decomposition; Thermal decomposition of wood.***

Cleveland O'Neal, Jr.

IV. Diffusion Flames

Rasbash, D. J., Rogowski, Z. W., and Stark, G. W. V. (Joint Fire Research Organization, Boreham Woods, England) "Properties of Fires of Liquids," *Fuel*, 35, 94–107 (1956)

This paper is concerned with the growth and development of the flame from the moment of ignition up to the establishment of the steady state since it had been shown in a previous paper* that the ease of extinction was partly dependent on the length of time that the fire had been alight. This earlier paper ("Extinction of Liquid Fires with Water Sprays") should be read in conjunction with the one under review since it is more concerned with the practical significance and application of the results reviewed here.

The flame properties of four liquids were examined; the liquids being, in order of volatility: alcohol, benzol, petrol, and kerosene. The experimental system was a cylindrical bath 30 in. diameter and 12.5 in. deep, made of sheet brass, with various attachments leading into the bath to supply the fuel, to maintain the liquid level 2 cm.

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* See page 18

below the top of the vessel, and to measure the liquid temperature at different depths. The flames were photographed in profile with a cinecamera so that measurements could be made of the flame shape, volume and upward velocity of the rising incandescent gases. Other measurements included rate of burning, flame temperature by the two-color method using a disappearing filament pyrometer, and flame temperature by the Schmidt method so that emissivity could also be calculated.

The results are concerned more with flame mechanism than with extinction mechanism. They are one step removed from direct application to flame suppression, but they should be valuable for interpreting extinction results. The chief result was that the relative importance of heat transfer by radiation and by convection/conduction varied with the type of fuel. For the alcohol fire, conduction predominated; but for the other three fuels, radiation was more important. This can be explained by the findings on emissivity which, for approximately similar flame widths, had values: alcohol, 0.066; petrol, 0.36; kerosene, 0.37; and benzol 0.6 to 0.7. Although the authors did not relate these values to the carbon percentage or C/H ratio of the fuels the reader may be aware that such correlations have been found in furnace measurements (e.g., Holliday & Thring *J. Inst. Fuel* March, 1957). Emissivity may also account for the characteristic flame shape finally attained by the flame of each fuel when the steady state had been established. The development of shape with time was qualitatively similar for all four fuels, but for each fuel the shape was arrested at different stages of the development. The authors represented stages in the development by five characteristic shapes, and the flames were arrested as follows: alcohol, stage 1; kerosene and petrol, stage 3; benzol, stage 5. The main part of each flame was a roughly cylindrical column with a diameter smaller than that of the vessel and with the base of the column characteristically shaped. Initially the curved base of the flame column touched the surface over an appreciable area (stage 1), then, as each flame developed, the base rose from the liquid surface leaving a vapor layer between the two. The alcohol flames were arrested in the first stage with the flame column sitting on the liquid. With the kerosene and petrol flames, the base of the column finally attained an inverted saucer shape with a vapor layer 3–5 cm. thick. The benzol flame developed even further. The thickness of vapor layer and general behaviour seem to be directly related to emissivity.

All values of burning rate, flame volume, velocity of the rising flame, and liquid temperature increased with time. Rate of burning and flame volume appear to be closely related, which is reasonable. Benzol had the greatest burning rate, flame volume, and rate of increase of both quantities; followed by petrol, and then by kerosene and alcohol about the same. This may suggest to the reader that rate of burning is influenced by volatility as well as by emissivity.

Radiation heat transfer also affected the temperature profiles in the liquid; excluding the alcohol, the depth of radiation penetration flattened the temperature profile near the liquid surface, caused the surface to bubble, and in the benzol set up convection currents so that at 1 and 3 mm. below the surface the temperature was the same. Samples of the hydrocarbon fuels taken towards the end of a run 0.5 mm. below the surface showed that with kerosene and petrol there was some preferential evaporation since the samples of these two liquids were significantly less volatile than the original liquid. This is likely to affect ease of extinction.

In their practical significance, the reader may conclude that the results indicate that the ease of extinction of a flame and type of spray required depend mainly on: (1) the emissivity (or C/H ratio) of the fuel, (2) the volatility of the fuel, and (3) the length of time it has been burning.

Subject Headings: ***Fires of liquids.***

R. H. Essenhigh

V. Combustion Principles

Burgoyne, J. (Imperial College, London) "Mist and Spray Explosions," *Chemical Engineering Progress*, **53**, 121–124 (1957)

The flammability limits for condensed mists, in which the drop diameters are mostly less than 10 microns, are approximately equal to those for the corresponding vapors, since vaporization is essentially complete prior to contact with the flame. Similarly, the requisite addition of inert gas for suppression of flammability and the burning velocity are likewise equal to those for the corresponding vapors. It is found that there is little variation in either the concentration (in weight of fuel per unit volume of air) of various hydrocarbons at the lower limit or the extinguishing additions of inert gas. For the case of a condensed mist formed from the saturated vapor of a liquid hydrocarbon of high boiling point, however, prolonged contact with a heat source may result in thermal cracking, so that the products of decomposition may tend to reduce the lower limit of flammability, raise the necessary amount of inert additive for flame suppression, and increase the burning velocity. Upper flammability limits for uniform mists appear to agree well with those for the corresponding vapors.

Although lower limit concentrations increase with the average diameter of a mist or spray, it is found that the product of volume concentration and flame front velocity relative to the falling drops remains essentially constant. The requisite addition of inert gas for flame suppression was found to increase with drop size although some investigators reported a subsequent decrease for drops larger than 200 microns. Burning velocity appears to increase with drop size, probably because of the corresponding growth of reaction zone thickness.

Explosion pressures for fuel mists in a closed vessel were somewhat lower than those for the corresponding vapors, although the rate of pressure rise for mists was appreciably higher than that of the vapor. Hence mist explosions are potentially more difficult to relieve than those of the corresponding vapor. No information on the closed vessel explosion of sprays was available.

Subject Headings: *Mist explosions; Spray explosions; Explosions of mists and sprays.*

C. C. Miesse

Hartmann, I. (U. S. Bureau of Mines) "Dust Explosions," *Chemical Engineering Progress*, **53**, 107–111 (1957)

Present investigations of dust explosions at the U. S. Bureau of Mines are grouped into three phases:

1) Laboratory evaluation of the explosive characteristics of all types of combustible dusts and powders, and studies conducted on various parameters that affect explosibility. Special studies have been made on the effect of admixtures of inert dusts with the combustible, effect of particle size, effect of moisture, effect of elevated initial pressure, effect of oxygen-enriched atmospheres, and effect of nature of ignition source on explosibility.
2) Basic research on the mechanism of ignition of dust particles and the propagation of combustion waves through dust clouds. Use is made of stationary laminar and turbulent dust-air flames of the Bunsen type, and those with flat flame fronts. Normal burning velocities of flames are measured as functions of dust concentration, oxygen partial pressure, and particle size; and the effects of radiation, turbulence, and oxygen diffusion are investigated with the aim of achieving a theoretical understanding of dust flames and explosions.

3) Investigations in partly open chambers of galleries, ranging in volume from 1 to 216 cu.ft., and in ducts on explosion venting, flame speeds, flame quenching, and related problems.

References to previous work at the Bureau are given.

Recent studies have concerned the effect of water on flame propagation in dusts, measurement of flame velocities in dust explosions, the confinement of explosion flames with wire screens, the quenching of incipient explosions and prevention of secondary explosions. Each of these topics is briefly discussed.

Some possible ways in which water can affect ignition and combustion in dust clouds are indicated. Laboratory experiments with coal dusts showed that moisture had little effect on flammability when present in amounts less than 5 per cent but had a pronounced palliative effect at higher moisture concentrations. The effect was greater the coarser the coal particles.

Flame velocities in ducts leading from galleries of various dust explosions were measured by photocell, ionization probe, and/or photographic techniques. The flame velocity increased almost linearly with distance along the duct. Terminal velocities between 600 and 1200 ft/sec were found for cork, cornstarch, cellulose acetate, sugar, coal, and wood flour. The velocity increased with dust concentration up to a maximum at a concentration which was above stoichiometric. The smaller the dust particles the greater the velocity. The effect of the duct geometry and venting of the duct and the gallery on flame velocity was also studied. Velocities were reduced several fold by proper venting. References giving explosion venting recommendations for specific situations are listed.

The effectiveness of wire mesh screens (14- by 18-mesh/in. bronze screens in one satisfactory arrangement) in confining the flame while providing an escape vent for explosions has been investigated and the results to date indicate that it is possible with the aid of screen devices to arrest flames of many industrial dust explosions within a short distance of their point of origin.

Quenching agents such as water, limestone, and salt were used to quench or to reduce the severity of incipient coal dust explosions. Quenching was successful when the time interval between ignition and dispersion of the quenching agent was 5-35 msec; partial control was achieved up to about 80 msec as evidenced by appreciable decreases in maximum recorded explosion pressure. With aluminum dusts complete control resulted only when water was dispersed simultaneously with the aluminum. Partial control was achieved in several tests when the time interval was 5 msec.

These same agents were found effective in preventing secondary explosions in a neighboring gallery when dispersed in a duct leading to the gallery of the primary explosion of various organic dusts. Providing vents in the connecting duct was also found effective in some cases. Aluminum dust explosions were controlled only with water.

Subject Headings: ***Dust explosions; Explosions of dusts.***

Claude P. Talley

Bouchet, R., Delbourgo, R., and Laffitte, P. "On the Extinction of Flames by Pulverized Substances," *Comptes Rendus*, **242**, 2152–2154 (1956).

Rockdust, chiefly consisting of $CaCO_3$, is widely used for quenching coal dust fires in mines.[1] $NaHCO_3$ is the main constituent of "dry chemical" fire extinguishers.[2] Flame extinguishing properties of salts have been extensively studied recently.[3]

Thomas and Hochwalt[4] injected sprays of aqueous solutions into oil fires, and found potassium hydrogen tartarate more efficient than other salts. Dufraisse and Co-workers [5] confirmed this for flames travelling through combustible gas mixtures in which pulverized salts are dispersed. They found the efficiency of different salts in HH_2-, CH_4-, CO-, air flames. Oxygen rich anions like NO_3- or ClO_3- are not much less efficient than Cl-, but organic anions like tartrates are by far superior, probably because these salts decompose at lower temperatures.

Laffitte and co-workers measured flame velocities photographically in methane- or propane-air mixtures, ignited at the open end of a vertical, 3 cm. diameter glass tube, 125 cm. long. Pulverized material deposited on a brass disc 90 cm. below the open end was dispersed by the compression wave ahead of accelerating or vibrating flames, e.g., a 5.4 per cent propane-air flame moving at 150 msec. The quantity required for extinction is found to decrease with decreasing particle size, except for silica and alumina. On diminishing the average particle diameter of fractions obtained by sieving from 100 to −25 microns the efficiencies of sodium and potassium salts become practically equal. Therefore, the authors question the previously claimed superiority of potassium over sodium salts.

Since in the reviewed work actual dust concentrations were not determined, further investigation is needed, such as initiated meanwhile by Dolan[3] and by McCamy, Shoub and Lee.[2] Regarding ion concentrations in flames the reader is referred to Gaydon and Wolfhard's book[6] and regarding chain-breaking mechanisms to that of Lewis and von Elbe.[7]

1. Hartmann, I. and Co-Workers *Bureau of Mines Report of Investigations 4688* (April 1950)
2. McCamy, C. S., Shoub, H., and Lee, T. G. *Sixth Symposium (International) on Combustion*, p. 795 (1957)
3. Dolan, J. E. Ibidem, p. 787
4. Thomas, C. A. and Hochwalt, C. A. *Industrial and Engineering Chemistry*, 20, 575 (1928)
5. Dufraisse, C. and Co-workers *Comptes Rendu*, 236, 164 (1953)
6. Gaydon, A. G. and Wolfhard, H. G. *Flames* (London), 281 (1953)
7. Lewis, B. and von Elbe, G. *Combustion, Flames and Explosions of Gases*, Academic Press, N. Y., p. 9 (1951)

Subject Headings: *Extinguishment by powders; Powders, flame extinguishment.*

Hans M. Cassel

VII. Suppression of Combustion

Rasbash, D. J., and Rogowski, Z. W. (Joint Fire Research Organization, Boreham Wood, England) "Extinction of Fires in Liquids by Cooling with Water Sprays," *Combustion and Flame*, **1**, 453–466 (1957)

Water sprays can be used to extinguish fires in burning liquids by a number of techniques. The most reliable methods are those which depend upon the reduction of evolution of vapor from the burning liquid to a value lower than that quantity which is required to sustain a flame. A particular method of extinction which falls into this category is the cooling of the burning liquid to the fire point. To extinguish a liquid fire by cooling, it is necessary that the flow rate of the coolant be above a certain critical value. At lower rates cooling occurs at a temperature which is higher than the fire point and is, therefore, ineffective.

From a practical point of view, it is important to predict the extinction time of a fire. This feature is particularly important when designing protective installations where rapid fire extinction is quite essential. Rasbash and Rogowski have conducted tests with water sprays on burning liquid fires. They show that, for sprays which extinguish fires by cooling the liquid, there is a correlation between the extinction time and the properties of the sprays and the fires. All of their experiments were conducted with the sprays projecting downward from fixed nozzles to a horizontal surface of the burning liquid.

Liquid fires on transformer oil, kerosene, and gas oil in circular open vessels having diameters ranging from 4.3 to 47.2 in. were utilized in the experiments. Sprays were produced by single nozzles of various types or by a battery of impinging jets. The single nozzles were employed in an investigation to determine the best type of spray for the protection of factories containing oils having high boiling temperatures such as those found in stations generating electricity. The other type of spray was produced from impinging jet nozzles and from swirl nozzles. Both directional and nondirectional sprays were utilized. The nozzles were located at heights above the burning surfaces ranging from 69 to 180 in. Mean flow rates of spray to the combustion vessels were varied from 0.06 to 1.2 gal/sq ft/min. Mass median drop sizes of the spray were altered from 0.012 to 0.12 in. Nozzle pressures from 10 to 100 psi were utilized.

The main evidence used by the authors to decide whether an extinction of the fire occurred by cooling was that the temperature shown by a thermocouple placed near the liquid surface is reduced to the fire point of the liquid prior to extinction. In some instances the fire continued to burn after the indicated temperature was lower than the fire point. This deviation was ascribed partly to unevenness in the spray pattern giving rise to different degrees of cooling at various parts of the liquid surface. In addition, however, some evidence indicated that the flames under these conditions consisted of burning oil droplets that were splashed upwards by the water spray.

When the flames were extinguished by cooling, it was characteristic that after an initial upsurge, the size of the flames was reduced gradually, until in the last stages the flames were about 6 in. high and were usually present only at the edge of the test vessel. A lighted taper placed near the liquid surface did not give immediate re-ignition after the initial extinction. Time-temperature records showed that the liquid continued to cool for a considerable time after the spray was terminated, which was within several seconds after fire extinction.

The nature of liquid burning, the time of initial burning, and the diameter of the burning vessel were the main properties of the fires that were varied during the tests. To obtain an estimate of the effect of the burning liquid, experiments were conducted in which extinctions took place under conditions wherein only the liquid itself was changed. A comparison was obtained by plotting the extinction time against the temperature difference between the fire point of the liquid under test and the ambient atmospheric temperature. The results show that there was a rapid decrease in extinction time as the temperature difference (defined above) increased; the extinction time was approximately proportional to the temperature difference raised to the -1.75 power. Despite a wide scatter of results, the extinction time was approximately proportional to the initial burning time of the liquid. There appeared to be no significant difference between the extinction times for vessels having diameters of 35 or 47 in.

Rasbash and Rogowski found that, in general, it was not possible to ascertain directly from their results the effect of the various spray properties on the extinction time, since over a major portion of conditions in which extinctions by cooling occurred it was not possible to control these properties independently. In some instances a direct estimate was possible. A coarse spray took longer to extinguish the fires tested than did a fine spray. A direct indication of the effect of difference in the velocity of the entrained current of two sprays was obtained. These two sprays had nearly the same drop size and flow rate. When the spray with the low entrained air velocity was applied to the initial extinction. Time-temperature drecords showed that the liquid continued to air current, however, the spray pushed the flames downwards and there was a reduction in the extinction time. Within the residual error the extinction time was shown to be directly proportional to the drop size and inversely proportional to the rate of flow of water spray to the fire area. A significant decrease in the extinction time was noted as the entrained air velocity increased.

The extinction times in all tests where extinction was by cooling were plotted against a parameter A, where

$$A=(D/M)(Y/\Delta T^{1.75})$$

where D(mm) is the mass median drop size of the spray, M($g \cdot cm^{-2} \cdot min^{-1}$) is the rate of flow of spray to the fire area, ΔT(°C) is the difference between the fire point of the liquid and ambient temperature, and Y (min) is the initial burning time. The resultant curve showed that, except for two groups of tests, the data fall fairly well about a straight line having a positive slope of unity. All of the data for the groups of tests not falling on the straight line were obtained during experiments wherein the entrained air velocity was less than 8 ft/sec (the approximate upward velocity of the flame gases) and it was characteristic of these tests that the flames moved upwards against the sprays. In general, it was shown that the deviation from the straight line increased as the entrained air velocity decreased.

The equation of the straight line having unit slope is $t=34{,}000\ A$ where t denotes the extinction time in seconds. All extinction times obtained in the tests, except for those extinction times associated with sprays having low entrained air velocities, fell within a distance of this line that was generally within the range of reproducibility of the tests. From the empirical expression for extinction time, it can be seen that under given conditions liquids with high fire points are extinguished much more rapidly than those with low fire points. Also, the efficiency of the spray, as measured by the reciprocal of the extinction time, is proportional to the flow rate of spray to the liquid surface. The efficiency of the spray increases as the drop size of the spray is reduced. This factor can be expected to hold only if the spray drops have a momentum sufficiently large to penetrate the flame and reach the burning liquid.

The size (diameter) of the fire, which varied from 4.3 to 47 in., was not an important factor in determining the extinction time. Also, the method of spray production, whether accomplished by impinging jets or swirl nozzles or even air atomization, did not affect the extinction time noticeably. Factors like the pressure at which the spray was produced and the cone angle at which the spray was directed from the nozzles affected the extinction times only in so far as they affected the properties of the spray reaching the fire, that is, the drop size, the flow rate, and the entrained air velocity in the spray.

Three mechanisms may be suggested to account for the cooling of the burning liquid: (1) heat transfer from the hot oil to the water drops, (2) mixing of hot oil near the surface with cold oil well below the surface, and (3) the formation of an oil-in-water emulsion followed or accompanied by heat transfer from the hot oil drops to the continuous water phase. The manner in which the extinction time depends upon the factors of the parameter A is most consistent with the view that the cooling to the fire point of the surface layers of the oil was due to the abstraction of heat from the liquid by water drops within the liquid. Thus, the amount of heat which had to be removed increased as the initial burning time increased; the ability of the spray drops to remove this heat increased as the flow rate of the spray increased, as the drop size decreased, and as the temperature difference between the fire point and the ambient temperature increased.

The derived empirical equation gives an estimate of the extinction time for a liquid fire burning from a horizontal layer when the spray is projected vertically downwards from a fixed system with the requirement that the water spray drops should be able to reach the liquid surface. Splash fires are not covered by this empirical equation. It is unlikely for most liquids that an increase in initial burning times beyond 10 to 20 min. will give the increase in extinction time predicted by the empirical equation since the sensible heat in the liquid above the fire-point temperature does not increase significantly after this time.

Subject Headings: ***Extinguishment by water sprays; Water sprays, flame extinguishment; Fires of liquids.***

L. E. Bollinger

Rasbash, D. J., and Rogowski, Z. W. (Joint Fire Research Organization, Boreham Wood, England) "Extinction of Liquid Fires with Water Sprays," *Chemistry and Industry*, **24**, 693 (1954)

This short letter outlines some of the factors that have been found to affect the ease of extinction of liquid fires by water sprays such as volatility of the fuel, drop size of the water spray and the "preburning" or duration of burning after ignition before the spray was applied.

Six liquids were tested, in order of volatility: alcohol, benzol, petrol, kerosene, gas oil, and transformer oil; they were burned in a cylindrical bath 30 cm. diameter and 12.5 cm. deep. Three water sprays were tested which at the same pressure (85 psi and rate of water flow ⅓ gal/sq ft/min), generated drops of diameter 0.28, 0.39, and 0.49 mm. The chief results were:

1) The extinction time varied with the preburning time.
2) The extinction time generally increased with the volatility of the fuel.
3) For alcohol, benzol, petrol, and kerosene the extinction time increased with the coarseness of the water spray, so the efficacy decreased with increasing coarseness.
4) For gas oil and transformer oil, the coarsest spray was the best.

Investigation of the effect of extinction time showed that with benzol, petrol, and kerosene, the ease of extinction suddenly improved (with a discontinuous drop in extinction time) after the flame had been burning for 6–8 secs. More extensive tests with kerosene showed that the results could be plotted on two separate, partially overlapping, curves. At short preburning times, the extinction time increased with preburning time from 5 to 500 secs., the mechanism of extinction evidently being cooling of the liquid surface to the fire point. At longer preburning times (greater than 6 secs.) extinction generally occurred, possibly by steam formation, in under 20 secs. without necessarily. cooling the liquid surface down to the fire point.

In general the authors conclude that coarse sprays should be used for high boiling point liquids and finer sprays for more volatile liquids.

Subject Headings: ***Extinguishment by water sprays; Water sprays, flame extinguishment; Fires of liquids.***

R. H. Essenhigh

Grove, C. S., *et al.* (Syracuse University Research Institute) "Additives to Improve the Fire-Fighting Characteristics of Water," *Bureau of Yards and Docks, Department of the Navy Contract NBy 13027, Progress Report*, **3** (April 1958)

Additives have been incorporated with water to improve its fire-fighting characteristics: viscosity additives to increase the contact time between the burning surface and water, and opacifiers to reduce the heat energy radiated from the flames. The runoff simulator apparatus (ROSA) used in previous viscosity studies has been modified to permit operation with a constant flow of liquid down the inclined heated plate at variable flow rates. Previous data had indicated that a greater plate cooling effect was to be expected in the 10–40 centipoise region. In the present experiments, owing to incomplete coverage of the plate and the imbedded thermocouples by the liquid as it is discharged from the pipe system, a plate temperature drop lower than that obtained with water was measured in the lower viscosity region at a flow rate of 2.27 l/min, but rapid cooling rates, longer time below re-ignition temperature and less vaporization of the water have been noted when using various Polyox compounds and Acrysol ASE-60 as viscosity additives. From the plate temperature drops and weights of vaporized water, cooling factors have been determined from which cooling ratios, the ratios of the cooling factors of the various solutions to that of water, have been calculated. With Acrysol ASE-60 a pronounced peak of *ca.* 2.35 was observed in the cooling ratio-viscosity curve at a viscosity value of *ca.* 10 centipoise. The use of a saw-toothed distribution system and of a movable thermocouple made of a pointed constantan wire in contact with the iron plate are modifications which are envisaged to improve the present apparatus for future work. A fire test apparatus consisting of a steel chimney 4 x 4 x 5 ft. high similar to the design of the standard fire test units used in the evaluation of spray nozzles is also under construction for testing viscosity additives under actual fire conditions.

For the radiant energy studies, the effectiveness of opacifiers has been evaluated by measuring with an ektron detector, having a 2 x 2 mm. PbS photo-conductor surface, the fraction of red radiation emitted by a tungsten filament lamp which is transmitted through a 1.75 mm. layer thickness of suspension of the opacifier in water. The photosignal was received by an oscilloscope following amplification and compared with that obtained with water in the cell. Results are reported for ZnO, Columbia coating clay, Cliffstone whiting, Titan clay, Mississippi clay, New Columbia water washed filler clay, K.B. clay, and Aluminum flake powder at concentrations varying between 0.004 and 0.5 per cent by weight. A 50 per cent reduction in transmission may be obtained by using concentrations between 0.03 and 0.15 per cent of suspension. Aluminum powder and ZnO have been found the most effective materials for reducing transmission under the conditions of the experiments. The use of a strobotac as light source showed that transmission of this radiation through water is higher than that from the tungsten filament lamp although the screening of solids is just as efficient in both cases. The apparatus is described.

Subject Headings: *Additives, fire-fighting improvement; Water, improvement by additives.*

J. Rene Jutras

Simmons, R. F. and Wolfhard, H. G. (R. A. E. Westcott, England) "The Influence of Methyl Bromide on Flames. I. Premixed Flames," *Transactions of the Faraday Society*, **51**, 1211–1217 (1955)

The effect of methyl bromide and bromine on premixed methane-air, ethane-air, hydrogen-air, and ethylene-air flames has been studied. For the methane-air and ethane-air systems it has been found that the flammability limits, as determined in a cylindrical Pyrex tube, 7.5 by 30 cm. at 380 mm. Hg and 50°C., are sharply contracted by both methyl bromide and bromine. The percentages of each required to prevent burning at any composition were, for methane, about 4.8 mole per cent methyl bromide and about 2.4 mole per cent bromine. For ethane the values were about 5.8 mole per cent methyl bromide and about 2.9 per cent bromine. When correction is made for the fuel portion of the methyl bromide molecule, it is found that the effect on the flammability limits of the methane-air and ethane-air systems depends only on the number of bromine atoms. One molecule of methyl bromide is half as effective as one molecule of bromine.

For the ternary system hydrogen-air-bromine it was found that flammability limits could not be described by Le Chatelier's rule. Burning velocity measurements of the ethylene-air systems by the burner method showed that methyl bromide lowered the burning velocity for stoichiometric, rich, and lean mixtures, the last-named being least affected.

Flame temperatures were calculated for limit mixtures for the hydrogen, methane and ethane systems. For the last two the presence of bromine decreased the limit temperature by about one hundred degrees.

The limit temperature calculations lend further support for the idea that this type of inhibiting agent works by a chemical rather than by a thermal effect. The flammability limit data for the hydrocarbon-air systems hint strongly that halogen atoms are the important species in this chemical effect, something suspected in the past, but until these papers, unsubstantiated by experimental proof.

Subject Headings: ***Extinguishment by methyl bromide; Premixed flames, influence of methyl bromide; Methyl bromide in premixed flames.***

Joseph B. Levy

Simmons, R. F. and Wolfhard, H. G. (R. A. E. Westcott, England) "The Influence of Methyl Bromide on Flames. II. Diffusion Flames," *Transactions of the Faraday Society*, **52**, 53–59 (1956)

The effect of methyl bromide on diffusion flames with air of methane, ethane, ethylene, acetylene, and hydrogen has been studied using a concentric tube type burner. The inhibitor was added to the air or fuel stream and the concentrations required to cause the flame to lift off were determined. Methyl bromide was much more effective in extinguishing the flame when added to the air rather than to the fuel stream, the concentrations required in the former case being comparable to the peak concentrations found for premixed flames. This was true for all the systems studied and is consistent with the idea that the main reaction zone in a diffusion flame occurs where the fuel and oxidant meet in approximately stoichiometric proportions.

Spectroscopic studies were carried out on the methyl bromide-oxygen diffusion flame and on the carbon monoxide-air, the hydrogen-air, the ethane-air, and the ethylene-air flames, all with methyl bromide added. The effect of the inhibitor on the flame structures is discussed.

Subject Headings: ***Extinguishment by methyl bromide; Diffusion flames, influence of methyl bromide; Methyl bromide in diffusion flames.***

Joseph B. Levy

Miller, J., Inami, H., Rosser, W. A., and Wise, H. (Stanford Research Institute, Menlo Park, California) "Mechanism of Flame Inhibition," *Corps of Engineers, U.S. Army, Engineer Research and Development Laboratories, Fort Belvoir, Virginia, Contract DA44-009-Eng-2863 Phase II Progress Report*, **3** (February 1958)

This is the third quarterly progress report on the inhibiting effect of chemical agents in combustion. The work described is divided into two parts: (1) emission spectroscopy in which the spectral intensities of excited radicals (OH, CH, and C_2) in premixed methane-air-inhibitor flames were measured, and (2) quenching distances of similar mixtures. Very small amounts (a few tenths of one per cent) of bromine, hydrogen bromide, and methyl bromide were used as inhibitors.

In the spectroscopic portion of the work the authors used an inverted flame to avoid absorption of radical emission by cooled product gases. A quartz-window photomultiplier tube was used as the detector of the excited radicals. The readings were taken directly from a microvoltmeter whose output was generally in the range of 10 to 2000 μv.

Noise and drift fluctuations were of the order of 5 per cent, and in the worst case the fluctuations were as high as 20–25 per cent. Even so, trends in the data were still observable.

The OH emission intensity was found to decrease considerably more for Br_2 addition than for HBr or CH_3Br in lean flames. In rich or stoichiometric flames, all three additives reduced the intensity at about the same rate. Very convincing straight lines were obtained when intensity was plotted against inhibitor concentration for mixtures of varying methane content. Similar plots made for the C_2 radical were not particularly clear and easy to interpret. However, the behavior in rich and lean flames was distinctly different. To look at the emission from the CH radical, only CH_3Br was used as inhibitor. In this case radiation intensity was found to increase continually in lean flames; in stoichiometric mixtures, it increased, then leveled off; and in rich mixtures, an increase, followed by a level-off, then a decrease, of the intensity was observed. The authors conclude that no single mechanism appears to account for all the phenomena.

In the quenching distance experiments a conical tube was employed. Methane-air-inhibitor mixtures were ignited by a high energy spark produced from tungsten electrodes, and the extinction point of the ascending flame was recorded photographically. The diameter of the tube at the extinction point was taken as the quenching distance. Here again, only CH_3Br was utilized as inhibitor. A seemingly happy consequence of these experiments is the fact that the quenching distance per se is not important, but it is the inverse of this property which linearizes the plot of 1/d versus mole fraction of additive. The rate of change of the reciprocal quenching distance with additive mole fraction varied linearly with methane concentration. These results led to the conclusion that the product of quenching distance and flame speed is constant. The latter has been discussed from another view previously as the authors clearly pointed out.

Throughout the paper the writers failed to discuss how these inhibitors do their job, which is what the title would lead one to expect. Even so, the data are generally informative and should be of some use.

Subject Headings: ***Flame inhibition mechanism.***

Cleveland O'Neal, Jr.

Friedrich, M. (Research Division for Technique of Extinguishing Fires, Karlsruhe Polytechnical Institute, Germany) "Research on the Extinguishing Effect of Halogenated Hydrocarbons," *VFDB-Zeitschrift* (*Forschung und Technik im Brandschutz*), Heft 2, (1957). Translated by Malcolm and Borst, U.S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia.

It is well known that volatile halogen-containing compounds, methyl bromide for example, are effective fire-extinguishing agents. The search for even more effective agents may be guided by the results of fundamental combustion studies, but it will probably be necessary to make the actual selection on the basis of practical tests such as those described in this study.

The experiments involved a number of flammable liquids and extinguishing agents and were performed in the following manner. A selected agent was sprayed from an electric atomizer onto a burning liquid a short distance away. The quantity of inhibitor required to extinguish the flame was determined as a function of the application rate. The results are presented graphically for nine inhibitors* and a large number of flammable liquids. These include about a dozen hydrocarbons and hydrocarbon mix-

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* Bromochloromethane, carbon tetrachloride, ethylene tetrachloride, methyl iodide, ethyl iodide, n-propyl iodide, ethyl bromide, n-propyl bromide, and water.

tures, five alcohols, three acetates, three ketones, ether, carbon disulfide, napalm, and five lacquers.

With such an extensive list it is therefore easy to order the various inhibitors according to relative ability to extinguish a given flame, and to arrange the flammable liquids according to sensitivity to chemical quenching by a given agent. The principal value of the experimental data lies in this relative ordering. Applicability to situations which differ substantially from those described in the study is limited, as the author recognizes, by the fact that the experimental results depend implicitly on the characteristics of the spray gun, the distance between the flame and the atomizer, and such physical properties of the extinguishing agent as viscosity, density, and volatility.

Subject Headings: *Extinguishment by halogenated hydrocarbons; Halogenated hydrocarbons, extinguishing effects.*

Willis A. Rosser

Levy, J. B., and Friedman, R. (Atlantic Research Corporation, Alexandria, Virginia) "Study of the Mechanism of Flame Extinguishment by Aluminum Chloride," *Wright Air Development Center, Aeronautical Accessories Laboratory Contract AF 33(616)-3527.* WADC Technical Note 58–1 (October 18, 1957).

The burning velocity at 200°C. of premixed methane-air-aluminum chloride mixtures decreased with increasing concentration of aluminum chloride vapor. Stoichiometric and rich mixtures were inhibited slightly more than lean mixtures, and the decrease in burning velocity tended to flatten slightly at higher inhibitor concentrations. Similar trends were observed by Simmons and Wolfhard [Transactions of the Faraday Society, 51, 1211–1217 (1955)]* in the inhibition of ethylene-air flames with methyl bromide.

Burning velocity was measured from luminosity photographs of a Bunsen flame cone. Concentrations were 7.75–12 per cent methane and 0–1.4 per cent Al_2Cl_6. Higher inhibitor concentration gave unsteady flames. Equipment is described. Aluminum chloride vapor was added through a capillary from a molten salt reservoir.

The authors concluded that Al_2Cl_6 vapor is about as effective on a mole basis as carbon tetrachloride† and that inhibition in the present work involved chemical reaction in the vapor, possibly by Al_2Cl_6 reacting with a hydrogen atom and thus breaking a chain reaction. The possibility of surface reaction on Al_2Cl_6 particles (or Al_2O_3 particles from hydrolysis) is discussed but discounted, although surfaces are often effective chain breakers.

The lesser effectiveness of Al_2Cl_6 as an inhibitor in the present work compared to work by Dolan [Sixth Symposium (International) on Combustion, 787 (1957)] was attributed to differences in experimental ignition conditions. The present work appears more significant.

Subject Headings: *Extinguishment by aluminum chloride; Aluminum chloride, extinguishing effect.*

Welby G. Courtney

Dolan, J. E. and Dempster, P. B. (Imperial Chemical Industries, Ltd., Stevenston, England) "The Suppression of Methane-Air Ignition by Fine Powders," *Journal of Applied Chemistry*, 5, 510–517 (1955)

The effect of particle size of several inorganic compounds on their efficiency as ignition suppressors in methane-air mixtures was determined. The study has application

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* See page 19.

† Rosser, Willis A., Jr. and Wise, H. (Stanford Research Institute) "Mechanism of Flame Inhibition," for Engineer Research and Development Laboratories, Fort Belvoir, Virginia Phase I Final Report (May 1957).

in understanding the effect of chemical diluents of explosives on the safety of use of these explosives which are fired in mixtures of flammable gases and air. Dusts with average particle diameters of 5–10 microns were dispersed in methane-air streams of several compositions which were subsequently ignited by a spark discharge in an ignition tube. A "suppression point" is defined as the value of the dust surface area such that on sparking the dust-laden gas, a flame is not propagated through the gas but is confined to a small kernel at the spark gap. A "quenching point" is defined as the value of the dust surface area such that a flame just propagates the entire length of the ignition tube. At all values of surface area between these two points, the dust is considered to quench the methane-air flame. Both the suppression point and the quenching point are shown to be functions of the methane-air mixture composition.

Quenching points and suppression points were measured for sodium bicarbonate, six alkali halides, and 13 other materials capable of quenching methane-air ignitions. Materials arranged in decreasing order of effectiveness in the quenching of methane-air ignitions are aluminum chloride, potassium fluoride, ammonium bicarbonate, potassium iodide, sodium sulfite, sodium aluminum fluoride, potassium chloride, sodium silicofluoride, sodium bicarbonate, ammonium chloride, sodium acetate trihydrate, potassium carbonate, cuprous oxide, sodium carbonate, cobaltous chloride hexahydrate, sodium sulfate decahydrate, sodium chloride, barium chloride, barium hydroxide octahydrate, and copper acetate monohydrate. Materials shown to be ineffective in suppressing or quenching methane-air flames under the conditions of the experiment are chalk, magnesium carbonate, copper carbonate, lead acetate, barium sulfate, cupric oxide, silicon, alum, magnesium sulfate tetrahydrate, ammonium nitrate, litharge, sodium thiosulfate, zinc sulfate, hydrated zinc sulfite, and talc. Suitable dust clouds of some materials could not be obtained because of the tendencies of the powders to form aggregates. These materials were bismuth nitrate, lithium chloride, sodium iodide, and lithium carbonate.

The generalization is made that, apart from chemical specificity, the major physical factor which determines the ability of an inorganic dust suspension to inhibit the explosion of methane-air mixtures is the surface area of the dust exposed to the advancing flame. Several other generalizations are made: e.g., salts with melting points below 200°C. are more effective than those with melting points above 200°C. with the exceptions of the alkali salts and cuprous oxide; the alkali salts are the most effective group of compounds; salts which decompose are generally effective if their decomposition temperatures are below 200°C. It is suggested that these dusts suppress the methane-air flames by reducing the temperature of the burning gases below a critical temperature, 1330°C., for flame propagation. The alkali halide dusts are shown to have an efficiency that cannot be fully explained by the thermal characteristics of their powders. An explanation of this apparent anomaly is suggested.

Subject Headings: ***Extinguishment by powders; Powders, extinguishing effect.***

L. R. Griffith

VIII. Model Studies and Scaling Laws

Fons, W. L. (California Forest and Range Experiment Station, Berkeley, California) "Analysis of Fire Spread in Light Forest Fuels," *Journal of Agricultural Research*, **72**, 93–121 (1946)

In the study of fire control a serious lack of information persists regarding the rate at which a forest fire may be expected to spread under various conditions of forest cover, weather, and topography. This paper presents an analysis of the rate of fire spread in light forest fuels and the fundamental laws governing this rate of spread.

The rate of fire spread in a fuel bed may be visualized as proceeding by a series of successive ignitions, its magnitude controlled primarily by the ignition time of the particles and the distance between them. The rate of spread as a function of particle spacing and ignition time is derived assuming an ideal bed of identical rodlike fuel particles standing upright at equal distances from each other. If θ_i is the time for the n particle to burst into flame after the (n-1) particle has ignited and if L is the distance between the particles, it follows that the rate of spread R is

$$R = \frac{L}{\theta_i} \tag{1}$$

where $R = \frac{dr}{d\theta}$ in the r direction down the row of fuel particles.

The ignition time in equation (1) depends on two types of variables. Those dealing with (a) the fuel particles and (b) the atmosphere surrounding the particle. From an analysis of heat transfer in the system the ignition time θ_i can be expressed in terms of the physical properties of the light fuel particle, the flame temperature, and the heat transfer factors as

$$\theta_i = \frac{\bar{\gamma}\bar{C}_p}{\sigma(f_c + f_r)} \ln\left(\frac{t_f - t_1}{t_f - t_i}\right) \tag*{* (10)}$$

From the equation of θ_i the rate of spread can be now expressed as

$$R = \frac{(f_c + f_r)\sigma L}{\bar{\gamma}\bar{C}_p \ln\left(\frac{t_f - t_1}{t_f - t_i}\right)} \tag{11}$$

In this equation R is expressed in terms of certain fundamental variables that control the spread of a fire in light forest fuels. Such quantities as wind velocity, moisture content, time and topography, which are ordinarily regarded as controlling spread do not appear in the equation. They affect the rate of spread indirectly through their influence on the more fundamental variables.

The film conductance factor f_c for convection is evaluated from the equation based on experimental data for heat transfer from gases to single cylindrical rods, with the gas flowing at right angles to the rod axis. This equation is

$$\frac{f_c D}{k_f} = 0.45 + 0.33\left(\frac{VD}{\nu_f}\right)^{0.56} \tag{12}$$

The net rate of heat transfer by radiation to a small particle surrounded by flame gives an equation for the radiation heat transfer coefficient.

$$fr = \frac{0.172\epsilon\left[\left(\frac{T_f}{100}\right)^4 - \left(\frac{T_1}{100}\right)^4\right]}{t_f - t_1} \tag{14}$$

The values of ϵ and t_f which were evaluated from experimental data are 0.23° and 1500°F., respectively. The fuel temperature t_1 was approximated by using the arithmetic mean of the ignition temperature t_i and the fuel temperature t_o, far from the flame front.

The ignition temperature t_i of a light forest fuel particle surrounded by ambient hot gases is the average specimen temperature at the instant a flame appears. An arbitrary

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* $\bar{\gamma}$ = density of moist fuel particle; σ = surface-volume ratio of fuel particle; t_i = ignition temperature.

value of 550°F. is recommended for all light forest fuels irrespective of fuel size and moisture content. This value is based on equation (10) in which the time θ_i was determined experimentally.

To calculate the rate of fire spread in a fuel bed by equation (11), the spacing L must be related to the measurable fuel and fuel-bed variables. The equation

$$\sigma L = E\ (1+\sigma\lambda)^{1/2} \tag{21}$$

expresses the particle spacing in terms of the shape factor E, the surface-volume ratio of the fuel particle σ, and the ratio of voids to fuel surface area of the bed λ. The reciprocal of λ may be thought of as the compactness of the fuel.

Since the fuel particles nearly always carry absorbed water, the specific heat of the moist fuel $\overline{C}_p$ may be expressed in terms of the specific heat of the dry fuel, its moisture content, and the heat of absorption. From an analysis of the total heat required to raise a moist fuel particle at temperature t_o to ignition temperature t_i the specific heat of the moist fuel can be expressed as

$$\overline{C}_p = \frac{1}{1+M}\left[M\left(\frac{1{,}089+0.46\ \ t_i-t_o}{t_i-t_o}\right)+\frac{h}{t_i-t_o}+C_p\right] \tag{27}$$

The relation between the density of the moist fuel and dry fuel γ, is $\overline{\gamma} = (1+M)\gamma$, where M is the moisture content.

Temperature t_i varies with the flame angle from the horizontal and the size of the flame front.

Temperature t_i is not easily measured even for the ideal condition. Temperature t_o of the fuel far removed from the advancing flame front is, however, readily determined. Temperature t_i may be eliminated by substituting t_o for t_i and correcting this new temperature-difference ratio in equation (11) by a coefficient C_t. The temperature-difference ratio coefficient is primarily a function of wind velocity, slope, size of the flame, and time from the start of the fire and must be evaluated experimentally. For the field conditions of $t_o = 80°$F. and $t_i = 550°$F., C_t will vary from 0.67 to more than 1.00 depending upon the wind condition and the fire itself.

In the idealized fuel bed all particles were assumed to be vertically oriented with equal spacing. In the natural homogeneous bed, such as a mass of fallen pine needles, more or less horizontally oriented at random, the spacing is not equal but has voids of varying sizes as well as occasional direct contact, different orientation with gas flow, and possible fuel-moisture gradients in the fuel bed.

By the theory of similitude, if the processes of burning in the two beds follow the same laws and the respective variables stand in a constant ratio to each other over their whole range, the application of equation (11), derived for ideal beds, can be applied to fires in natural beds.

On the assumption that the individual variables in the two processes are relatively proportional, as required by laws of similarity, equations replacing these variables may be written. Equation (11) can be rewritten as

$$R = \frac{C(f_c+f_r)\sigma L}{\overline{\gamma}\,\overline{C}_p \ln\left[C_i\left(\frac{t_f-t_o}{t_f-t_i}\right)\right]} \tag{32}$$

where

$$C = \frac{C_f C\sigma C_L}{C\gamma C_{cp}}$$

Thus C represents a proportionality constant relating the rate in a natural bed with the rate in a standard bed under identical conditions. The coefficients C_t and C in equation (32) are evaluated experimentally.

Fuel beds of the homogeneous type are of rare occurrence in nature. Normally a natural bed is composed of particles varying in size, shape, density, and specific heat. Since the ignition time θ_i is dependent on the material and dimensions of the particles, it follows that the rate of spread will be different for different particles. An expression for the gross rate of spread is presented in the report for the heterogeneous fuel beds. However, no experimental verification is presented.

The coefficient C_t was evaluated for Ponderosa pine needles and they were chosen as the natural fuel for the standard bed in the experimental phase of the report. Beds of needles 2 in. deep, 3 ft. wide, and 8–12 ft. long were prepared in trays with controlled compactness. These beds were placed in a low velocity wind tunnel and were burned on the horizontal at zero slope. The beds were ignited and were allowed to burn under various conditions of compactness, wind velocity, air temperature, and moisture content.

In order to simulate a standing type of fuel such as brush, fuel beds were prepared by standing uniform twigs vertically at equal spacings in sawdust which had been treated with a fire retardant chemical. The twigs were 7½ in. long and were cut from dead branches of Ponderosa pine. Three diameter sizes were tested.

Numerical values of C_t were computed for each pine-needle fire by equation (32) using the observed rates of spread and assuming C as equal to unity. C_t was plotted as a function of the wind velocity. Experimental rates of spread were compared with computed rates of spread using C_t from the C_t versus wind velocity curve. Good agreement between experimental and calculated values was obtained.

The values of C, using C_t from the curve, for twigs varied widely around the mean value of 1.61. This was mainly due to the experimental technique.

Curves were drawn for the effects of the measurable variables—wind velocity, fuel temperature, compactness, fuel size, fuel density, and moisture content—on the rate of forward spread of fires.

The rate of spread is approximately proportional to the first power of the wind velocity for velocities less than 5 mph and to the 1.5 power of wind velocity for velocities from 5 to at least 12 mph. This is caused by the fact that wind velocity influences fire spread by causing changes in the magnitude of film conductance f_c and temperature ratio coefficient C_t.

The surface-volume ratio σ of the fuel particle has been used to express the fuel size. Representative values of σ for various fuels are:

Dead Ponderosa pine twigs (of diameter D): $\frac{4}{D}$ in.$^{-1}$
Ponderosa pine needles: 128 in.$^{-1}$
Fir needles: 124 in.$^{-1}$

With all other variables constant, σ varies with rate of spread R as

$$R=(a\sigma+b\sigma^{0.47}+c)(1+d\sigma)^{1/2}$$

where, a, b, c, and d are the proper constants for the given values of wind velocity, initial fuel temperature, compactness, and moisture content. For fine fuels this expression approximates a straight line having positive slope.

The reciprocal of the ratio of volume of voids to the surface area of the fuel in a bed is denoted by $\frac{1}{\lambda}$ and may be used as a direct measure of the variable combining fineness and crowdedness. Representative values of $\frac{1}{\lambda}$ for various fuel beds are:

Dense brush: 0.2 in.$^{-1}$
Pine needles: 6.0 in.$^{-1}$
Fir needles: 20.0 in.$^{-1}$

The rate of spread varies as the square root of λ by definition. There is a limiting value of λ at which fires would fail since for a fuel particle of a given size, it is necessary to increase the distance L between particles to obtain greater values of λ.

The important effect of initial fuel temperature on fire spread is that a change in temperature changes the ignition time θ_i as shown by equation (10).

The ignition time for fuel particles of a given volume is directly proportional to the density (equation (10)) and by the same token fire spread is inversely proportional to density.

Fire spread varies inversely with the fuel-moisture content. Moisture content can be expected to have the same effect on the rate of spread as density has, in that the greater the moisture the more heat is required to bring the fuel to the ignition point and the slower it will burn. Slope has the same effect as wind on the rate of spread since it brings the flames closer to the fuel.

The rate of spread varies as the logarithm of time since immediately after the start of a fire the volume of hot gases at its head increases progressively increasing the radiant heat to the fuel particle.

A set of tables is included at the end of the report and contains values for a group of fundamental variables in terms of measurable variables.

Subject Headings: *Fire spread; Forest fire spread.*

Alan W. McMasters

Byram, G. M. (Southeastern Forest Experiment Station, Asheville, North Carolina) "Some Principles of Combustion and Their Significance in Forest Fire Behavior," *Fire Control Notes*, **18**, 47–57 (1957)

A survey of various principles involved in the combustion process is presented in this paper, and their significance in forest fire behavior is discussed. Combustion has three rather definite phases, each overlapping and all existing simultaneously in a moving fire. In the first phase the fuel ahead of the fire is preheated, partially distilled, and ignited. Distillation of gaseous substances continues in the second phase but is accompanied by the burning or oxidation of the volatile fractions. Ignition is regarded as the link between the first and second phase. In the third and final phase, the charcoal left from the second phase is burned leaving a residual ash. Depending on the degree to which the fuel is dried, the third phase may be incomplete and result in a burned-over area which appears black instead of gray.

Heat that is derived from combustion is very important in forest fire behavior. For most forest fuels the heat energy released from one pound of dried fuel varies between 8000 and 9000 Btu. In most instances, however, fuels do not burn with maximum efficiency. The efficiency may be as high as 80 per cent for a small fire burning in dry fuel with little smoke. In large fires with dense smoke, the efficiency would be less.

Besides the three primary ways by which heat is transferred, *i.e.*, conduction, convection, and radiation, a fourth means of heat transfer in forest fires is described. In this mechanism, embers and firebrands are carried ahead of the fire by convection currents and this results in "spotting."

The factors that affect combustion are so complex that they are not fully understood; this is especially true in the burning of solid fuels. There are, however, two factors which have obvious and definite effects on the combustion rate of woody substances and are important in forest fire suppression. These are fuel moisture and fuel size and arrangement.

Moisture in the fuel greatly diminishes the preheating effect of fire which occurs in the first phase of combustion. Much of the heat that would normally be used in heating the fuel is used in evaporating the water present in the fuel. The resulting water vapor dilutes the oxygen in the air which interferes with the second or gaseous combustion phase. This dilution also affects the carbon-combustion phase. It is probable that moisture may also have considerable effect in reducing the heat yield or combustion efficiency of the fuel.

The effect of size and arrangement of the fuel is presented by means of an illustration. In the illustration similar piles of logs are set up differing only in fuel size and arrangement. In each case reducing the size of the fuel and rearranging the fuel to provide greater ventilation increased the combustion rate considerably. Under such conditions the rate of combustion becomes less dependent on conduction and is governed more by convection and radiation.

It is more difficult to apply what is known of ignition and combustion to the behavior of very high-intensity fires than to the behavior of more frequent low-intensity fires. Ordinary fires generally behave as one would expect from the principles of combustion. In a conflagration or blowup, however, factors are in operation which are absent in small fires. Low-intensity fires are essentially two dimensional phenomena, while high-intensity fires become three dimensional. The third dimension permits the conversion of part of the heat energy into kinetic energy of motion which changes the relative significance of various combustion factors and greatly modifies the expected effects of the basic processes. Because of this, high-intensity fires cannot be considered as enlarged models of low-intensity fires.

Fire behavior is related to the combustion process by a group of basic fuel factors: (1) combustion period, (2) critical burnout time, (3) available fuel energy, (4) total fuel energy, and (5) quantity of firebrand material available for spotting.

The combustion period is defined as the time required for complete combustion of the fuel. This factor is primarily dependent on fuel size, fuel arrangement, fire intensity, and fuel moisture. Critical burnout time is the maximum length of time fuel can burn and still feed its energy into the base of the forward moving convection column. The magnitude of this factor depends primarily on fire intensity or the rate of a fire's energy output. The available fuel energy is that part of the total fuel energy which is fed into the convection column. For fuels which have a combustion period equal to or less than the critical burnout time, the available fuel energy is equal to the total fuel energy. If the combustion period is longer than the critical burnout time, the available fuel energy is less than the total fuel energy. The total fuel energy is determined by the quantity of fuel per acre and the combustion efficiency.

The fifth fuel factor, quantity of firebrand material available for spotting, becomes increasingly important as fire intensity increases. Of equal importance is the relation of fuel moisture and the probability of ignition from firebrands. Ignition probability is essentially zero at 25 to 30 per cent moisture content but increases rapidly with decreasing fuel moisture. Both ignition probability and combustion rate are greatest for oven-dry fuels, and in the lower moisture ranges are considerably affected by slight changes in fuel moisture. Ignition probability is also dependent on other factors such as the nature of the surface fuel in which firebrands fall and the ground coverage of the fuel.

The initial phases of a blowup are directly related to the combustion process and the basic fuel factors. A decrease in fuel moisture results in a higher combustion rate and a shorter combustion period. This in turn results in an increase in available fuel energy and is accompanied by an increase in fire intensity. With an increase in fire intensity, the critical burnout time is lengthened which further increases the available fuel energy. Thus, a reinforcing cycle is established which favors the growth of fire intensity. As intensity increases, atmospheric factors become increasingly important. As a result, spotting and ignition probability become dominant fire behavior factors.

Subject Headings: ***Forest fire combustion principles.***

W. Y. Pong

Burgoyne, J. H. and Katan, L. L. (Imperial College, London) "Fires in Open Tanks of Petroleum Products—Some Fundamental Aspects," *Journal of the Institute of Petroleum*, **33**, 158–185 (1947)

Careful observations of temperature, composition, and combustion rate were made of the burning of petroleum products in an open-topped (vertical) tank 22 in. diameter and 40 in. deep. The petroleum products are classified according to their tendency in burning to form a liquid floating mass (called a "hot zone") stripped of lighter fractions, which grows in thickness as burning progresses. The hot zone maintains a relatively high temperature level but the remaining underlying oil is unaffected until it is converted into hot zone by layer-wise light-end stripping.

The hot-zone-forming materials investigated were three fuel oils, three crudes, and leaded and unleaded gasoline. When the burning of fuel oil progressed until the tank contents were all converted to hot zone, boilover occurred and another cycle began with a second hot zone (higher temperature) forming at the top surface. The occurrence of boilover is attributed to the presence of small amounts of water (e.g., 0.3 per cent). Frothing and sudden eruptions were encountered with very wet oils. Crude oils produced boilover without the presence of measurable water. After the hot zone of gasoline reached the tank bottom no second hot zone was formed. Instead, the temperature rose uniformly sometimes with apparent superheating and consequent eruptions.

The non-hot-zone-forming combustibles tested were a gas oil, a diesel oil, a transformer oil, and four lubricating oils. When these burn the flames are fed by complete vaporization of the oil from the surface layer without forming a liquid residue and without affecting the composition and temperature of the bulk of the liquid.

The forementioned tests were followed by a brief study of agitation (by air and oil injection) of the tank contents to reduce the liquid surface temperature and thereby effect fire control. By injecting air at the tank bottom, fires of the non-hot-zone-forming oils were extinguished unless the flash point was too low (below 40°C.) or the viscosity too high.

In the class of hot-zone-forming materials, fuel oil fires were successfully extinguished by air agitation. The burning rate of crude oils was reduced drastically but complete extinguishment did not occur. Air mixing apparently does not reduce the burning rate of gasoline sufficiently for effective fire control. However, the occurrence of superheating leading to eruptions is averted by agitation.

It is concluded that for non-hot-zone-forming materials agitation possesses no advantage over the top application of foam in fire extinction. In the case of hot-zone-forming-substances (except gasoline) agitation as a pretreatment for the application of foam is recommended. The hazard of eruptions and boilovers in the application of aqueous foams to a hot oil is reduced by circulation and by the attendant surface temperature reduction. Several tests with fuel oil burning in a 9 ft. diameter tank gave limited indication of the promise of utilizing agitation in fighting large fires.

Subject Headings: ***Petroleum fires; Tank fires.***

George A. Agoston

X. Meteorological Interactions

Byram, G. M. (Southeastern Forest Experiment Station, Asheville, North Carolina) "Atmospheric Conditions Related to Blowup Fires," Station Paper, **35**, 34 pp. (April 1954)

This report presents the results of a four-year study by the Southeastern Forest Experiment Station of certain atmospheric factors connected with the problem of extreme fire behavior. This study was conducted in an attempt to answer the question, "What can we do to recognize the conditions causing extreme fire behavior and how can we predict them in advance?"

A fire which exhibits extreme fire behavior is termed a "blowup" fire and occurs when a fire suddenly and unexpectedly burns with an intensity which seems to be far out of proportion to apparent burning conditions.

From a study of atmospheric conditions accompanying a number of blowup fires, the following main features appear:

1) Fuels are dry and plentiful.
2) The atmosphere is either unstable or was unstable for some hours, and possibly days, prior to the fire.
3) The wind speed of the free air is 18 mph or more at an elevation equal to, or not much above, the elevation of the fire.
4) The wind decreases with height for several thousand feet above the fire with the possible exception of the first few hundred feet.

The approach used in this study was the case-history method preceded by analytical work on the energy processes in fire behavior and the manner in which these processes are affected by atmospheric conditions. The data for the case histories were obtained from climatological data and soundings, fire reports, and eye-witness accounts of the fires.

The analytical work indicated in advance some of the fire behavior characteristics one might expect, as well as some of the conditions to look for in the upper atmosphere. A complete analysis of the energy conversion process was beyond the scope of the report but is discussed briefly in the appendix to the report.

The facts of extreme fire behavior were taken from known conditions associated with blowup fires. Many seeming contradictions which any effective solution must resolve are noted in the following list:

1) Blowup fires have occurred during the turbulent and unstable conditions of the afternoon and during the evening when the lower layers of the atmosphere were usually stable.
2) These fires have occurred in both rough and nearly flat or rolling country.
3) These fires have traveled at times with the wind and at other times against it. They have also traveled upslope and downslope, which indicates that terrain had no influence on their behavior.

4) Although extreme fire behavior is connected with turbulent, warm, sunny days, sometimes a fire will not build up to extreme intensity on these days.
5) Intense fires have occurred on windy as well as relatively calm days.
6) Blowup fires have burned on both high temperature and low temperature days if the relative humidity was low.

Other facts of extreme fire behavior which are not contradictory include the following:

1) The amount of fuel available to a fire is an important factor and an increase in fuel may cause a more than proportionate increase in fire intensity.
2) Arrangement and quantity of fuel are important. Extreme fire behavior seems most likely to occur in dense growths of trees or brush.
3) An obvious and well developed convection column which may extend high into the atmosphere is present in blowup fires.
4) Blowup fires have caused convection columns which have reached a height of 25,000 ft. or more. These columns were volume phenomena and had storm characteristics like certain other disturbances in the atmosphere.

The apparent contradictions in extreme fire behavior, plus certain basic physical principles, indicate the existence of a single over-all unifying concept which would be consistent with all of the facts of fire behavior. The energy concept seems to meet the unifying requirements. It can be reduced to three groups of factors:

1) Stability conditions in the atmosphere
2) Wind speed and wind shear in the atmosphere
3) Fuel and stand conditions

The atmosphere is unstable if the temperature decreases upward at a rate of 5.3 degrees or more per thousand feet. Instability is a condition which causes turbulence. Turbulence seems to affect the behavior of fires both directly and indirectly.

The direct effects of turbulence occur during the period of instability in the afternoon and causes fires to crown easily and travel rapidly upslope. Winds are gusty and variable, especially near the fire. The direct effects reach their peak when relative humidity and fuel moisture are lowest.

The greatest and most dangerous effect of turbulence is its indirect influence on fire behavior. The lower air moves faster than the upper air and the maximum speed occurs at or near the elevation of the fire. This action creates a miniature model of a jet stream which is called a jet current. The altitude of maximum velocity in this jet current is termed the jet point and is somewhere between ground level and a height of 1000 ft.

The decrease of wind velocity with altitude permits a fire to build its convection column. During this building the fire converts part of its heat energy into turbulent energy, which in turn drives the fire to an ever increasing intensity. The blowup fire is in effect a large heat engine capable of transforming a part of its heat energy into the destructive turbulent or kinetic energy of motion. A convection column is produced in which the expansion and cooling of hot gases completes the energy transformation. Some of the technical aspects of the convection column and the energy conversion process are given in the appendix to the paper.

A group of wind speed profiles observed on blowup fire days is presented in graphical form for five large blowup fires. These are the Hoffman fire and Buckle Island fire in North and South Carolina, respectively; the McVey fire in South Dakota; the Rattlesnake fire in California; and the Mann Gulch fire in Montana.

In addition to the general decrease in wind speed with altitude during these fires, the wind speed profiles are comparable for all five fires.

The average wind speed near the fire elevation for these fires was 21–22 mph. These speeds seem to fall into a critical wind zone in which the power of the wind surpasses the power developed by the fire heat engine. Perhaps the critical wind speed zone should be regarded as a "tug-of-war" region in which fire behavior dominance passes alternately from the wind to the fire. Also the wind speeds in this zone may be those which enable the heat zone to operate most efficiently.

The tendency of the wind speed profiles to fall in fairly definite classes at those times when extreme fire behavior exists suggests the possibility of some type of simple classification such as numerical or graphical classification. However, for a preliminary system and for simplicity the author felt it was desirable to use either the actual profiles at the time of specific case-history fires, or composites of actual profiles.

This was the procedure followed in the report and can be thought of as the beginning of a "rogues' gallery" of extreme fire behavior information. It is known that extreme fire behavior came on days when the wind speed profile could be classed in one of the six types listed in the report. It is also known that there was a considerable difference in behavior between certain types and even within a single type. With a description of each of the profile types listed in the report there is given a description of the corresponding fire behavior characteristics, which the author believes may occur with a given wind profile type.

No temperature profiles were included in the report since little work had been done on them at the time of preparation of the report.

For convenience, the case-history fires in this study were summarized in a table which lists the name of each fire, its location, the date, the wind-speed profile type, the final size of the fire, and brief comments on the fire's particular charateristics. Seventeen blowup type fires are listed; in five of these there was loss of life, and there were narrow escapes in others.

In recognizing and predicting conditions which may cause extreme fire behavior the first important factor is recognizing when a dangerous wind-speed profile exists, and the second factor is recognizing when an area becomes safe. The pilot balloon is one of the simplest devices for aiding in this analysis.

The prediction of jet currents and their growth and decline is a problem in basic meteorology and is beyond the scope of this report. Turbulence, stability, and jet currents appear to be related and possibly turbulence could have a delayed action in its effect on the strength of jet currents at a later time. Long range predictions of 12 hrs. or so are not possible yet but the prospect of an accurate 3–4 hr. prediction of wind-speed profile and direction profile seems good.

Even without instruments, there are signs that give warning of unusual burning conditions. They include:

1) High burning index and high buildup index
2) Gusty and variable winds with wind speeds of 15 to 25 mph at the weather bureau stations
3) Convection column tending to curve upwards and becoming nearly vertical in its upward parts
4) Spot fires occurring more than 600 ft. ahead of the main fire
5) Spot fires forming straight line or curved patterns
6) Passage of a dry cold front
7) Turbulent winds before the passage of a cold front due to changing of wind direction

8) Dust devils or dust whirls over plowed fields
9) Towermen or lookout men on 4000 to 5000 ft. peaks reporting lower wind velocities than exist at lower elevations and airport wind velocities of 15 to 20 mph.
10) Bumpy flying earlier than usual in the morning

These points should be noted in future observations on unusual fire behavior since all of them are valuable to the researcher studying the problem of blowup fires.

When blowup conditions are known to exist, the only effective period for controlling a fire is when it is small since actual blowup probability increases rapidly with increasing size.

Concepts of what may cause extreme fire behavior are becoming sufficiently developed and specific to be tested experimentally. However, even before the final answers to the problem are obtained, the group now studying blowup fires should provide increasingly effective guidelines to the fire fighter.

The appendix includes wind-speed profiles and direction profiles for several blowup fires. The McVey fire, which occurred in the Black Hills of South Dakota in 1939, is analyzed in detail as an example of an actual blowup fire. The energy conversion, convection column structure, and wind profile of a hypothetical blowup fire is discussed briefly.

Subject Headings: ***Blowup fires; Atmospheric conditions related to blowup fires.***

Alan W. McMasters

Small, R. T. (U.S. Weather Bureau Airport Station, Boise, Idaho) "The Relationship of Weather Factors to the Rate of Spread of the Robie Creek Fire," *Monthly Weather Review*, **85**, 1–8 (1957)

This article is a case study of the behavior of a large fire (8310 acres) as it responded to changing weather during its five-day existence (September 5–9, 1955). Weather conditions could be closely followed as the fire was only 10–15 airline miles east-northeast of the Boise Weather Bureau Airport Station (elevation 2858 ft.), where there is a complete program of surface and upper air observations. Weather was also observed at Shafer Butte Lookout (7590 ft.) and Idaho City Ranger Station (3950 ft.), 6 mi. northwest of the fire and 12 mi. northeast of the fire, respectively.

The fire itself was located on the southeast facing slopes of a 5000 to 6000 ft. ridge running north-south between Boise and the fire. Starting at about 5000 ft. elevation, the fire eventually spread over a range of 4000 to 5500 ft. It burned in fuels consisting of dry grass, several kinds of brush, and second-growth Ponderosa pine. Fuel moisture had been reduced by 21 days of above normal maximum temperatures and a period of 45 days since measurable rain.

The fire started in dry grass and chokeberry on a southeast slope at 2 P.M. September 5. The extreme burning conditions then present are indicated by the 101°F. temperature and 6 per cent relative humidity reported by Idaho City Ranger Station. Although surface and upper winds were light, spread on the first day was so rapid as to defy the efforts of fire fighters. Twelve hundred acres burned the first day and 3700 acres the second under similar weather conditions. Fire behavior was similar on these two days and was characterized by a cumulus cloud-capped smoke column producing a " 'chimney effect' reaching to an estimated 25,000 to 30,000 feet which induced a strong draft at the base of the column." The author suggests that this is a type of blowup fire that would be classed by Arnold and Buck as "fire burning near a cell of vertical air circulation."

Weather on the third day was similar to that of the preceding two except that winds above 10,000 ft. were definitely stronger. The fire, however, was comparatively inactive, burning only 300 acres, mostly at night. Maximum temperatures near the fire were lower than on the previous day although there was no decrease in temperature of the air mass on the 8 P.M. raob. This is believed to indicate a shallower superadiabatic layer during the day, a condition possibly related to fire behavior.

The fire became active on the fourth day driven by steady westerly winds bringing in a cooler, more stable air mass with slightly higher humidities. Boise winds at fire level and the Shafer Butte wind were near 20 mph. The smoke column was inclined toward the east and did not extend so high, though occasional cumulus puffs did appear. Moving with the wind, the fire covered another 3100 acres under blowup conditions classified by the author as "fire exposed to steady-flow convection wind" in the Buck-Arnold types.

On the fifth day, temperatures remained cool and the winds at fire elevations were light, although a layer of faster winds developed in the afternoon at around 8000 ft. The fire remained quiet although dust devils were observed within the burn. By this time fire lines were well established.

The author gives considerable attention to interpreting the winds aloft at Boise in terms of Byram's wind-speed profiles. Although the profile on the first day is a "safe" 4-c, the presence of the fire on a slope converts the profile to the dangerous 1-a type with fast wind near the surface. On the second day, the presence of faster winds or "jet point" immediately above the fire elevations is similar to type 3-a which is said to be conducive to whirlwinds and rapid spread. Observed spotting ¼ mi. ahead of the fire was thought to indicate the presence of whirlwinds. On the third day a type 1-b profile prevailed with stronger winds above 10,000 ft. tending to prevent formation of a convective column which might have induced strong winds at the surface. The faster surface winds and increasing speed aloft on the fourth day were typical of type 4-a which produces "intense and fast-spreading fires" that are not erratic or unusual and "could not be considered dangerous to experienced crews." The wind profile on the fifth day was similar to types 1-a and 2-a and showed faster winds aloft that would have been important had they descended to fire elevations. The author stressed that important differences in fire behavior were explained by profile differences, whereas they were not explained by the other weather variables.

In conclusion, the author notes that it is difficult in predicting to distinguish between blowup days and quiet days. He suggests that additional research may find ways of utilizing such information as the depth of the superadiabatic layer. Although he found merit in Byram's wind profile types, these also would be difficult to predict. Current upper-air observations with a mobile rawinsonde unit are recommended for the fire-weather forecaster at going fires.

The significance of this case study lies in the use of the latest hypotheses relating weather conditions to fire behavior. The author gives careful attention to Byram's wind profile types and to the Buck-Arnold classification of atmospheric conditions leading to blowup fires. This study is also significant because of the fire's proximity to an upper-air observation station. An unusual feature is the striking photographs of the fire convection column. Although no new basic information is presented, the manner in which this fire's behavior is investigated is new.

Although most accounts of fires neglect the role of weather, this article may be open to criticism for its neglect of non-meteorological factors. The impression is created that the Robie Creek fire was a meteorological phenomenon that responded in expected ways to certain weather conditions. Neglected are the location of the burning edge in relation to topography, the diurnal wind effects, the effect of nonhomogeneity of fuels, and the effects of fire suppression activities. Pertinent comments on the action of the fire front itself would have been helpful for interpreting the influence of the weather on fire behavior and the existence of blowup conditions. Without this additional information, one cannot judge whether or not the fire acted in a normal and predictable manner as influenced by surface conditions alone.

The term "blowup" is used as if to describe a definite and well-known phenomenon. This is probably undesirable in a scientific account of fire behavior. The author's application of the Buck-Arnold classification of atmospheric conditions under which blowups may occur is also open to question. On the first and second days the fire may or may not have been "burning near a cell of vertical air circulation", although it certainly produced such a cell of its own. Nor is there any indication that the fire was exposed to a "steady-flow convection wind" on the fourth day. Certainly the wind was steady, but the inflow of cold air following a cold front is not usually considered a convection wind. There is, therefore, a lack of evidence that there was actual blowup behavior under the given definitions.

Despite possible criticisms, the article is quite interesting and accomplishes the valuable service of introducing fire behavior to the meteorologists and meteorology to fire control specialists.

Subject Headings: ***Weather factors related to fire spread; Fire spread, weather factors.***

Owen P. Cramer

Schaefer, V. J. (The Munitalp Foundation, Inc., Schenectady, New York) "Relationship of Jet Streams to Forest Wildfires," *Journal of Forestry*, **55**, 419–425 (1957)

In this paper the author emphasizes the fact that the combination of a number of meteorological conditions (prolonged rise in the burning index, onset of local subsidence, presence of a jet current) results in an environment conducive to blowup fires. The information concerning the relationship of meteorological conditions, particularly jet streams, to forest wildfires was obtained by direct observations in the field and by analysis of jet charts in conjunction with records of recent blowup fires.

Although the jet stream is usually at the 25,000 to 35,000 ft. level, gusty winds may be observed at ground level. These winds are warm and dry, becoming a driving force for catastrophic wildfires. Frequently "clouds" of positive ions are observed concurrently with the low-level gusty winds; the significance of the ionization is not clearly understood. When the gusty ground winds, which are related to a high-level jet stream, occur it is commonly found that the axis of the jet stream is swinging. Two immense jet streams may form a zone of conflict which also results in ground level winds. The author states that the primary atmospheric structure associated with the occurrence of gusty ground winds in connection with a jet stream is the horizontal Bénard cell.

The author personally observed and studied the 1956 Dudley Lake fire in Arizona. Low relative humidity coupled with 35–50 mph winds caused the fire to burn until it ran out of fuel. Smoke remained as a coherent stream for at least 300 mi. Time-lapse movies revealed a Bénard cell having a diameter of about 6000 ft. Corona current measurements at the leading edge of the fire were correlated with the smoke density. Data relating jet streams to other large blowup fires in western forests during 1955 and 1956 are also given.

The energy necessary to produce the widespread effects for extended periods of time can be accounted for by consideration of the jet stream. The author concludes that additional study is required before the physical mechanism involved is sufficiently well understood to enable forecasting of dangerous conditions.

Subject Headings: ***Forest fires related to jet streams; Jet streams related to forest fires.***

A. E. Fuhs

Faure, M. and Pugnet, M. (National Hydraulic Laboratory, 6 Quai Watier, Chatou (S. and O.), France) "Report on the Tests Relative to Convectional Currents Due to Large Surface Fires," *Ministry of the Interior, National Services of Civil Protection, Special Report Series A* (September 1956). Translated by Malcolm, U.S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia.

The purpose of this report, as stated by the authors, is to determine the distribution of pressure, temperature, and velocity resulting from convective currents associated with large surface fires. It was felt that such knowledge would be useful in establishing rational techniques for controlling large surface fires.

The first portion of the report is concerned with the theoretical aspects of convective heat transfer. A short discussion of forced and natural convection is presented in which the physical mechanism of natural convection is emphasized. The steady state, three dimensional equations expressing conservation of mass, momentum, and energy are presented. The momentum equation includes a gravitational body force arising because of density gradients within the fluid. The energy equation includes convective enthalpy transport and transport by conduction. It is shown that if the conservation equations are written in a nondimensional form, three familiar dimensionless groups appear, namely, the Reynolds number, Prandtl number, and Grashof number. The equations are then applied to the problem of free convective heat transfer from a point source of heat. The solution to the equations is based on the work of Chia-Sun-Yih.* The mathematical treatment leaves much to be desired from the standpoint of clarity, and the results are rather difficult to interpret because of the sketchiness of the mathematical treatment. There is a lack of continuity between the theoretical treatment and the experimental phase of the report.

The experimental studies described in the report are of two types. The first part of the experimental investigation was concerned with the measurements of temperature, pressure, and velocity above heated metallic plates. The second part of the experimental investigation was a qualitative observation of fires of liquid fuels burning in large pans.

Five tests were performed with heated plates, two with a 50 cm. plate and three with a 100 cm. plate. The plates were heated electrically, and each test was performed at a different plate temperature. The plates were embedded in sand to the top surface of the plate in order to eliminate disturbing convective currents originating from the heating coils underneath the plate. All measurements were made along the vertical axis of the plates, the plates being oriented horizontally.

Pressure measurements, made with a micromanometer which read to 1/100 mm. of water, indicated no measurable change in pressure along the plate axis.

Velocity measurements were made by means of a flow visualization technique using the lint of goose down as the flow tracer. The only quantitative velocity data presented indicated that the lateral velocity of the incoming air near the surface of the plate varied from 10 to 15 cm/sec for all plates and all temperatures. The vertical velocity at a height of one plate diameter above the plate surface ranged from 70 to 140 cm/sec, depending on the plate size and temperature. There is insufficient data presented to gain an insight into the entire velocity field.

The temperature measurements indicated that the temperature along the plate axis could be described exponentially by the relationship:

$$\Delta T = C_1 e^{-C_2 \frac{h}{D}}$$

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* Chia-Sun-Yih "Free Convection Due to a Point Source of Heat" *Proceedings First U. S. National Congress of Applied Mechanics*, p. 941 (1951).

where ΔT = temperature difference between point of measurement and the ambient temperature

h = height above plate at which the temperature was measured

C_1 and C_2 are empirical constants which depend on the plate diameter and the power dissipated per unit area of plate surface

The second part of the experimental investigation was primarily a photographic study of the burning of liquid fuels in pans. The data also included a pressure-time study of the pressure above the fires during the time interval between initiation of combustion and extinction of the fire. The point at which the pressure was measured was not stated. The pressure-time trace was considered by the authors to substantiate a three-stage combustion process for fires of the type investigated, *i.e.*, (1) ignition, (2) combustion, and (3) extinction. The ignition stage was characterized by a pressure rise followed by a decrease in pressure to a negative value (relative to the ambient pressure). A similar pressure-time pattern was observed for the combustion stage except of a larger order. The pressure was negative over approximately the last half of the total time interval between initiation of combustion and extinction. The maximum pressure variation observed was of the order of 2 mm. of water.

There is little to be said concerning the numerous photographs of the pan fires presented in the report. The authors do not interpret the photographs, and this is understandable if one asks critically what fundamental information could be expected from direct flame photographs.

In summary, while it may be said that the laboratory approach to large surface fires described in this report is certainly worthwhile, the theoretical and experimental data presented in the report are inadequate for a generalized description of the significant parameters governing fires of this type.

Subject Headings: ***Surface fires, convectional currents; Convectional currents in surface fires.***

William T. Snyder

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Volume I January 1959 Number 2

Fire Research Abstracts and Reviews

Committee on Fire Research
and
Fire Research Conference

Division of Engineering and Industrial Research
NATIONAL ACADEMY OF SCIENCES—NATIONAL RESEARCH COUNCIL
Washington, D. C.

FIRE RESEARCH ABSTRACTS AND REVIEWS is published three times a year by the Committee on Fire Research and the Fire Research Conference of the National Academy of Sciences — National Research Council, 2101 Constitution Avenue, Washington 25, D. C. It is supported by the Office of Civil and Defense Mobilization, the U. S. Department of Agriculture through the Forest Service, and the Department of Defense under Contract CD-SR-58-45. The opinions expressed by contributors are their own and are not necessarily those of the Committee on Fire Research and the Fire Research Conference.

Fire research abstracts and reviews. v. 1–
Sept. 1958–
Washington, Division of Engineering and Industrial Research, National Academy of Sciences, National Research Council.

v. 26 cm. 3 no. a year.

Issued by the Committee on Fire Research and the Fire Research Conference.

1. Fire extinction—Abstracts. 2. Fire prevention—Abstracts. 3. Combustion—Abstracts. I. National Research Council. Committee on Fire Research. II. National Research Council. Fire Research Conference.

TH9111.F77 614.84082 58–60075 rev

Library of Congress

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FOREWORD

The organization and aims of *Fire Research Abstracts and Reviews* should become more apparent with this issue. This publication is to be a focus for the more scientific aspects of the fire problem. It is not intended, however, to be merely a repository of highly specialized abstracts and reviews, thereby neglecting a larger audience whose interest in fire is mainly in its prevention or extinction. Discoveries in the fire field will find rapid application only if the practitioner has been trained to keep a watchful eye on current developments and has been taught to understand the basic principles. To meet this goal, reviews will be included dealing with such topics as Model Fires, Flame Suppression, Water Sprays, etc. The current work and programs at research establishments where fire research plays a prominent part will be presented. This will serve to give a better perspective of the directions in which the fire problem is being attacked, and indicate where new and useful ideas are developing.

Thus, the scientists who contribute to the solution of the many difficult and intricate research problems will find in *Fire Research Abstracts and Reviews* a means of observing what progress is made in the several scientific disciplines. The practitioner in the art of fire suppression and prevention, on the other hand, may use this journal to keep posted on promising trends, and through deeper understanding, be prepared to accomplish his goals with greater confidence.

The appalling toll taken by fires in the United States alone (11,000 persons killed and a property loss of 1.3 billion dollars in 1958) demonstrates the magnitude and seriousness of the problem. For its solution the support and encouragement of all who are in a position to help is needed.

The response to the first issue of *Fire Research Abstracts and Reviews* was encouraging. Such interest from readers is of great value, particularly in suggesting topics of interest that are not now included. It would also be of great aid if authors of articles relating to fire problems were to forward their manuscripts or reprints for early review. This is particularly true for publications from Europe and Asia which are not easily and rapidly obtainable in the United States.

WALTER G. BERL

REVIEW

Certain Laws Governing Diffusive Burning of Liquids

by

V. I. Blinov and G. N. Khudiakov[*]

(*Reviewed by Hoyt C. Hottel*)

An interesting scientific paper dealing with fires burning from the surface of liquid fuels was published in 1957 in the Proceedings of the Academy of Sciences, USSR. This paper is an important contribution to the studies of model fires. It also indicates something of the scale of the Russian effort in this particular area. In his review, Professor Hoyt C. Hottel has added some interpretive comments of his own.—EDITOR

This paper on the natural burning of liquid petroleum products in pans is especially significant because of the wide range of pan size covered, sufficient to block out clearly the various burning regimes and to indicate, to investigators of fire modeling, the hazards associated with drawing conclusions from studies of too limited size range.

Gasoline, tractor kerosene, diesel oil, and solar oil (and, to a limited extent, household kerosene and transformer oil) were burned in cylindrical pans (depth not indicated) of diameters 0.37 cm. to 22.9 *meters*. Liquid burning rates and flame heights were measured, and visual and photographic observations of the flames were recorded. The quantitative results were presented in the original article in tabular form; they are summarized in the accompanying figure for which the present reviewer takes full responsibility.

The photographs indicate that as the pan diameter increases the flame structure, for any of the fuels, changes from a conical steady flame (1.1 cm. pans) to a pulsating-tip flame, of maximum frequency about 18–20 cycles per second (3 cm. pans). Further increase in pan diameter reduces the pulsations, but the unstable portion of the flame shifts downward until, for a 15 cm. pan, the entire flame is changing continuously in structure everywhere; and with 1.3 meter pans the random turbulent motion is fully established.

The lower curves in the accompanying plot show the liquid burning velocity v(log scale) plotted versus pan diameter d(log scale). Since the product of these is approximately proportional[†] to the Reynolds number (Re) of upward flow of vapor leaving the pan, it is possible to superimpose on the plot lines of constant Re running diagonally up to the left with a slope of -1. The burning velocity-pan diameter relation has the same general structure for all the oils. It first de-

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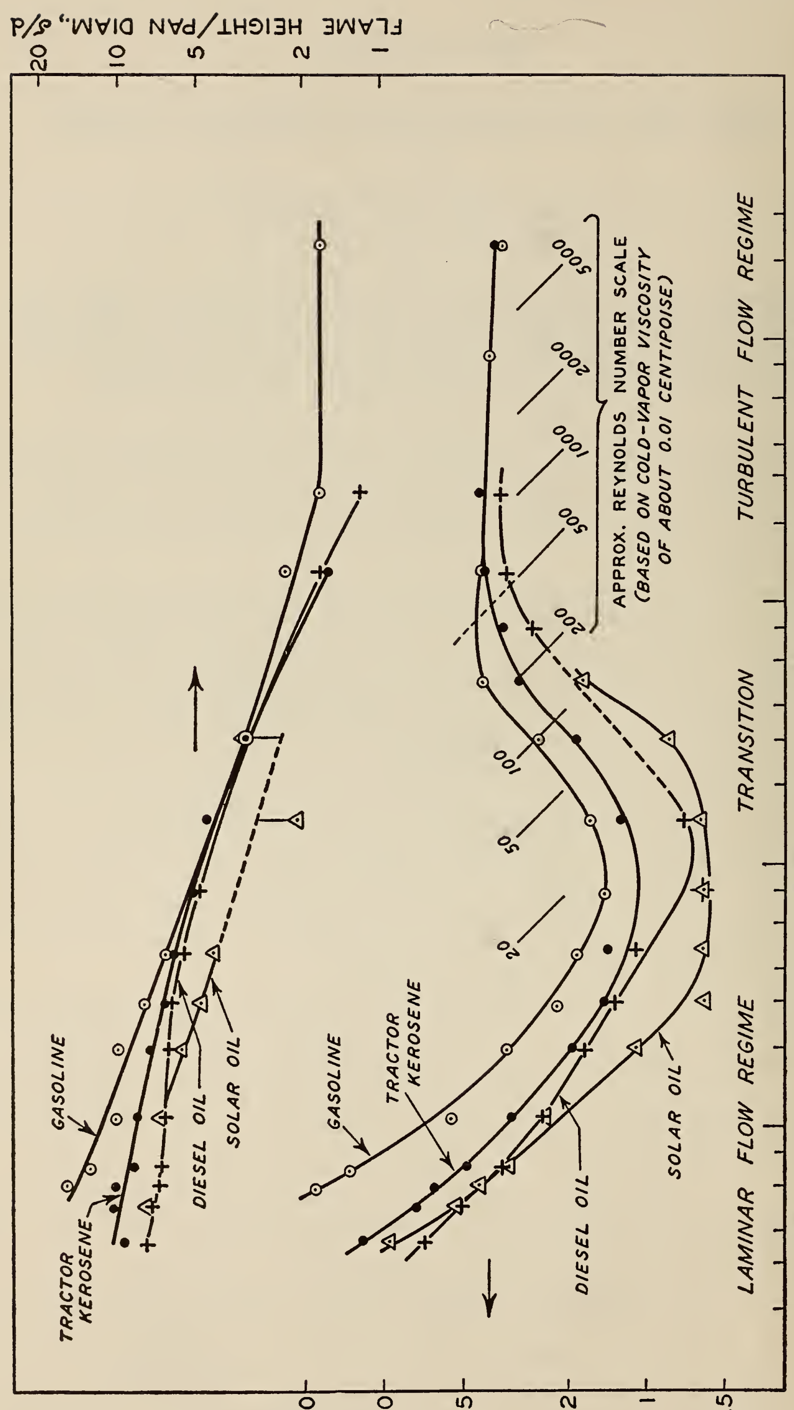
[*] Blinov, V. I. and Khudiakov, G. N. (Institute of Energetics of the Academy of Sciences, USSR) "Certain Laws Governing Diffusive Burning of Liquids," Academiia Nauk, SSSR Doklady, 113, 1094–1098 (1957).

[†] The original article gives no indication of properties used in evaluating Re in the tabulation, and the table adds some confusion by containing at least 2 numerical inconsistencies (e.g., for gasoline in 2 cm. pan, Re = 90, not 140). If d = pan diameter, (cm.), v = liquid burning velocity (mm/min) as given, then Re $(= dU_G\rho_G/\mu_G \equiv dU_L\rho_L/\mu_G) = (dv) \times \left(\frac{\rho_L,\ \text{gms/ml}}{600\ \mu_G\ \text{poises}}\right)$. The last term would be 1.33 if $\rho_L = 0.8$ and $\mu_G = 0.0001$ poise (reasonable values). That same term, inferred from values of Re and dv in table, is 1.24, 1.37, 1.40 for gasoline, tractor kerosene, and Diesel fuel, respectively. Your reviewer then used 1.4 for solar oil for which the table reported no Re; he further used a single factor 1.3 to establish the Re scale that appears on the plot.

factor of 10

factor of 10


FLAME HEIGHT/PAN DIAM., ℓ/d
20
10
5
2
1
v, LIQUID BURNING VELOCITY, mm/min
20
10
5
2
1
0.5
PAN DIAMETER, CENTIMETERS
(d)
0.4
1
2
3
4
6
8
10
2
3
4
6
8
100
2
3
4
6
1000
3000
LAMINAR FLOW REGIME
TRANSITION
TURBULENT FLOW REGIME
GASOLINE
TRACTOR KEROSENE
DIESEL OIL
SOLAR OIL
GASOLINE
TRACTOR KEROSENE
DIESEL OIL
SOLAR OIL
APPROX. REYNOLDS NUMBER SCALE
(BASED ON COLD-VAPOR VISCOSITY
OF ABOUT 0.01 CENTIPOISE)
20
50
100
200
500
1000
2000
5000

creases with increasing pan diameter, with an almost constant product of the two. This is the laminar flow regime, with Re less than about 20 (based on properties of the non-burning fuel vapor). With further increase in pan diameter the velocity decrease decreases, changes sign, rises rapidly in the range of Re from 20 to 200, and finally levels off again at a pan diameter about 1 meter or a Reynolds number of about 500. Above that value the burning is turbulent and the burning velocity is substantially uninfluenced by pan diameter or fuel type.

Flame lengths δ, expressed as ratios to pan diameter, appear in the top plot. A continuous decrease in the length ratio persists out to the turbulent regime where it becomes constant for the one fuel adequately studied (gasoline). Consider first the laminar regime. A constant negative slope corresponds to the relation $(\delta/d) \propto d^{-n}$. In the same regime the burning-rate curves may be expressed by the relation $v \propto d^{-m}$. These relations may be combined to give $(v)(d/\delta) \propto d^{n-m}$,

or
$$vd^2/\delta \propto d^{n+1-m}.$$

It will be noted from the plot that $-n$ is in the range -0.1 to -0.3 and that $-m$ is about -1.1 to -1.3, or that the exponent $n+1-m$ is near zero. Then vd^2/δ, which is proportional to the ratio of volumetric burning rate of liquid to flame height, is substantially constant in the laminar regime. This is a well-known result in studies of short laminar flames of fuel jets, where the flame length is found to be dependent on and roughly proportional to the volumetric flow rate of the fuel gas and independent of the nozzle diameter.

In the turbulent regime the flame length/pan diameter ratio is constant at high Reynolds numbers. This is also analogous to findings from studies of turbulent flames of fuel jets, where the flame length-diameter ratio is found to be independent of Reynolds number. The result is a consequence of air-fuel mixing by turbulent rather than by molecular transport.

The burning rate keeps pace with the fuel vaporization rate, which is heat transfer-controlled. The rate of heating q is the sum of q_1, q_2, q_3 representing the transfer rates from the pan rim, by convection, and by flame radiation, respectively. The authors call attention to the fact that in large reservoirs q_1 and q_2 are smaller than q_3 and that in consequence the constancy of burning velocity v for turbulent combustion indicates that the irradiation rate per unit of the liquid surface is independent of reservoir diameter. It is tempting to add, to this qualitative treatment of the authors, a simplified semiquantitative analysis. Let

$$q_1=k_1\pi d(T_F-T_B);\ q_2=U(\pi d^2/4)(T_F-T_B);\ q_3=(\pi d^2/4)\sigma F(T_F^4-T_B^4)(1-e^{-\kappa d}),$$

where U = convection coefficient; F = geometrical view-factor that the liquid has of the flame; κ = Beer's law extinction coefficient of the flame to allow for increasing opacity with thickness. Then the vaporization rate per unit of surface is given by

$$\frac{q}{\pi d_2/4}=\frac{k_1(T_F-T_B)}{d}+U(T_F-T_B)+\sigma F(T_F^4-T_B^4)(1-e^{-\kappa d})$$

Even with k_1, U, F, T_F and κ assumed constant (which they are not), this relation has a form which can be fitted to the burning-rate curves. At small d's the first term on the right will be large and cause the burning rate to be high. At large d's the first term will have disappeared completely, the second will be constant, and the third and dominant term will be constant because κd is so large. At intermediate d's the third term will be low because of the thinness of the flame but the pan will be too large for the first term to be significant; hence a minimum burning rate. Calculations based on the gasoline results indicate that on the basis of U = 1 (English units), F = ¼, and d large enough to make the flame opaque, the burning rate corresponds to radiation and convection from a flame at about 1600°F. or 1100°K.

Subject Headings: *Diffusion flames, burning rates of; Flame, diffusion, length of; Liquids, diffusive burning of; Petroleum products, burning rates of.*

ABSTRACTS

I. Ignition Phenomena

Lawson, D. I., and Simms, D. L. (Joint Fire Research Organization, Boreham Wood, England) "The Ignition of Wood by Radiation," *British Journal of Applied Physics,* 3, 288–292 (1952)

The time required to ignite wood spontaneously and in the presence of a pilot flame has been determined at varying irradiation intensities. For most species of wood, the minimum irradiation necessary for ignition was found to be constant for a given type of ignition. Equations relating time to ignition, intensity of irradiation, and thermal properties of the woods have been derived.

The materials examined ranged in density from 0.24 to 0.72 g/cm^3. Dried samples of fiber insulation board, western red cedar, American whitewood, African mahogany, freijo, oak, and iroko were irradiated by a one square foot surface combustion heater burning a coal gas-air mixture. The intensity of irradiation was varied between 0.15 and 1.5 cal/cm^2/sec by varying the sample distance from the radiator. A pilot flame was placed one-half inch above and in front of the wood. The time was measured for the pilot flame to ignite the combustible gases liberated from the sample. In the spontaneous ignition experiments, the time was measured for the specimen to burst into flames spontaneously. Maximum spontaneous ignition times were approximately 70 secs. whereas the maximum time for pilot ignition extended to 1000 secs. Mean variation of the measurements was ± 10 per cent while extreme variation approached ± 25 per cent.

Analysis of the results involves two assumptions: that the wood is inert, and that the surface cooling is Newtonian with no appreciable rise in temperature of the back surface. Thus the surface temperature rise θ, is given by

$$\theta=\frac{I}{\Psi}\left[1-\frac{1}{\Psi}\left(\frac{K\rho s}{\pi t}\right)^{1/2}\right]$$

where

K = thermal conductivity
ρ = density
s = specific heat
Ψ = rate of loss of heat per unit area for each degree rise in temperature
I = intensity of irradiation

A plot of I *vs.* $I/\sqrt{t}$ yielded straight lines with more or less common intercepts of the intensity axis as $I/\sqrt{t}\rightarrow 0$. For pilot ignition, this minimum intensity of irradiation, or I_0, was approximately 0.35 cal/cm^2/sec, except for fiber insulation board at 0.15 cal/cm^2/sec. For spontaneous ignition, the critical intensity was approximately 0.61 cal/cm^2/sec except for iroko which had a much higher value.

It is not unreasonable to expect that the critical intensity should be independent of the species of wood since it represents the energy required to ignite the wood after a long time, when transfer of heat into the wood has virtually ceased. At this point, the controlling parameters for ignition are the emissivity of the wood surface which is similar for most woods and the nature and proportion of the gaseous decomposition products. The differences in the critical irradiation intensities for iroko and fiber insulation board may be due to differences in their decomposition products.

A more pertinent relation between ignition time and intensity of irradiation was sought via the difference between the actual intensity and the critical intensity. A plot of log $(I-I_o)$ *vs.* log t gave straight lines. For pilot ignition, the equation derived is

$$(I-I_p)t^{2/3}=A$$

where A is a constant varying with the species investigated. For spontaneous ignition, the equation is

$$(I-I_s)t^{4/5}=B$$

where B varies with the species. Since it seemed reasonable to include in these equations an expression for the thermal properties of the materials, the values equated to A and B above were plotted *vs.* $K\rho s$. Straight lines were obtained. The final expressions linked the thermal properties of the woods, their time to ignition and the difference between the measured intensity of irradiation and the critical minimum irradiation. For intensities greater than the critical intensity the time t taken for pilot ignition is

$$(I-I_p)t^{2/3}=0.025\times10^6(K\rho s+68\times10^{-6})$$

while for spontaneous ignition it is

$$(I-I_s)t^{4/5}=0.05\times10^6(K\rho s+35\times10^{-6}).$$

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

G. M. Steffan

Stout, H. P. (Imperial Chemical Industries, Stevenston, Scotland) "Ignition of Wood by Radiation," *British Journal of Applied Physics,* **3,** 394–396 (1952)

The paper by Lawson and Simms* describes the ignition of various species of wood by radiation, both with and without a pilot flame. Their work is summarized in equations linking the difference between the measured irradiation and a critical intensity, $(I-I_o)$, time t, and the thermal conductivity K, density ρ, and specific heat s. Dr. Stout comments that the underlying significance of these equations is not clear. He proposes that a study of the total radiation energy would reflect more clearly the physical processes involved.

The total energy supplied before ignition is It cal/cm^2 and it increases as the time to ignition increases. Extrapolation of the energy-time curves to zero time gives the energy $(It)_0$ necessary for instantaneous ignition. For each wood these values were similar for both the pilot and the spontaneous ignition experiments. These energies divided by ρs, which is proportional to the thermal capacity of the wood, yielded reasonably constant values for all of the woods. Thus Dr. Stout suggests that all woods ignite instantaneously at a common temperature. Assuming a 0.5 mm. surface layer heated, the temperature rise would be 720°C, a reasonable value.

With increasing time, the energy required for ignition increases because of the loss of heat via conduction. This loss depends on $K/\rho s$, the thermal diffusivity, which Dr. Stout terms conductivity. This value proves to be much lower for fiber board than for the other woods and suggests why the required ignition energy was lower for fiber board.

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* See page 45.

Dr. Stout concludes by stating that wood ignition seems to require a critical amount of energy. It is at a minimum when generated instantaneously in a limited volume of the medium.

In reply, Lawson and Simms state that the minimum energy for instantaneous ignition would be reached more correctly through the expression $(I\sqrt{t}/(\rho s))_{t\to 0}=$ constant instead of $(It/(\rho s))_{t\to 0}=$constant as Dr. Stout suggested. Their supporting analysis attacks the problem as one similar to heat conduction in a thick plate exposed to steady radiation. It allows x, the depth of penetration of heat to approach zero to obtain the surface temperature, with time incidentally approaching zero also. The surface temperature, θ, is presented by

$$\theta=2I\sqrt{t/(\pi K\rho s)} \qquad (1)$$

although for this model, the temperature should be given by

$$\theta=2I\sqrt{tK/(\pi\rho s)} \qquad (2)$$

The simplified equation (1) applies only to times much shorter than those measured in their work. Consequently another approximation is presented.

$$\theta=2I\sqrt{\frac{t}{\pi K\rho s}}\left[1-\frac{\Psi}{2}\sqrt{\frac{\pi t}{K\rho s}}\right] \qquad (3)$$

A plot of $I\sqrt{t}$ *vs.* It proved to be linear, indicating the validity of this expanded expression. On this basis, the authors conclude that the simplified expression (1) is probably legitimate also within its range. Thus they conclude that the expression $(I\sqrt{t}/(\rho s))_{t\to 0}$ would be constant rather than Dr. Stout's expression $(It/(\rho s))_{t\to 0}$.

Finally, they suggest that the ignition of wood occurs when the surface reaches a fixed temperature rather than when it has received a fixed quantity of energy. The energy concept must be accompanied by an element of time or volume to be completely definitive. The conflicting expressions are due to the difference in choice of models, with the model of Lawson and Simms interpreting the experiments more closely.

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

G. M. Steffan

Lawson, D. I., and McGuire, J. H. (Joint Fire Research Organization, Boreham Wood, England) "The Prediction of Distance of Ignition of Wood from an Atomic Explosion," *Fire Research Note 227* (1955)

Prediction of the distance of ignition of wood from an atomic explosion to a first approximation, based upon constant radiation intensity for 3 secs., is refined to consider time-variant radiation intensity. It is shown that, for low density materials (fiber insulation board) under perfectly clear atmospheric conditions, the increase in distance from ground zero at which ignition takes place may be as much as 40 per cent greater than previous estimates; and that for medium or high density wood the increase is just over 10 per cent. The lower the visibility the less the percentage discrepancy between the present estimates and previous work. If a given quantity of radiation is applied rapidly, there is little time for an appreciable quantity of heat to be conducted away from the surface layers and the surface temperature is higher; conversely, less heat is required to bring the surface of wood to a given value the more rapidly the heat is applied.

Analogous electrical networks are used to represent one-dimensional flow of heat inside a slab and the simultaneous loss of heat by reradiation and convection. Lawson and Simms* have determined the minimum intensities of radiation to cause spontaneous ignition of wood after long-continued exposure; a constant value of 0.6 cal/cm^2/sec was found to apply to nearly all woods tested. Applying this value to the electrical analogue made to represent constant radiation intensity, the surface temperature at which wood ignites is found to be 480°C.

With the electrical analogue arranged to represent a time-variant radiation intensity similar in form to the heat pulse developed by an atomic explosion, the peak intensity necessary to raise the surface temperature to 480°C is determined for woods of various densities. Then, knowing the intensity required for ignition and the energy released by the bomb, the distance from ground zero at which ignition will take place under various atmospheric conditions can be determined.

Subject Headings: ***Atomic explosion, ignition of wood; Ignition, of wood by radiation; Radiation, ignition of wood; Wood, ignition distance; Wood, ignition by radiation.***

W. G. Labes

Wolfhard, H. G., and Burgess, D. S. (U. S. Bureau of Mines, Pittsburgh, Pennsylvania) "The Ignition of Combustible Gases by Flames," *Combustion and Flame,* 2, 3–12 (1958)

The authors report the results of experiments on the ignition of stoichiometric methane-nitric oxide mixtures by pilot flames burning in the mixture. These are preliminary experiments to attempt some clarification of the wider problem indicated in the title. The mixture chosen was amenable to simple experimentation whereas hydrocarbon-air or hydrocarbon-oxygen mixtures are difficult to investigate due to the very small ignition energies involved.

The experiments were conducted using a vertical tube 6.0 cm. in diameter and 50 cm. long with the small pilot burner mounted concentrically in the lower portion. The stoichiometric methane-nitric oxide mixture was passed round the pilot flame and filled the outer tube, back diffusion of air being prevented. The premixed laminar pilot flame consisted of carbon monoxide-oxygen, hydrogen-oxygen, acetylene-oxygen, and methane-oxygen in stoichiometric proportions and diluted by nitrogen admixture, the pilot burner diameter being varied as required to maintain laminar flow. Some experiments with rich and lean carbon monoxide-oxygen pilot flames are also reported. Ignition was observed by a loud report or the spreading of flame throughout the tube.

The results are given graphically with plots of the heat input of the pilot flame, assuming complete combustion, against the volume flow of the pilot required just to cause ignition.

For $(CO+0.5\,O_2)+N_2$ pilot flames the higher the flow the more nitrogen can be added. At pilot rates of about 60 cm^3/secs a stoichiometric carbon monoxide-air flame will just cause ignition. Similar results are obtained with the stoichiometric hydrogen, acetylene, and methane flames, but hydrogen-air and methane-air flames cannot ignite the methane-nitric oxide mixture. A rich pilot, $(CO+0.3\,O_2)+N_2$, gives identical results to the stoichiometric flame suggesting

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* See page 45.

that these pilots act as neutral heat sources. On the other hand lean pilot mixtures $(CO+0.75\,O_2)+N_2$, ignite more readily. Even allowing for the possible methane combustion from the surrounding mixture deviations from the previous two cases exist, though these tend to disappear as flow rate is increased.

By calculating the adiabatic flame temperature the limiting (*i.e.* just-igniting) pilot flames are reported by plotting ignition temperature against volume flow. To test the relative importance of flame temperature and total heat input, argon and carbon dioxide were substituted for nitrogen in carbon monoxide-oxygen-inert gas pilots. Although the critical heat input was altered by using argon and carbon dioxide in place of nitrogen, the limiting flame temperatures coincided with those using nitrogen as diluent for equivalent pilot flame mass flows.

With the larger and cooler pilot flames, ignition could be observed to be spreading from the column of hot burned gases above the pilot flame. Luminosity in this column is first observed, and by slightly reducing the nitrogen flow, flame spreads from this column throughout the outer tube. For the carbon monoxide, methane, and acetylene pilots the temperature approaches a constant value as the volume flow increases. The hydrogen pilot flame, on the other hand, does not reach a constant value.

Extrapolation of the curves to zero pilot flow gives the minimum energy (cals/sec) required to ignite methane-nitric oxide mixtures, if the energy is delivered at a point source at a very high temperature.

Since the temperature of a laminar pilot flame required for ignition becomes independent of size and is not identical with the spontaneous ignition temperature, heated surfaces and heterogeneous reactions being absent, the authors propose to call this temperature the "hot-gas ignition temperature." This temperature is significantly higher than the spontaneous ignition temperature (1110°C) determined separately by the authors for stoichiometric methane-nitric oxide.

In the future, the authors intend to report on hydrocarbon ignition, which is likely to have important practical applications.

Subject Headings: *Flame, ignition of combustible gases by; Gases, combustible, ignition by flames; Ignition, of combustible gases by flames.*

M. G. Perry

II. Thermal Decomposition

Madorsky, S. L., Hart, V. E., and Straus, S. (National Bureau of Standards, Washington, D. C.) "Pyrolysis of Cellulose in a Vacuum," *Journal of Research of the National Bureau of Standards,* 56, 343–354 (1956)

The paper under review is one of a series dealing with the thermal degradation of various high polymers at elevated temperatures. From the fire research point of view the effects of temperature on the decomposition of cellulose are of considerable interest in explaining how this material decomposes and burns and how fire-resistant treatments affect the decomposition reaction.

It is postulated that flaming of cellulose takes place in two principal steps. The high-polymer cellulose is first degraded under the influence of heat to form volatile and nonvolatile products. The flammable constituents then ignite, the heat thus evolved promoting further decomposition. A lowering of the amount of the volatile and combustible material by chemical treatment should contribute to increasing the fire-resistance of the material.

Experiments were carried out to investigate the nature of the decomposition products and the rate of decomposition with and without inorganic additives (sodium carbonate, sodium chloride). The reactions were run in a vacuum (10^{-3} to 10^{-5} mm. Hg) to prevent further interaction of the decomposition products with the surrounding gas and to insure rapid removal of the products away from the reaction zone to minimize secondary side reactions.

Cotton, hydrocellulose (cotton treated with 6N hydrochloric acid) and regenerated cellulose (viscose) were investigated. The apparatus consisted of an all-glass system where the cellulose was rapidly heated and then held at constant temperature in a furnace. The products of decomposition were pumped away with a mercury pump. The volatile fractions were separated by freezeout at −80°C and −190°C. Five fractions were obtained, the nonvolatile residue resulting from the heat treatment, a pyrolysis fraction which was volatile at furnace temperature but not at room temperature (V_{pyr}), a fraction volatile at 25°C but not at −80°C (V_{25}), a fraction volatile at −80°C but not at −190°C (V_{-80}) and a noncondensable fraction (V_{-190}).

With all cellulose samples, V_{-190} consisted almost entirely of carbon monoxide, V_{-80} was mainly carbon dioxide, V_{25} was composed of water with small amounts of acetaldehyde, while V_{pyr} was identified as levoglucosan ($C_6H_{11}O_6$) with a small amount of another unidentified substance. The identity of levoglucosan was established by similarity of mass peaks in a mass spectrometer with a sample of pure levoglucosan, by its infrared spectrum and by molecular weight determination. The decomposition temperatures were chosen near 300°C where the reactions proceeded with reasonable speed. The behavior of cellulose and hydrocellulose were quite similar, while the viscose decomposition was somewhat slower. A typical decomposition of cellulose after 11 hours at 200°C yielded 70 per cent volatile products, which were made up of 65 per cent tar (V_{pyr}), 27 per cent water, 6 per cent carbon dioxide, and 2 per cent carbon monoxide. Impregnation with sodium chloride or sodium carbonate produced a marked shift in the distribution of the volatile products, the tar now representing only 12 per cent of the volatile fraction.

Rates of reaction were obtained by heating the cellulose in a boat suspended on a tungsten spring. The weight changes were obtained by observing the change in extension of the spring as a function of time. Excepting the salt-impregnated fibers, the reactions would start slowly, reach a peak rate, beyond which they slowed down in a linear manner. The curves can be extrapolated to zero time to give "initial" rates or extrapolated to zero reaction rate to obtain the carbonization end point.

With impregnation, the initial rates were fast from the beginning, indicating that the thermal stability of the cellulose chain was much reduced. Thus, the effect of sodium carbonate and sodium chloride on the pyrolysis is considerable, reducing the tar yield drastically, increasing the amount of nonvolatile residue and giving high initial reaction rates, followed by relatively rapid reaction.

The results of the study indicate that for pure cellulose in vacuum, half of the structural units of the cellulose are converted to levoglucosan. Additional units are broken down to carbon dioxide, carbon monoxide, and coke. By far the most important volatile combustible breakdown product is levoglucosan. Presence of salts has a catalytic effect on the dehydration and bond scission, resulting in increased yields of water, carbon dioxide, and carbon monoxide at the expense of levoglucosan, and also in an increased rate of degradation of the cellulose, particularly in the initial stages.

These experiments are of considerable interest in identifying some of the early steps in the complex reactions during the combustion of organic high-molecular weight compounds. The modifying effect of inorganic additives on the rate of formation and the nature of the products is noteworthy.

Subject Headings: ***Cellulose, thermal decomposition; Thermal decomposition, of cellulose.***

W. G. Berl

Madorsky, S. L., Hart, V. E., and Straus, S. (National Bureau of Standards, Washington, D. C.) "Thermal Degradation of Cellulosic Materials," *Journal of Research of the National Bureau of Standards,* **60,** 343–349 (1958)

This paper is a continuation of an investigation on cellulose,* extending it to cellulose derivatives (cellulose triacetate, NO_2-oxidized cellulose). Several new experiments with cellulose are also reported which supplement the earlier report. In particular, pyrolysis of cotton in nitrogen at atmospheric pressure was carried out and compared with the vacuum experiments previously reported. It was found that in the presence of nitrogen the rates of formation of volatile products did not change appreciably. However, the composition was altered in favor of increased amounts of water, carbon dioxide, and carbon monoxide at the expense of the tarry material.

This indicates that in the presence of gas the tar molecules remain in the hot reaction zone long enough so that an appreciable part will undergo secondary decomposition. In vacuum, on the other hand, the larger tar fragments escape from the hot decomposition zone without further decomposition.

Subject Headings: ***Cellulose, thermal degradation; Thermal degradation, of cellulose.***

W. G. Berl

Schwenker, R. F., Jr., and Pacsu, E. (Textile Research Institute, Princeton, New Jersey) "Chemically Modifying Cellulose for Flame Resistance," *Industrial and Engineering Chemistry,* **50,** 91–96 (1958)

Pyrolysis in air at 350°C of unmodified cellulose and of oxidized cellulose indicated that the former gave appreciably more levoglucosan (1,6-anhydro-β-D-glucopyranose). Important differences in burning behavior also were noted; unmodified cotton flamed vigorously, and quickly produced a small quantity of char that was completely reduced by afterglow to an ash residue. By contrast, the oxidized cellulose burned in a desultory manner leaving a bulky char with practically no afterglow. This seems to be related to the fact that for oxidized (modified) cellulose eliminating the hydroxyl groups in the number 6 position by oxidation had prevented formation of levoglucosan. This work thus provides support for the theory that the thermal degradation of cellulose proceeds by depolymerization and intramolecular rearrangement to give levoglucosan as an intermediate and that the flammability is due to the further breakdown of the intermediate to give flammable gases and tars. The implication is that prevention

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* See page 49.

of levoglucosan formation by chemical means could result in decreased flammability of the resultant cellulose derivative.

The working hypothesis based on this work is that suitable chemical modification of the primary alcohol group at the number 6 carbon of the glucose anhydride unit of the cellulose chain prevents formation of levoglucosan in those glucose residues so modified. A modifying agent was sought having preferential reaction with the number 6 hydroxyl group, of low molecular weight, preferably without a benzene nucleus, and replaceable by halogen to produce a modification stable over a reasonable pH range.

Methanesulfonyl (mesyl) chloride was selected but "mesylation" was found insufficient to give flame resistance and further modification by introducing flame retardants was tried. A suitable method was discovered for preparing partially substituted iodo, bromo, chloro, and fluoro derivatives of mesyl cellulose. This involved esterifying cellulose hydroxyl groups with methanesulfonyl chloride and partially replacing mesyloxy groups by halogen.

While chlorine and fluorine seem to have little value as flame retardants, bromine is quite satisfactory. Iodine is the most effective retardant. It is suggested that a more complete reaction occurs during iodine replacement.

Glow resistance was improved by introducing phosphorus-containing groups in another esterification reaction. The resultant derivatives using cellulosic fabrics as starting material constitute new textile materials. They have not yet been produced in sufficient quantity for full mechanical tests but preliminary tests are encouraging.

It is concluded that the efficiency of the halogens as flame retardants in chemical combination with cellulose is in the order: iodine>bromine>chlorine>fluorine. The flame resistance is caused by a reduction in the amount of flammable products and by the release of bromine or iodine in elemental or free radical form to act as a chemical inhibitor to flaming.

Subject Headings: *Celluose, modification for flame resistance; Flame, resistance of cellulose to.*

R. Long

Flynn, J. H., Wilson, W. K., and Morrow, W. L. (National Bureau of Standards, Washington, D. C.) "Degradation of Cellulose in a Vacuum with Ultraviolet Light," *Journal of Research of the National Bureau of Standards,* 60, 229–233 (1958)

The photochemical degradation of cellulose has been extensively investigated since it is an important cause of deterioration of textiles and paper. Sheets of cotton cellulose, dried and purified, were irradiated in a vacuum at 40°C with light of 2537 Å. The amount of degradation was independent of the presence of oxygen during irradiation and was inhibited by water vapor. Some decomposition took place subsequent to the irradiation period indicating the presence of labile dissociation products in the irradiated polymer.

The composition and rate of evolution of gaseous products were measured and changes in functional group content and degree of polymerization of the irradiated cellulose were determined. The cellulose was enclosed in an evacuated vessel and maintained at constant temperature. The samples were irradiated with five calibrated Hanovia quartz low-pressure mercury lamps spaced evenly about the interior of an etched cylindrical aluminum reflector.

Hydrogen (87.5 mole per cent), carbon dioxide (4.3 per cent), and carbon monoxide (8.2 per cent) were evolved during irradiation. The fraction of hydrogen decreased with increase in irradiation time. A plot of the square of the reciprocal of the rate of hydrogen evolution versus irradiation time gave a linear relationship. The rate of evolution of carbon dioxide and of carbon monoxide remained relatively constant and was proportional to the first power of the intensity.

The degree of polymerization decreased approximately threefold in a particular run. Simultaneously, the number of CHO groups increased twentyfold while the carboxyl ($-COOH$) content increased fourfold.

Interruption of irradiation and evacuation for several days did not change the rate of gas evolution. A period of treatment with hydrogen followed by evacuation also had no effect. Treatment with oxygen caused a temporary decrease in the rate of gas evolution when irradiation was resumed.

This is the first recorded evidence of hydrogen evolution by cellulose during irradiation with ultraviolet light. The prolonged degassing of the cellulose and the condition of high vacuum during irradiation may have removed traces of absorbed oxygen, water, or other materials that either inhibited hydrogen formation or reacted with hydrogen atoms before they could combine to form hydrogen.

A possible explanation for the source of the hydrogen is given. From previous work it is known that alcohols when irradiated in gaseous or liquid phase below 2000 Å yield ketones and hydrogen. Simple aldehydes and ketones are decomposed photochemically in the gas phase to produce carbon monoxide and other products. Thus any primary hydroxyl groups which are oxidized to CHO groups during irradiation might be expected to produce hydrogen and carbon monoxide. Oxidation of secondary hydroxyl groups in cellulose will lead to ketones which subsequently break down to carbon monoxide and other products. The increasing carbonyl concentration at the surface of the polymer acts as an inhibitor for additional hydrogen production. On the other hand, decomposition of a larger number of carbonyl groups will lead to an increase in the appearance of carbon monoxide. This might explain the decrease in rate of hydrogen evolution and increase in carbon monoxide evolution after longer irradiation periods.

Subject Headings: *Cellulose, degradation by ultraviolet light.*

P. Breisacher

III. Heat and Material Transfer in Surface-Burning Solids and Liquids

Pavlov, P. P., and Khovanova, A. M. "Heat Transfer in Oil Products Burning from a Free Surface," *Symposium on Chemical Means for Fire Extinction and Fire Prevention, Moscow,* 100–116 (1954) Library Translation No. 113 Department of Scientific and Industrial Research and Fire Officers' Committee Joint Fire Research Organization (England)

Tests were conducted to clarify the behavior of oil burning at a free surface in an open-top tank, and particularly to investigate the mechanism of formation of a heated layer, which in some cases progresses downward to reach water at the tank bottom causing boiling and ejection of oil, sometimes called a "boilover." This information was sought as an aid in the development of apparatus and techniques for combating oil-tank fires.

Open-top metal tanks 1.0, 2.6, 4.6 and 8.6 feet in diameter were used. Oils tested were three crudes, fuel oil, gasoline, kerosene, and lubricating oil. Burning rate and progress of the heated layer were determined by periodic readings of thermocouples mounted at various levels in the tank. Fifty-three tests were run, but only some of them are reported in detail.

Burning rates for the three larger tanks increased slightly with increase in diameter; rates for the smallest tank were distinctly lower. Typical figures were: gasoline, 0.9 ft/hr; kerosene, 0.62 ft/hr; two crudes, containing less than 1 per cent water, 0.25 and 0.30 ft/hr. For a crude containing between 1 and 2 per cent water, the burning rate was initially very slow, but became normal after about two hours, when it was presumed that all the water had been evaporated. No burning rates were given for the other oils tested.

In the burning of crude oil, a gradually deepening layer of oil heated to 480–680°F. was observed to form. The lower boundary of this layer (also known as "heat wave") was sharply defined, and progressed downward at more than twice the burning rate. The authors note that conduction of heat through the oil cannot account for the rapid progress of this heat wave, which must result principally from convection within the hot upper layer. Burning rate, viscosity, container diameter, and water content of the oil are said to be factors which control the rate of advance.

The authors' statement that burning of oil from a free surface has been little studied indicates that they were unaware of the extensive work done by the petroleum industry fire protection engineers in the United States, beginning at least as early as 1924. Some of this work is summarized by Hall * who states that the convection which produces the heat wave is the result of partial distillation at the surface producing a residue which, although very hot, is still more dense than the underlying colder oil, and hence sinks through it; that this can occur only during burning of oil having components covering a wide range of boiling points; and hence that the heat wave cannot progress far in advance of the burning surface during the burning of narrow-cut refined oils. This latter conclusion is barely alluded to in the current work.

That the behavior of oil burning in open-top tanks is a matter of common knowledge is indicated by references in "Fire Protection in Refineries," published by the American Petroleum Institute in 1933, 1939, and 1941.

In the reviewer's opinion, this work confirms previous conclusions concerning burning rates and the development of the heat wave, but contributes nothing new.

Subject Headings: ***Heat transfer, in surface burning; Oil, heat transfer in surface burning of.***

O. W. Johnson

V. Combustion Principles

Essenhigh, R. H., and Thring, M. W. (University of Sheffield, Sheffield, England) "Measurement of Burning Times of Single Coal Particles," *Conference on Science in the Use of Coal, Sheffield, England,* Paper 29, Sec. IV (April 1958)

This work dealt with the development of a method for measuring the burning time of single captive particles of coal in order to check the constants in the theoretically predicted equation

$$t_c = K.d_o^n$$

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* Hall, H. H. "Oil Tank Fire Boilovers," *Mechanical Engineering,* 47, 540–544 (1925).

where t_c is the burning time of a particle, d_0 is the initial particle diameter, and K and n are constants.

The burning time was measured by monitoring with a photocell and fast pen recorder the radiation emanating from individual particles of coal burning in air. The particles were cemented onto fine silica threads and placed between flat spirals of electrically heated Nichrome V resistance wire located above and below the particle. The heater coils were maintained at 1000°C; particle temperatures between 900 and 950°C were measured during burning. Six different types of coals were studied whose volatile content ranged from 17 to 40 per cent. Coal specimens approximating cubes and ranging from 0.3 to 4 mm. across were selected from crushed and sieved coal samples.

The well-known phenomenon of volatile combustion followed by combustion of the residue was easily observed visually as well as on the photocell trace because of the marked difference in radiation characteristics. This allowed the total burning time to be divided into two parts, the volatile combustion and residue combustion periods. Between the volatile and residue combustion periods the radiation intensity oscillated momentarily first below and then above that corresponding to residue combustion. The glow of carbon monoxide combustion in a thin film around the particle was also observed. All the coals swelled to some degree during combustion.

The experimentally determined values of the constant n were in general only slightly higher than the theoretically predicted value of 2. K values of about 100 sec/cm^2 for volatile combustion and about 1000 sec/cm^2 for residue combustion were found compared to a value of 2000 sec/cm^2 predicted theoretically for carbon. The average burning rate during volatile combustion increased considerably with increasing volatile content whereas no consistent trend was found for the residue combustion.

Coal particles were precarbonized at temperatures between 280° and 1020°C. It was found that the characteristic volatile flame vanished when the particles were precarbonized at temperatures above 500°C. By quenching burning particles at the end of the volatile combustion period it appeared that nearly all the volatile material had been evolved. However, a small fraction apparently remained, which was thought to be hydrogen.

Subject Headings: ***Coal, burning time.***

C. P. Talley

Palmer, K. N. (Joint Fire Research Organization, Boreham Wood, England) "Smouldering Combustion in Dusts and Fibrous Materials," *Combustion and Flame,* **1,** 129–154 (1957)

The work described in this paper was intended to furnish information on the rates of smouldering of dusts and fibrous materials under various conditions. It can best be dealt with under three headings.

1. The smouldering of small trains of dust

The materials used in this investigation were cork dust, beech and deal sawdusts, and grass dust. Smouldering was initiated by applying a small flame to one end of the train, the combustion zone (as observed visually) being allowed to advance 2 or 3 cm. before commencing measurements of the time of travel at intervals over a total distance of 10 cm. From these results the mean linear smouldering rate was calculated. If combustion ceased before the completion of the 10 cm. interval, the train was classified as not smouldering. Rates were determined in still air and also under air flow conditions in wind tunnels, the direction of flow being either in the direction of the progress of smouldering, or opposed to it. In the experiments in still air, thermocouples buried in the train were used for temperature measurement. Under air flow conditions the external temperature of the smouldering zone was measured by an optical pyrometer. Observations on the transition from smouldering to combustion with flame were also made. The minimum depth of dust layer necessary for sustained smouldering was found by initiating smouldering at the thicker end of a wedge-shaped train, and noting the depth of dust at the point where smouldering ceased.

The results of these experiments, which are reported in graphical and tabular form, may be summarized as follows:

The smouldering rate

a) increased as particle size was diminished.
b) under air flow conditions, was greater with flow in the direction of smouldering than when opposed.
c) increased with air velocity for air flow in the direction of smouldering.
d) increased initially and then levelled off or fell with increase in opposing air velocity.
e) decreased with increasing depth of dust train for the finer dusts.
f) in still air, decreased with increasing moisture content. This effect was less significant under air flow conditions.

The minimum depth of dust necessary to sustain smouldering

a) increased with particle size (up to approximately 2 mm/diam).
b) decreased with increasing air velocity.

The smouldering temperature increased with air velocity.

For coarser dusts (mean particle diam.$>$1 mm.) in an air stream smouldering was frequently accompanied by the sudden appearance of flame at the surface of the train.

2. The smouldering of board strips

Four samples of fiber insulating board were used in these experiments; strips were cut from the boards replacing the dust trains of the previous section. The experimental procedure was as before, except in the method of supporting the strip, which was held in a clamp at one end, smouldering being initiated at the free end. The inclination of the strip to the horizontal was varied to determine the effect of this factor on the smouldering rate. The experimental results may be summarized as follows:

The smouldering rate

a) decreased with increasing width of strip for a fixed thickness.
b), c), d) was as in the previous experiments on trains.
e) varied with the inclination of the strip to the horizontal, being greatest when smouldering vertically upwards, and least when smouldering horizontally. The rate when smouldering vertically downwards was intermediate between the two.

The temperature of the smouldering zone was little affected by air velocity in these experiments.

3. Smouldering in the interior of dust deposits

Combustion under these conditions is known in waste heaps and in some fires in solid materials which are stored or transported in bulk.

The materials used in the experiments were cork dust, elm sawdust, and a commercial mixed wood sawdust. In some cases the dust heap took the form of the frustrum of a cone. The smouldering was initiated by applying a small flame to the base of the cone when still in the mould, the time being measured from turning out the mould to the appearance of charring on the top surface. In the rest of the experiments, in the bottom of a cubical box, a small heap of dust was ignited and the remainder of the dust then piled on top, the time being measured from filling the box to the appearance of charring on the top surface. The results of the experiments were as follows:

The time for smouldering to penetrate the deposit increased with

a) the depth of the deposit.
b) the moisture content.
c) the density of packing.

Subject Headings: ***Dusts, smouldering; Smouldering, combustion in dusts.***

R. G. Siddall

Knewstubb, P. F., and Sugden, T. M. (University of Cambridge, Cambridge, England) "Mass-spectrometric Observations of Ions in Flames," *Nature* 181, 474–475 (1958)

Preliminary qualitative results obtained by direct mass-spectrometric analysis of ions drawn from some premixed flames burning at atmospheric pressure (flame temperatures *ca.* 2200°K) are given. Ion concentrations down to 10^7 ions/cc were readily detectable. Many ion-hydrates were found, but it is not certain whether these occur actually in the flame, or whether they are formed during sampling. In hydrogen-air flames, without additives, H_3O^+ and H_2O^+ appeared to be prominent, with some $H_2O_2^+$ in addition. In the presence of alkali metal salts Li^+, Na^+, K^+, Cs^+ appear strongly, together with hydrates, the peaks for the latter becoming weaker as hydration increased. With $SrCl_2$ peaks correlating with $SrOH^+ \cdot nH_2O$ up to n=3 appear in addition to Sr^+ and hydrates. Similar observations were made with calcium and barium salts, though Ba^+, if present, is below the limit of detection, and $BaOH^+$ is predominant.

The acetylene flame is more complex and no analysis of the primary reaction zone was attempted. In the gases above this zone, all the peaks observed in the hydrogen flames were present together with a prominent peak at mass number 30, probably CH_2O^+ or NO^+. No C^+ was found, so that CH_2O^+, if present, is probably ionized formaldehyde.

Subject Headings: **Flame, ions in; Ions, mass spectroscopic observation in flames.**

G. Dixon-Lewis

VI. Radiation

Lawson, D. I., and Hird, D. (Joint Fire Research Organization, Boreham Wood, England) "A Photometric Method of Determining Configuration Factors," *British Journal of Applied Physics,* 5, 72–74 (1954)

Heat transfer problems, such as studies on the growth of fires, frequently require calculation of the intensity of radiation transmitted from a radiator to a surface. This intensity depends not only on the temperature but also on the size of the radiating area and on the distance and orientation of the receiver. The intensity of radiation at any point of a receiving surface can be expressed by

$$I = \Phi \sigma T^4$$

where σ is the Stefan-Boltzman constant and Φ is the configuration factor that takes into account the geometry of the problem. Calculations of the magnitude of the configuration factor is not easy except for simple geometric cases. It is also not possible to estimate the reverse problem, *i.e.,* to find at what position with respect to the radiator there is a given configuration factor.

The principle of the method described in this paper rests on the substitution of light intensity measurement for heat measurement. This is possible since both heat and light propagation follow the same laws.

The apparatus for the determination of the configuration factor consists of a light-tight box within which is mounted a model of the radiating area, cut out from black paper and covered with a diffusing layer of material uniformly illuminated from behind. The light intensity is measured by means of a photocell at various distances in front of the radiator. Thus, once the model of the radiator is set up the configuration factor can be found quickly at any position. Since Φ is a pure number, linear dimensions of the radiator can be scaled provided the receiver distance is scaled by the same factor.

If the total heat transfer between two surfaces is desired the configuration factor of the entire receiving element is required. A close approximation for this can be obtained by taking the configuration factor at several points by the above optical method and averaging these values.

If the radiator is three-dimensional, the photometric method may also be used since it is the contour of the surface which determines the value of Φ. The surface of the radiator is replaced by an equivalent flat surface provided the angular coverage at the receiver is the same.

This analogue method is particularly useful if the configuration factor at many positions with respect to a radiator is to be found.

Subject Headings: ***Photometry, configuration factors; Configuration factors, determination by photometry.***

W. G. Berl

VII. Suppression of Combustion

Aidun, A. R., Walker, E. J., Gabriel, S., Buckman, W. R., and Grove, C. S., Jr. (Syracuse University Research Institute) "Additives to Improve the Fire-Fighting Characteristics of Water," *Bureau of Yards and Docks, Department of the Navy Contract NBy 13027, Quarterly Progress Report No. 4* (July 1958)

The study has as its objective the improvement of water as a fire extinguishing agent by suitable additives. The study includes several phases.

1) Evaluation of the influence of viscosity additives on the retention of water on heated surfaces
2) Evaluation of the influence of various surface-active agents on the mechanical stability of liquid films
3) Evaluation of various materials as opacifying additives in water
4) Practical evaluation of additives by scaled model fires

In selecting these avenues of study, the authors point out that by increasing the residence time of water at the locus of fire, the gross potential heat absorption of the water would be increased, in contrast to the condition where a large fraction of the water rapidly "runs off" surfaces to which it is applied. [It is noted elsewhere* that Bentonite clay (oil well drilling mud) has rendered water more effective in forest fire-fighting operations, and the same mechanism has been postulated for the effect.]

The methods of investigation were as follows. A runoff test device was constructed for the runoff studies, in which solutions to be evaluated were allowed to flow down an inclined heated plate, on which thermocouples were located at the plate surface. Heating could be discontinued as desired for actual test determination, and reheat time after solution application could be determined, as well as temperature drop on the plate during application of solution. When the last of the flowing solution leaves the plate a liquid film remains. As the plate is reheated, this film evaporates. If the amount of water held on the plate can be increased by viscosity additives, the plate reheat rate should be less and more cooling is available to prevent reignition of a combustible material.

Film stability was determined in a specially constructed device, which allowed the generation of a liquid film on a nichrome wire frame measuring 3.9 x 1.2 cm. in a vertical plane. For various solutions, the progress of the second-order dark interference band with sodium lamp illumination was observed using a cathometer; and the distance of this dark band from the top of the wire frame was measured at time intervals. In addition, the film lifetime was recorded.

For the fire tests eight pieces of wood, 2½" x 12" x ¾", soaked in kerosene, were arranged in a two-tier crib. Radiant heat recordings were made by means of a thermocouple. At the "peak temperature" following ignition, application of the extinguishing solution was initiated by means of a spray nozzle. The spray continued until extinction.

The rate of reheat in the runoff test varied in opposite directions when Acrypol ASE-60 or Polyox WSR-35 were used as viscosity additives even though both substances improved the exectiveness of water for fire extinguishment. As yet no explanation is available for this puzzling behavior.

In the scaled model fire tests, 3.5 minutes of application of water at a rate of 0.5 gal/min was required to completely extinguish the test fire without reignition and *ca.* 6 liters of runoff were collected. The best performing additive formulation was Polyox WSR-35 with 1 per cent Alkanol WXN (surfactant) and 0.05 per cent aluminum powder. At the same rate of application, only 0.175 minutes were required for extinguishment, and 0.325 liters of runoff were collected. The function of the surfactant was stated to be that of suspending the aluminum

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* Wilson, Carl C. "Fire Fighting Aircraft—The New Look in Forest Fire Control," *An Address to the Third Agricultural Aviation Research Conference* (November 1958).

powder in solutions, although the "blanketing" effect of aluminum was indicated to be better without a surfactant (*i.e.,* the aluminum powder spreading as a film over the liquid surface rather than being dispersed in the solution). Further study was proposed using a different means of injecting the aluminum powder into the spray stream, rather than dispersion with a surfactant. A second mechanism postulated for the effect of aluminum powder in the extinguishing formulation was that of reflecting radiant energy from fuel surfaces.

Since the studies are still in progress, and the report concerns progress in the fourth quarter of the investigation, the authors have not attempted to correlate the relationship of each phase of the investigation with the others by means of the experimental data generated to date, nor have they indicated the relationship of the test fire configuration to a large scale situation, or the basis on which the particular configuration was chosen.

Subject Headings: *Additives, fire-fighting improvement; Water, improvement by additives.*

J. E. Malcolm

Friedrich, M. (Research Division for Technique of Extinguishing Fires, Karlsruhe Polytechnical Institute, Germany) "On the Extinguishing Effect of Polyhalogenated and Mixed Halogenated Hydrocarbons," *Chemiker-Zeitung,* **81,** 526–531 (1957) Translated by J. E. Malcolm (U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia.)

This report is the third in a series of papers covering a search for more effective extinguishing agents with low freezing points. A previous report by M. Friedrich* dealt with the following liquid halogenated hydrocarbons: bromochloromethane, carbon tetrachloride, ethylene tetrachloride, methyl iodide, ethyl iodide, n-propyl iodide, ethyl bromide, n-propyl bromide, and water, and their effect on surface-burning fuels such as aliphatics, aromatics, alcohols, esters, ethers, ketones, JP (kerosene) fuels, carbon disulfide, varnish and lacquer, linseed oil and similar paint components, and napalm.

This subsequent study investigated the following compounds as extinguishing agents: dichloromethane, trichloromethane, 1,1,2 trichloroethane, 1,1,2,2 tetrachloroethane, pentachloroethane, dibromomethane, tribromomethane, 1,2 dibromoethane, 1,1,2,2 tetrabromoethane, dibromodifluoromethane, tetrafluorodibromoethane. Two sets of preliminary experiments were performed: (1) impinging experiments to determine spray patterns and the actual quantity of halogen arriving at a burning surface at some distance from the atomizing spray gun, and (2) pyrolysis experiments to determine the rate of pyrolysis and the nature of the decomposition products.

The results of fire extinguishment tests showed that dichloromethane has no extinguishing ability. Of the chlorinated methanes, carbon tetrachloride had previously been shown to be from 25 to 30 per cent better than trichloromethane. Of the chlorinated ethanes, monochloroethane and 1,2 dichloroethane are flammable, trichloroethane is slightly worse (5 per cent) than tetrachloroethane as an extinguishing agent but is about 45 per cent better than pentachloroethane. None of the chlorinated compounds extinguished a methanol fire. Of the brominated methanes, tribromomethane is from 45 to 50 per cent better than dibromomethane. Of the brominated ethanes, the tetrabromoethane is 15 per cent better than the dibromoethane which is 22 per cent better than the monoethylbromide.

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* FIRE RESEARCH ABSTRACTS AND REVIEWS, Vol. I No. 1 p. 21 (1958).

Dibromodifluoromethane was found to be the best extinguishing agent of the halogenated compounds studied; next is dibromotetrafluoroethane. Both of these are superior to all monohalogenated hydrocarbons.

The conclusion from these studies is that increasing the halogenation of a hydrocarbon increases the extinguishing ability, not in proportion to the number of halogens introduced but rather with the amount and rate of free halogens liberated upon decomposition. The hydrocarbon acts merely as a binder and the free halogen dissociated from the hydrocarbon is the principal carrier of the extinguishing effect.

Although the results of such experiments cannot be generalized to other situations, being limited to the specific experimental conditions employed, such as the kind of spray apparatus used, the distances involved, and the physical characteristics of both flame and extinguishing agent, the author has made an attempt to provide more than a simple ordering of relative extinguishing abilities of halogen-containing compounds. These tests, therefore, provide both a practical means for developing more effective fire extinguishing agents and a qualitative understanding of the role of the halogen in flame extinguishment.

Subject Headings: *Extinguishment, by halogenated hydrocarbons; Halogenated hydrocarbons, extinguishment by.*

D. W. Dembrow

Neill, R. R. (U. S. Naval Research Laboratory, Washington, D.C.) "The Hydrocarbon Flame Extinguishing Efficiencies of Sodium and Potassium Bicarbonate Powders," *NRL Report 5183* (August 1958)

Evidence of an increasing extinguishing effect with increasing atomic number for the alkali metals, in addition to the excellent over-all fire-suppressing properties of dry-powder chemicals, suggested better fire-fighting properties for potassium bicarbonate than the presently used sodium bicarbonate.

In controlled indoor and outdoor experiments, made to determine the fire-suppressing properties of both compounds, it was found that the critical rate of application and weight of potassium bicarbonate applied were one-half of the corresponding quantities for sodium bicarbonate, indicating a superior efficiency for the potassium compound.

Although in general the dry chemicals have better extinguishing qualities than the foam-type extinguishers the danger of reignition is great when the rate of powder application is low and ignition sources still remain. This failing has limited the use of dry chemical powders to a secondary role in the fighting of naval aircraft fires. Work is continuing on the development and improvement of potassium bicarbonate and other types of foam-compatible dry-chemical powders.

In comparing the sodium and potassium powders, it was necessary to maintain the same average particle size for both groups in order to eliminate extinguishing advantages due to the fineness of the powder particles. Uniformity of application technique and regulation of environment were other controlling factors in this study.

To avoid wind effects, the first series of tests were made indoors with 3′ x 3′ gasoline spill-type fires. For both powders, the minimum rate of powder application necessary to barely extinguish the fire was determined. For sodium bicarbonate this minimum rate was 4 grams of powder per second per square foot of fire area, while for potassium bicarbonate only 2 grams of powder per second per square foot were necessary. Eight hundred grams of sodium compound were needed as compared to four hundred grams of potassium powder. This difference of the minimum rates necessary to extinguish the gasoline fire is attributed to the chemical mechanism acting to produce extinction. It is believed that the radicals produced in the combustion reactions must be intercepted by the flame-suppressing agent. Earlier experiments also indicated that for related alkali-metal compounds, the chemical extinguishing effect increases with increasing atomic number.

At higher powder rates, sufficient to extinguish the 3′ x 3′ flame in 2 secs. (as compared with 15 or 20 secs. at low application rates) it is believed that the chemical effects do not operate. Physical suppression mechanisms such as cooling, smothering, oxygen dilution, and overcoming flame propagation become the controlling factors. Since the physical characteristics of the two powders differed very little, it is not surprising that no difference between the two powders is measurable at high application rates.

The test program was expanded to include larger outdoor fires. Testing times were selected when the wind velocities were from 0.5 to 2 miles per hour. The outdoor tests were performed on square areas ranging in size from 6′ x 6′ to 13′ x 13′. An extinguisher having a ten-pound dry chemical capacity was chosen as being of an optimum handling size. Since the flow rate through the extinguisher decreased with time, it was necessary to utilize an average application rate. This was taken as 300 g/sec. It was found that the maximum area that could be extinguished by sodium bicarbonate at the given flow rate was 57 sq. ft. while the corresponding area for potassium bicarbonate was approximately twice as much. These areas corresponded to application rates of 5.3 and 2.7 g/sec/sq ft for the sodium and potassium powders respectively.

As in the indoor tests, a doubling in effectiveness for the potassium compound was indicated. The outdoor tests also indicated that the differences between the two powders were reduced at higher application rates, becoming equal for extinguishing times of 4 or 5 seconds.

Other tests with 30-pound extinguishers again indicated similar advantages for potassium bicarbonate over sodium bicarbonate.

A study of the flame-zone enlargement caused by both powders indicated that a maximum flareup of two and one-half times the original flame volume could be attributed to acceleration of the burning process caused by air entrained into the powder cloud and air intermixing with the combustible vapor displaced from fuel surface. As measured by the visible spectra, the increase in flame radiation upon introduction of either of the dry chemicals into the flame zone was found to be relatively constant for constant powder application rates.

Subject Headings: ***Extinguishment, by potassium bicarbonate; Extinguishment, by powders; Extinguishment, by sodium bicarbonate; Potassium bicarbonate, extinguishing effect; Powders, extinguishing effect; Sodium bicarbonate, extinguishing effect.***

A. L. Goldstein

Rosser, W. A., Miller, J. H., Inami, S. H., and Wise, H. (Stanford Research Institute, Menlo Park, California) "Mechanism of Flame Inhibition," *Corps of Engineer, U. S. Army, Engineer Research and Development Laboratories, Fort Belvoir, Virginia, Contract DA44–009–ENG 2863 Phase II Final Report* (June 30, 1958)

The final report in a study of flame inhibition is composed of four parts: (1) measurement of the maximum temperature of premixed methane-air flames, (2) flame spectra of premixed methane-air flames, (3) quenching of such flames by solid surfaces, and (4) low temperature oxidation of methane.

Temperatures of halogen-inhibited and uninhibited flames were measured by the sodium D-line reversal technique with a Bausch and Lomb 1.5 meter astigmatic grating spectrograph. It was concluded from these experiments that although flame speed is markedly affected by small quantities of halogen inhibitors, flame temperature is essentially unchanged.

The intensity of radiation emitted by OH, C_2 and CH in an inverted V-shaped flame at 3064 Å, 5165 Å, and 4315 Å respectively, was measured with the 1.5 meter spectrograph fitted with a scanning photomultiplier. To investigate the effect of each of these species on flame propagation, halogenated inhibitors (CH_3Br, HBr and Br_2) were added in small quantities and the spectrum changes resulting from these additions observed. The CH emission increased by as much as 50 per cent with addition of only 0.5 mole per cent CH_3Br. The C_2 emission intensity first decreased to a minimum, then increased with similar inhibitor additions. Since flame speed was found to be a monotonic function of inhibitor concentration, these results indicated that C_2 and CH emission intensity is not a significant feature of flame propagation. In contrast to these results, the OH emission intensity decreased with addition of inhibitor at approximately the same rate as flame speed decreased with corresponding inhibitor additions. It was concluded from these results that flame speed is proportional to the OH concentration.

Quenching distances of premixed methane-air mixtures were measured in a conical glass combustion tube. The extinction point of an ascending flame was determined photographically. The diameter of the conical tube at the point of extinction is defined as the quenching distance. The reciprocal of the quenching distance decreases linearly with increasing inhibitor concentration. The quenching distance is found to be independent of the nature of the confining surface. In view of this, heat loss rather than heterogeneous radical removal would seem to play the dominant role in flame quenching. It follows that the effect of an inhibitor on quenching distance can be predicted from a knowledge of the properties of an uninhibited flame. The primary effect of halogen inhibitors is to reduce flame speed.

The greater portion of this report is concerned with the low temperature (800°C) oxidation of methane. The experimental apparatus consists of a quartz reaction vessel housed in a cylindrical furnace, a tungsten lamp and hydrogen discharge lamp, and a monochromator and photomultiplier tube. The oxidation of HBr alone was followed by observing photometrically at 4200 Å the production of Br_2 as a function of time, reaction pressure, and temperature for 10^{-7} to 10^{-5} moles/cc of reactant. Rate equations and activation energies were determined for the production of Br_2 when $(O_2) >> (HBr)$ and $(O_2) << (HBr)$. Kinetic gas phase mechanisms are postulated for the oxidation reactions involved in these two situations. The activational energies compare favorably with other recent thermodynamic data.

The rate of pressure rise and optical density changes in CH_2O (2930 Å), Br_2 (4200 Å), and H_2O_2 (2200 Å) were used to investigate the oxidation of methane containing small quantities of HBr. For the uninhibited reactions an induction period was observed. In the inhibited oxidation the absence of this induction period was attributed to the reaction between HBr and O_2. The similarity in the pressure curves obtained in the oxidation of methane with HBr as inhibitor and Br_2 as inhibitor indicates that the HBr is first oxidized to Br_2.

In the absence of HBr the formaldehyde concentration follows closely the rate of pressure rise throughout the oxidation of methane. In contrast to this the formaldehyde concentration in the sensitized experiments shows the same general trend as the pressure, but reaches its maximum value within a few seconds after introducing the reactants. It is worth noting that the presence of HBr does not affect appreciably either the maximum rate of pressure rise or final pressure in these reactions.

HBr, CH_3Br and CH_2Br_2 all possess appreciable absorption constants in the spectrum region of the hydrogen peroxide absorption (2200 Å). Consequently, the hydrogen peroxide species is not easily followed photometrically in the inhibited reactions.

The large number of reactions involved in the oxidation of methane makes a quantitative investigation of the problem very difficult. However, a reasonably qualitative argument, mechanism-wise, is presented. It is to be noted that low-temperature oxidation kinetics are distinct from flame kinetics. Halogen compounds tend to catalyze low temperature oxidation, whereas they inhibit flame phenomena. For inhibited flames the mobile and highly reactive H, OH and O species are replaced by the less mobile and less reactive halogen species. This results in lower flame speeds.

Subject Headings: ***Flame, inhibition mechanism; Inhibition mechanism.***

H. E. Perlee

Radusch, R. (Research Division for Technique of Extinguishing Fires, Karlsruhe Polytechnical Institute, Germany) "Observations on the Most Favorable Size Drops for Extinguishing Fires with Atomized Water and on the Range of a Stream of Water Spray," *VFDB Zeitschrift Forschung und Technik im Brandschutz* **2**, 47–54 (1953)

I. The most favorable size drops

Water has a very high heat capacity which enables its cooling action to play a predominant part in the extinguishment of fires. The rate of heat absorption depends on the extent of the exposed surface. The first part of this report discusses the possibility of improving the fire-fighting ability of water to its maximum by increasing the speed of vaporization by means of very fine atomization. In practice it is required that water be discharged at a distance from and be brought to the surface of the burning object in sufficient quantities per unit of time to absorb the heat generated within that unit of time. Very fine droplets cannot be easily focused at an object from a distance to give proper coverage and they do not have sufficient energy to resist the upthrust of the combustion gases when entering the combustion zone.

It is possible theoretically to determine the most favorable size drops on the basis that the speed of vaporization for a drop of water is a function of its surface area and the heat transfer coefficient. In still air—a condition which prevails at the burning surface itself—this coefficient is inversely proportional to the diameter of the drop and heat will be absorbed in proportion to the extent of the exposed surface. However, when a relative motion exists between the drops of water and the surrounding air, as when water is used mainly to quench the flames, to reduce heat radiation, and to curtail the spreading of fire by cooling of the hot gases, then the heat transfer coefficient is greater and the speed of vaporization is increased. To determine the most favorable size drops under these conditions, the author makes use of Edeling's* equation of the heat transfer to small drops of water in motion:

$$\alpha = 0.75 \frac{\lambda}{\sqrt{b}} \cdot \sqrt{\frac{v}{d}}.$$

in which the heat transfer coefficient α is shown to be a function of the ratio of the velocity v of the drop to its diameter d, λ is the thermal conductivity and b the thermal diffusivity $\left(\frac{\lambda}{c\gamma}\right)$. At a constant velocity, the heat transfer coefficient will depend only on d and by assuming that the heat quantity dQ

$$dQ = \alpha \cdot 4\pi r^2 \cdot \Delta t \cdot dz$$

transmitted within unit time dz to the surface of the drop of radius r under a temperature difference Δt is made to vaporize a quantity dW of water, a vaporization equation can be obtained relating time of vaporization z to the radius of the drop r:

$$z = \frac{N \cdot \rho w \cdot \sqrt{2b}}{1.5 \cdot 0.75 \cdot \lambda \cdot \Delta t \cdot \sqrt{v}} \cdot \sqrt{r^{1.5}}$$

where N is the heat of vaporization of water, and ρw its density.

A series of tests aimed at measuring the vaporization time of a drop of water in a current of air at constant values of air velocity and temperature led to the conclusion that the exponent of d must be larger than 0.5 and should lie between 0.8 and 1.0. The influence of the air velocity could be analyzed in a similar manner by keeping temperature and diameter of the drop constant. No results were available as yet and the author makes use of results reported by Schmidt † on the transfer of heat from heated pipes, to infer that the exponent of v would have to correspond to, if not exceed, that of d.

Assuming equal exponents for both v and d, the influence of the quotient v/d on the heat transfer coefficient can be analyzed to determine for what value of d heat absorption will be maximum. For a drop of a given diameter, neglecting the loss of substance through evaporation during flight, the value of the heat transfer coefficient will be a function of the speed of the drop relative to the surrounding air. The horizontal component of this speed will decrease very rapidly to zero against the resistance of the air although there continues to exist a horizontal component of the absolute speed because of the air current created by the stream of water spray. On the other hand, the vertical component of the relative speed increases toward a limit value, the terminal speed of fall, which is unequivocally defined for any size drop and which determines the balance between the weight of the drop and the air resistance.

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* Edeling: Investigation of Atomization Drying (Untersuchunger zur Zerstaeubungstrocknung): Diss. 1949, Karlsruhe, Verlag Chemie, Weinheim, Germany.

† Schmidt: Introduction into Thermo-Dynamics (Einfuehrung in die Thermodynamik) Berlin 1944.

The author introduces this terminal speed of fall as the lower limit for the relative speed of the drop and, substituting its value for v in Edeling's equation of the heat transfer, he finds that the coefficient of heat transfer is maximum for a drop diameter of 0.35 mm. This is compared with optimum values of 0.4 to 0.6 mm. obtained in England* during tests on the extinguishment of liquid fires.

II. The range

The range of a solid stream of water is a function of the velocity of the stream at the nozzle which in turn is dependent on the pressure at that point. In the case of a stream of water spray, a certain quantity of energy A must be used to overcome the surface tension σ of the water during the atomization process:

$$A=\frac{6\sigma}{10d}\ \mathrm{kg/cm^2}$$

It is calculated that the production of drops with a 0.35 mm. diameter at an absolute pressure of 5 atmospheres consumes only 0.24 per cent of the water pressure.

If this energy required for atomization is taken into account in the pressure equation, the initial velocity (or nozzle velocity) v_0 of a drop of water of a diameter d (in mm.) is equal to:

$$v_0=\sqrt{\frac{2}{\rho w}\left(P_0-\frac{6\sigma}{10d}\right)+v_1^2}$$

where P_0 is the pressure within the pipe line and v_1 the speed of water in the line. Assuming a water flow of 100 1/min through a hose of 52 mm. diameter, v_1 would be equal to 0.79 m/sec. Water drops of 0.35 mm. diameter would have a velocity of about 30 m/sec for a nozzle pressure of 5 atmospheres, providing friction losses within the nozzle are kept low.

To determine the range of the water spray, consideration must be given to the air resistance which is a function of the diameter of the drops and of the dynamic pressure of the air. For a sufficiently short time interval Δz, the deceleration $-\Delta v_0$ of the drop would be

$$-\Delta v_0=-b_0\cdot\Delta z$$

where b_0 is the retardation factor. After Δz seconds, the speed v_1 of the drop would be:

$$v_1=v_0-\Delta v_0$$

and the corresponding distance travelled amounts to:

$$s_1=\frac{v_0+v_1}{2}\cdot\Delta z$$

The speed variations and the corresponding distances travelled can be integrated step by step to give the range S of the drop:

$$S=\sum_{i=1}^{i=n} s_i$$

This range is found to be about 1.50 m. for 0.35 mm. drops at an initial velocity of 30 m/sec. Loss of mass by the drop during flight would tend to reduce this

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* Rasbash, Rogowski, Skeet: "Some tests on the effect of water sprays on a hexane fire." *F. C. Note #45/1951.* Rasbash: "The effect of water sprays in burning kerosene." *F. C. Note #41/1951.*

value. If attempts were made to extend the range, say to 6 m., by increasing the pipe pressure, it would be found that very high pressures outside the range of practical possibilities would be required since range increases with the the 4th root of the pressure. Furthermore, owing to its low mechanical stability, a drop of water is incapable of opposing very high dynamic air pressures. Whenever the dynamic pressure resulting from the speed of the drop exceeds a certain value, the drop is flattened and broken down into smaller drops. The condition of stability which exists between the upper speed limit $v_{max.}$ and the diameter d of a drop is:

$$v_{max.} = \sqrt{\frac{8\sigma}{d \cdot \rho_L}}$$

where σ is the surface tension of the drop and ρ_L the specific density of the air. From this, it is found that a drop of 0.35 mm. diameter would become unstable and break down at velocities greater than 36.2 m/sec.

In practice, it is observed that, in a stream of water spray, the drops travel much farther than could be expected on the strength of the theoretical findings above. In a steady-state stream, only the very first drops encounter static air. They create in their path a current of air which rapidly attains a stationary state and reduces the air resistance for the following drops. For an examination of the range of a stream of water spray, the stationary state is, therefore, the determining factor.

Assuming very fine atomization of the water, a stream of water spray can be compared to a stream of air and would be expected to expand quite accurately and independently of the nozle velocity as a cone having a vertex angle of 14° at the nozzle opening, provided the Reynold's number is sufficiently large. If the drops are not infinitely small, and assuming steady conditions of water flow, the total free surface of the water would be smaller, friction would be reduced, and a smaller amount of air would be forced along. The reduction in the amount of air to be accelerated means that the volume of the cone becomes smaller. It is concluded that in a stream of water spray, the vertex angle which is a function of drop size would lie between the limits of 0° (solid stream) and 14° (fine atomization), providing all drops are emitted at the same speed and direction.

It is found that, in practice, the nonuniformity of drop sizes complicates the dynamics of the stream since small and large drops tend to collide in flight. It would be most important to develop atomizing nozzles which produce drops of uniform sizes, regardless of pipe pressure. With a properly designed nozzle, it would be possible for 50 per cent of the water to arrive at a vertical circular surface of 1 square meter area at a distance of 8 m. from the nozzle. This corresponds to an 11.4° vertex angle of spray. It is also concluded that, for a water flow of 100 1/min and an initial velocity of the drops of 30 m/sec, the absolute velocity of the drops at a distance of 8 m. would be of 4.2 m/sec which is presumed to be sufficiently high to allow the drops to reach the focal point of the fire against the upthrust of the combustion gases. The time of flight would be 0.45 sec. Gravity would make drops having a 0.35 mm. diameter fall a distance of 0.68 m.

Subject Headings: *Water, sprays for flame extinguishment; Water, sprays, range of; Extinguishment, by water sprays.*

J. R. Jutras

VIII. Model Studies and Scaling Laws

Lode and Dettmar (Leverkusen, Germany) "Study on the Quantities of Water for Extinction in a Model Fire," *VFDB Zeitschrift Forschung und Technik im Brandschutz,* 5, 141–142 (1956). Translated by U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia

In any extinction process, it would be helpful if the amount and rate of supply of extinguishing fluid was known. Such data would be applicable to the design of sprinkler systems for large buildings and smaller extinguishers of localized fires. A physico-mathematical model has been used to obtain a solution to extinction problems, and the solution evaluated for the case in which water extinguishes burning timber under the particular conditions of the model.

The model fire consists of an infinite solid, burning uniformly in one direction only, such that the flame and surface temperature is constant, and the temperature distribution from the burning surface into the solid, does not change with time.

The general equation for one dimensional heat transfer is

$$\lambda \frac{\partial^2 T}{\partial x^2} = c \frac{\partial T}{\partial z} \tag{1}$$

where

λ = thermal conductivity of material to be burnt
c = specific heat x density of material to be burnt
T = temperature
z = time
x = depth

and the temperature distribution is given by

$$T_{(x,z)} = T_0 + (T_1 - T_0)\, e^{-(x-x_1)gc/\lambda} \tag{2}$$

where

T_0 = ambient temperature
T_1 = surface temperature
x_1 = distance of burning surface from origin
g = burning speed of the material

The extinction process is assumed to correspond to a solution of the heat conduction equation as follows,

$$T_{(x,z)} = T_0 + \frac{T_1 - T_0}{2} \cdot \frac{1}{\sqrt{2\pi}} e^{-\gamma x[1-\Phi(u)/\varphi(v)]} \tag{3}$$

where

$$\gamma = \frac{gc}{\lambda}$$

$$v = a\sqrt{z}$$

$$a = \sqrt{\frac{2c}{\lambda}}$$

$$u = v - \frac{\gamma x}{v}$$

$$\Phi(u) = \frac{1}{\sqrt{2\pi}} \int_{-u}^{+u} e^{-v^2/2} dv; \quad \varphi(v) = \frac{1}{2\pi} e^{-v^2/2}$$

It is possible to calculate the rate of flow of heat from the surface and the variation of surface temperature with time during the extinction period.

From a numerical example, the following points can be deduced:

1) A time can be calculated at which the surface temperature falls below the ignition temperature, and the flame is extinguished.
2) From the temperature distribution within the burning material after extinction, a condition can be determined at which the temperature at the surface will not exceed the ignition temperature, and the extinction process can be discontinued.
3) If water is supplied to the surface at a rate predicted by the equation, the flow can be reduced when the flame has been extinguished.

The derivation of equation (3) is not given in the paper, and in its present form, it is unwieldly and difficult to work with. A simpler approach to the extinction problem, producing a more practical solution would be more valuable and the results equally applicable.

The model may be extended to include other variables such as forced and natural convection, and the effect of a fireproofing material on ignition.

Subject Headings: *Extinguishment, of model fires; Fires, model; Model fires; Water, quantities for extinguishment.*

P. L. Start

Lawson, D. I. (Joint Fire Research Organization, Boreham Wood, England) "Models and Fire Research," *The (London) Times Science Review,* Autumn 1958, p. 14.

The author presents a popular discussion of some of the problems involved in the study of fires in buildings and in the design of models of such fires. The author points out that the large sums spent annually in England alone to prevent and fight fires ($40 million) and large sums lost due to fires ($82 million) justify a more extensive effort toward understanding the mechanism governing the start and growth of fires.

Observation of accidental fires is judged to be an unsatisfactory way to study fires in buildings due to the uncontrolled and often unknown circumstances surrounding their start and development. Hence, controlled tests are necessary and, because of expense involved, these tests must be largely model tests. However, construction of models is difficult, even though basic phenomena are understood, due to the complexity of the processes involved in the initiation and growth of fires. Considerable study will be necessary before the important dimensionless parameters can be discovered and appropriate models devised. A new laboratory at the Fire Research Station, Elstre, England, has been erected for study of these modeling problems.

The author outlines four principal problem areas concerning fires: ignition, growth, extinction, and damage to building structure, and discusses in some detail the problems involved in setting up models for these processes. Two models of ignition are described: ignition of surface by thermal radiation, and spontaneous ignition of stored solids. Experimental results are now available which indicate the important parameters in surface ignition, and theoretical results satisfactorily describe certain examples of spontaneous ignition. Techniques for study of both phenomena are briefly mentioned.

The growth of a fire can be analyzed when either the fuel or oxidizer is in great excess. Thus, in a well ventilated fire the burning rate is proportional to the surface area of fuel. In a poorly ventilated fire, the rate is proportional to the rate of delivery of air. The supply of air to a building fire is usually fixed by convection currents produced by differences in density of the hot and cold gases. Thus, the ventilation will depend on the scale of the building. The air supply of a simple scale model will always be less than that in a full-scale building. Tests with buildings ranging from full scale to one-ninth scale models are being conducted to investigate these effects.

The damage to noncombustible structural members is largely due to thermally induced stresses, reduction of strength at high temperature and spalling. These effects depend on rate of heat transmission to and conduction of heat through the structural members. Spalling is the only process which is not well understood at present and which is not subject to analytical evaluation. Combustible support members are subject to burning. Experiments indicate that the strength reduction is proportional to the degree of charring.

The extinction of fires involves either reducing the temperature of the burning surface or replacement of air by inert gas. Model tests indicate extinction of fire in enclosed spaces is usually caused by replacement of air by steam. The author suggests that other inert gases, such as cooled combustion products of air from a turbojet engine, may be used instead of steam.

The author believes that model testing and development of scaling laws are of utmost importance in solution of fire problems, and that despite difficulties, efforts to develop useful scaling laws will be successful.

Subject Headings: ***Fires, model; Model fires.***

E. E. Zukoski

Krueger, A., and Radusch, R. (Karlsruhe Polytechnical Institute, Germany) "Experiments in the Determination of the Characteristics of Fires in Storage Tanks of Flammable Liquids," *Erdoel and Kohle,* 8, No. 7 (July 1955)

Conditions existing in ethyl alcohol and gasoline fires have been investigated on the basis of model studies and the results of some tests are reported. Previous experiments have shown that representative results can be obtained from model studies of this type if similarity between the actual storage tank and the model tank is maintained. Four different tanks were used in this study (12–30 cm. diameter); the ratio of tank diameter to tank height was kept constant. Measurements were made of the rate of consumption of the fuel (burning rate) and the temperature profile along the verticle axis of the tank as a function of time (temperature progression).

Initial experiments showed that slight air movements could produce a drastic increase in the burning rate. The temperature progression is also affected by wind, but only slightly. Alcohol burns more slowly and evenly than gasoline in the upper half of the tank. However, the burning rate for gasoline decreases as the liquid level falls. The maximum burning rate increases with increasing tank diameter, gasoline being affected more than alcohol. Gasoline requires a large amount of air for complete combustion and the possibility for incomplete combustion is greater for gasoline than for alcohol. Heavy soot formation in gasoline fires is evidence of this fact. Alcohol requires a longer time to reach the maximum burning rate than gasoline.

The temperature profile indicates that the burning liquid is heated strongly near the surface. The temperature falls off rapidly below the liquid surface even after long burning times. Temperatures in gasoline fires were only slightly greater than in alcohol fires although the heat release of gasoline is almost double that of alcohol, indicating that the gasoline does not burn completely. Vigorous boiling on the surface occurred quickly after the ignition of the liquid, particularly near the tank walls. Radiation measurements showed that the intensity of radiation increases with increasing tank diameter and that it depends also on the type of fuel and the liquid level in the tank.

Subject Headings: ***Fires, of liquids; Fires, in storage tanks; Tank fires.***

T. P. Anderson

Sesca, S., and Sauer, F. M. (California Forest and Range Experiment Station, Berkeley, California) "Possible Effects of Free Convection on Fire Behavior: Laminar and Turbulent Line and Point Sources of Heat," *California Forest and Range Experiment Station Technical Paper No. 8* (1954)

The theories of free convection from point and line sources of heat are reviewed for both laminar and turbulent flow. The theories are applied to atmospheric diffusion problems by appropriate modifications. The relation of these theories to the convective flow field above a surface fire is discussed. Only the thermal problem is considered; no attempt is made to include combustion effects.

To obtain a set of conservation equations which are amenable to analysis, the boundary layer equations are assumed to be applicable. Only incompressible flows are considered in detail; the temperature differences are assumed to be small in comparison with the absolute temperature. To relate the classical solutions of the free convection problem to atmospheric diffusion the concept of potential temperature is introduced. The solution of the laminar problem follows the method of E. Pohlhausen while the solution of the turbulent problem follows the method of W. Schmidt.* In the turbulent flow solution the Prandtl mixing length hypothesis is utilized for both the point and the line sources. The eddy diffusivities for heat and momentum are assumed to be equal. The mixing length is assumed to be proportional to altitude.

With source strengths representative of actual fires, inflow velocities and temperatures are found as a function of altitude. The results indicate that laminar sources tend to become uniform in cross section with large vertical velocities and high temperatures, as a result of the low lateral tendency to diffuse buoyancy and momentum. The turbulent sources diverge with a rapid diffusion of buoyancy and momentum depending upon the assumed value of the mixing length proportionality constant.

Despite the approximate nature of the analysis, the authors find sufficient differences between the laminar and turbulent solutions to conclude that turbulent source flows should be used for practical applications to large-scale fires.

By an approximate method the assumption of zero horizontal pressure gradient is verified. An attempt is also made to substantiate the use of incompressible flow theory. The methods of analysis are extended to finite source areas by introducing a virtual origin. With the point- or line-source moved some distance below the surface, the convective flow from a fire of finite area may be simulated.

Subject Headings: ***Convection, free, on fire behavior.***

D. L. Turcotte

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* Schmidt, v. W., Z. *angew. Math.* 21, 265–351 (1941).

Taylor, G. I. (University of Cambridge, Cambridge, England) "Flow Induced by Jets," *Journal of the Aero/Space Sciences,* **25**, 464–465 (1958)

This paper by G. I. Taylor is a comment on a recent article by A. M. Lippisch.* Sir Geoffrey did similar and additional work during World War II which has not been published except as internal reports to the British Ministry of Supply.†

The stream functions for flows induced by several types of jets are listed. The jets flow vertically upwards, are either forced or thermal, two- or three-dimensional, and issue either from a horizontal plane into the space above and are bounded by this plane, or they flow into unbounded space. Stream functions are given for seven of the eight possible cases; only the flow due to a line-heat source in an unbounded medium is omitted.

The method used for deriving the stream functions is described: each jet is replaced by an appropriate distribution of sinks and the corresponding potential flow pattern is calculated. Details of the computations are omitted. The stream functions are given by simple trigonometric expressions in five cases. Stream functions for the flows induced by a point-heat source on a horizontal bounding plane and in unbounded space are more complex, and for these two cases, plots of typical streamlines are shown.

Calculated streamlines are compared in two cases with streamlines observed experimentally by Lippisch. The streamlines of the flow induced by a forced, two-dimensional jet issuing from a horizontal plane are two sets of confocal parabolas with horizontal axes. Streamlines are convex upward, and the flows from either side curve down as they approach the vertical plane of symmetry.

Subject Headings: ***Jets, flow induced by.***

F. H. Wright

X. Meteorological Interactions

Gifford, F., Jr. (U. S. Weather Bureau) "Relative Atmospheric Diffusion of Smoke Puffs," *Journal of Meteorology,* **14**, 410–414 (1957) and "Further Data on Relative Atmospheric Diffusion," *Journal of Meteorology,* **14**, 475–476.

This paper presents a discussion on the application of Batchelor's similarity theory of relative atmospheric diffusion. The spreading of smoke puffs in the atmosphere should be governed by the laws of relative diffusion and not by the fixed-source diffusion law advanced by Taylor. According to Batchelor's theory, the mean-square dispersion is proportional to the cube of the time, once dependence on the initial puff size is lost. This differs from the fixed-source theory in that the latter theory assumes the mean-square dispersion is proportional to, at most, the second power of the time. The author's discussion emphasizes the fact that in smoke puff diffusion analysis no *a priori* assumption of a particular law of atmospheric diffusion is needed.

In his analysis of smoke-puff measurements reported by other researchers the author shows two definite dispersion regimes. Initially where time is small, the

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* Lippisch, A. M. "Flow Visualization," *Aeronautical Engineering Review,* 17, 24–32, 36 (1958).

† Walker, E. G., and Fox, D. A. "The Dispersal of Fog from Airfield Runways," *Ministry of Supply, London* (1946).

mean-square relative dispersion is proportional to the square of the time, with the initial puff size dominating the dispersion. In the other dispersion regime, the mean-square relative dispersion is proportional to the cube of the time. This regime begins at the "intermediate time" which is determined by the condition that the dependence of relative motion of two particles upon their initial separation has disappeared, but the dispersion is still dominated by the intertial subrange of eddy sizes. The author further states that the division between the two regimes is a function of the initial separation and energy dissipation rate. Values of the rate of eddy-energy dissipation are inferred from the smoke-puff data analyzed by the author.

Subject Heading: ***Diffusion, of smoke puffs; Smoke, atmospheric diffusion of.***

W. L. Fons

Smith, F. B. (University of Manchester, Manchester, England) "The Diffusion of Smoke from a Continuous Elevated Point-Source into a Turbulent Atmosphere," *Journal of Fluid Mechanics,* 2, 49–76 (1957)

This work consists of the highly mathematical treatment of a problem of interest in the field of atmospheric pollution, namely, the determination of the steady state concentration distribution of nonbuoyant smoke emitted from a continuous elevated source in a moving turbulent air stream. The treatment is based on solutions of the linear diffusion equation in which streamwise eddy diffusion is neglected compared with transverse diffusion. A one-parameter family of power-law velocity profiles in the vertical coordinate is assumed and transverse eddy diffusivities are taken to be independent of the position of the source. Anisotropy near the ground is accounted for by a difference in the two transverse components of the eddy diffusivity. Subject to these assumptions, and the conditions that the ground is impervious to the smoke and the concentration of smoke is zero at great heights, exact solutions are found for the zero and second moments of the concentration distribution along the ground in the crosswind direction for arbitrary values of the velocity profile parameter. For a particular value of this parameter the concentration distribution itself is found and is shown to be Gaussian. With the single hypothesis that these distributions are always Gaussian, explicit expressions for the surface concentrations in terms of the zero and second moments are obtained which were already found for arbitrary values of the velocity profile parameter. Finally, the combined effects of velocity profile and eddy diffusivity on the ground level concentrations are displayed graphically.

For eddy diffusivities which are independent of source position, a useful reciprocal or "reverse flow" theorem is proved, which generalizes earlier reciprocal theorems of Bosanquet and Pearson,* both as to velocity and diffusivity profiles. With its aid the problem of the transversely moving point source (*i.e.,* the "smoke-screen" problem) is treated, and the zero, first, and second moments of the crosswind concentration distributions are determined exactly, as well as the corresponding concentrations, subject only to assumption of Gaussian distribution.

Subject Headings: ***Atmosphere, turbulent diffusion of smoke in; Diffusion, of smoke; Smoke, diffusion.***

D. E. Rosner

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* Bosanquet, C. H., and Pearson, J. L. *Transactions of the Faraday Society,* 32, 1249 (1936).

Ball, F. K. (Division of Meteorological Physics, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia) "Some Observations of Bent Plumes," *Quarterly Journal of the Royal Meteorological Society,* **84,** 61–65 (1958)

Results of the measurements of the height of the smoke plume rising from four 10 kw. oil burners at distances of 30 and 60 feet downwind are presented and correlated with the previously published mathematical formulations of Priestley* and Sutton.† Using these formulations in conjunction with some simplifying assumptions, curves were drawn giving the height of the plume as a function of wind speed at a given distance from the source. The author develops a general nondimentional solution of Sutton's equation which, he states, can be applied to bent plumes on any scale.

The observations for low wind speeds in the range of 3 to 12 ft/sec scatter somewhat. For wind speeds exceeding 12 ft/sec buoyancy no longer dominates the motion of the plume. The experimental evidence thus favors neither Sutton's nor Priestley's formulation, both of which predict the height of the smoke plume as a function of wind speed as to reasonable accuracy. A third theory, that of Bosanquet, *et al.,*‡ is mentioned but not applied since it requires knowledge of the initial velocity and rate of emission of gas from the source, both of which are unknown in the present experiments.

Subject Headings: ***Smoke, plumes.***

A. Strasser

XII. Instrumentation

Halpern, C., and Ruegg, F. W. (National Bureau of Standards, Washington, D.C.) "A Study of Sampling of Flame Gases," *Journal of Research of the National Bureau of Standards,* ***60,*** 29–37 (1958)

This study was made to determine the effect of sampling conditions (velocity, quenching effectiveness, probe material, and design) on concentrations of carbon monoxide, carbon dioxide, hydrogen, and water. Samples were taken from a stable flame in a horizontal burner with a set of water-cooled probes 0.27 to 0.70 cm. internal diameter.

Methane-air and methane-oxygen mixtures were burned in bunsen flames at the discharge ports of various nozzles. Gas samples were dried and analyzed, either gravimetrically or volumetrically. Probes were mounted with the center of the tip coaxial with the flame cone.

Experimental results were compared with the calculated theoretical compositions for various mixtures burning at various temperatures.§ These calculations assume chemical equilibrium. Since sodium line-reversal temperatures are close to the theoretical values, the assumption seems justified. Experimental compositions

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* C. H. B. Priestley *Quarterly Journal Royal Meteorological Society,* 82, 165 (1956).

† O. G. Sutton *Journal of Meteorology,* 7, 307 (1950).

‡ C. H. Bosanquet, W. F. Cary, and E. M. Halton *Proceedings of Institution of Mechanical Engineers,* 162, 355 (1950).

§ Hottel, H. C., Williams, G. C., and Satterfield, C. N. "Thermodynamic Charts for Combustion Processes" (John Wiley & Sons, Inc., New York, N.Y. 1949).

were used to calculate an equilibrium constant and its associated temperature T_{aq} (apparent quenched temperature). This approximates the temperature to which a gas is slowly cooled under equilibrium conditions and then completely quenched. This temperature, when compared to the adiabatic flame temperature, gives an indication of the effectiveness of probe quenching.

The effect of sampling velocity was studied with a mixture having the mole proportions $CH_4:O_2:N_2=1:2:2$ burning on the port of a 0.457 cm. nozzle, with the probe positioned 0.36 cm. above the inner cone tip. Probes of various diameters were used and show that the ratios of CO/CO_2 and H_2/H_2O are constant for a range of sampling velocities and then decrease linearly as the sampling velocity increases. The decrease is caused by gas from the cooler regions of the flame being drawn into the probe. Sampling velocities ranged up to 92,000 cm/sec or about Mach 0.85.

The CO/CO_2 and H_2/H_2O data show T_{aq} to decrease linearly with increasing probe diameter. An extrapolation to zero diameter gives apparent temperatures below the adiabatic flame temperature for both cases, with the H_2/H_2O data having the greatest deviation.

Stainless steel, silver, and platinum probes were used and all gave the same quenching effectiveness. Some corrosion and scaling were observed for the steel and silver probes.

Only slight improvements were obtained if bends or nozzles were used as the probe tip. A probe L/D ratio of 35 to 1 was sufficient to cool the gas.

As the temperature of the gas increased, the effectiveness of the probe in quenching the reactions decreased. The apparent temperatures based on hydrogen were found to be lower than those based on carbon over most of the range. At 1600° K they appear to become equal and to coincide with the theoretical flame temperature. Below 2250° K only small composition differences were observed.

Subject Headings: ***Flame, gases, sampling of; Gases, flame, sampling of.***

J. M. Douglas

Thomas, A. (Imperial College, London) "An Isothermal Calorimeter for Measuring Low Rates of Heat Evolution Over Long Periods," *Transactions of the Faraday Society,* **47,** 569–573 (1951)

A constant temperature calorimeter has been developed which is useful for the measurement of heat release at low rates ($\frac{1}{2}$ to 1 cal/hr), characteristic of oxidation of solids in storage.

Basically, the device is a modified bunsen ice calorimeter which measures the volume change of naphthalene on melting after absorption of heat; the use of naphthalene is dictated by the reliability and precision of its melting point at the temperature of the experiment (75–80° C).

Oxidation of the solids takes place in a jacketed chamber. The space between the two walls is filled with mercury and naphthalene; the latter floats atop the mercury. Prior to the experiment, a mantle of solid naphthalene is deposited around the pyrex reaction chamber. The heat produced by the oxidized solids melts the solid mantle which increases in volume to the extent of 0.479 cm.^{3} for each 100 cals. liberated. The displaced mercury is measured in a long graduated capillary tube.

The solid reactant (e.g., oilseeds) is placed in the chamber which is filled with nitrogen to inhibit reaction, and installed in the brass pot. The thermostat bath oil surrounding the pot is heated and the naphthalene within the jacket is melted by a nichrome-wire electrical heater. Heating is terminated when the height of displaced mercury indicates that the naphthalene is completely melted. A mantle of solid naphthalene is formed by passing 1 $cm.^3$ of water through the reaction chamber. Fine adjustment of the thermostat temperature is made and after equilibrium conditions are reached, the nitrogen in the reaction chamber is displaced by oxygen.

The subsequent evolution of heat and changes in chamber pressure caused by oxidation are followed by observation of the mercury column position and a manometer. Calibration is achieved by substituting a heating coil for the solid reactant.

Variation in heat transfer to the surroundings introduces the greatest source of error. However, this error decreases relative to the total error as the heating rate increases in magnitude.

Subject Headings: ***Calorimeter, for low rates of heat evolution; Heat evolution, calorimeter for low rates.***

K. M. Foreman

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Errata – Volume I Number 1

page 15 line 1 for HH_2 read H_2
line 6 for vertical read horizontal
line 12 for -25 read <25

page 16 line 4 from bottom of page
delete entire line
insert—the fire, the flames moved upwards against the spray. With a spray of high entrained

page 24 equation 14 for fr read f_r
line 5 from bottom of page for 0.23° read 0.23

page 25 equation 32 for C_i read C_t

Volume I May 1959 Number 3

Fire Research Abstracts and Reviews

Committee on Fire Research
and
Fire Research Conference

Division of Engineering and Industrial Research
NATIONAL ACADEMY OF SCIENCES—NATIONAL RESEARCH COUNCIL
Washington, D. C.

FIRE RESEARCH ABSTRACTS AND REVIEWS is published three times a year by the Committee on Fire Research and the Fire Research Conference of the National Academy of Sciences — National Research Council, 2101 Constitution Avenue, Washington 25, D. C. It is supported by the Office of Civil and Defense Mobilization, the U. S. Department of Agriculture through the Forest Service, and the Department of Defense under Contract CD-SR-58-45. The opinions expressed by contributors are their own and are not necessarily those of the Committee on Fire Research and the Fire Research Conference.

Fire research abstracts and reviews. v. 1–
Sept. 1958–
Washington, Division of Engineering and Industrial Research, National Academy of Sciences, National Research Council.

v. 26 cm. 3 no. a year.

Issued by the Committee on Fire Research and the Fire Research Conference.

1. Fire extinction—Abstracts. 2. Fire prevention—Abstracts. 3. Combustion—Abstracts. I. National Research Council. Committee on Fire Research. II. National Research Council. Fire Research Conference.

TH9111.F77 614.84082 58–60075 rev

Library of Congress

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COMMENTS AND DISCUSSIONS

FOREWORD

It will be of interest to the readers of this Journal that a technical meeting on an international scale is being planned by the Committee on Fire Research. The subject of the symposium is "The Use of Models in Fire Research." The choice of this topic is particularly satisfying at this time since it emphasizes the point that a successful attack on the fire problem must be based on sound concepts and ideas of the over-all processes. Models, even though they generally oversimplify actual situations, stress the important parameters involved. Once they are known and understood, further search in depth can be carried out with profit. Without sound models it is difficult to decide what avenues of research should be taken.

Although the need for a sound fire research effort has long been recognized, a re-examination is taking place of the responsibility of the federal government to support the program, now that advances in various scientific disciplines may provide significant and fruitful solutions to the fire problem. The Committee on Fire Research has made representations to the National Science Foundation and to The President's Scientific Advisory Committee for sympathetic consideration of research proposals in the fire area, and such proposals have been requested from a number of people and organizations with interest and competence in this field.

Even though the publication of new scientific findings was not intended to be a function of *FIRE RESEARCH ABSTRACTS AND REVIEWS,* a new section of "Comments and Discussions" is added to this issue. In it short communications and announcements of significant findings can be presented prior to formal publication in technical journals or reports.

Walter G. Berl

REVIEW

Mechanisms of Action of Chemical Agents for Flame Extinguishment*

by

Raymond Friedman and Joseph B. Levy

The following review is based on a continuing effort by the authors to relate significant results of combustion research to the interpretation of fire extinguishment. Success in understanding the latter is intimately bound up with further knowledge of combustion principles in general. The authors, located at the Atlantic Research Corporation, Alexandria, Virginia, have made many significant contributions in the combustion field and are, therefore, well qualified to write this review.—EDITOR

Fire is one of the most common of our everyday phenomena. Yet fire, or a flame in air, represents an exceedingly complicated physico-chemical system. Despite the efforts of hundreds of research workers who have studied the propagation of flames and have advanced our knowledge so far in this area, our understanding of the combustion of even the simplest systems, such as methane burning in air, is incomplete. In this paper we shall deal with a subject which, although not as thoroughly studied as the propagation of combustion, is likewise very important and very complicated—the chemical extinguishment of flames. We shall be interested here only in the mechanism of chemical extinguishment, *i.e.,* just how those agents that we can call chemical extinguishers perform their functions. Other facts such as toxicity, cost, etc., which are very important from the point of view of practical application, will not be discussed here.

We start by considering the nature of flames, which we classify as arising from the burning of gases, liquids, or solids in air. In the combustion of liquids, vaporization from the liquid surface occurs so that the combustion system is really that of a gas in air. For solids it is likewise often true that evolved gases burning in air comprise the main part of the combustion system. Since the bulk of the experimental work has been done with gaseous systems, the knowledge gained there being applicable to the burning of liquids and, in most cases, to the burning of organic solids, we shall direct our discussion to the burning of gases in air or oxygen.

Gaseous flames may be classified as diffusion flames or premixed flames. Let us consider a stream of natural gas issuing from a pipe and burning in air, such as the old-fashioned gas lights. The air necessary for combustion diffuses into the fuel stream. This is a diffusion flame. An oxy-acetylene torch represents a premixed flame. The fuel and oxygen are first mixed and then ignited. Both types of flames have many things in common. Both have a very hot flame zone where the main reaction of fuel and oxidant is occurring. In both, heat is transferred to the unburned gases to heat them to a temperature high enough so that the combustion reactions occur. In both, a state of balance exists wherein the heat produced in the flame zone raises the temperature of the reactants so that further reaction can occur and the flame is sustained.

Let us now consider mechanisms whereby flames can be extinguished. It is

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* Note: Under sponsorship of Wright Air Development Center, U.S. Air Force, the writers have prepared a series of surveys [9, 10, 11] of the state of fundamental knowledge and current research dealing with the basic principles involved in flame extinguishment by chemical agents. The following discussion touches on some highlights. Research workers are referred to the original survey reports

at once clear that diffusion flames can be extinguished if the fuel and oxidant can be separated. This is called smothering or blanketing and it is the primary mechanism whereby a stream of carbon dioxide extinguishes a burning pool of gasoline, for example. This mechanism clearly cannot operate in premixed systems.

A second mechanism of extinguishment which we may call mechanical extinguishment is exemplified by the blowing-out of a match or the extinguishment of an oil fire by blasting. Here the flame zone is physically removed from the unburned gases so suddenly that propagation cannot be sustained. This mechanism can operate on both types of flame.

A third extinguishment mechanism is that of cooling. The state of thermal balance that exists for a flame results in a steady burning speed of the flame. The heat produced in the flame heats the reactants to a temperature where they in turn react to produce heat. If such a system is cooled, as by the injection of an inert gas, or the addition of a vaporizable liquid like water, the temperature falls, the reactions go more slowly, and the flame burns less vigorously. For all flames there is some minimum burning rate below which they are not stable and will go out. When the system has been cooled below this point extinguishment occurs by cooling.

The above mechanisms of extinguishment, by virtue of the nature of their modes of action, can properly be called physical mechanisms. There are, however, agents whose extinguishing action cannot be explained on the basis of the above mechanisms and which, although their action is not well-understood, appear to operate by affecting the chemistry of flame reactions. Their mechanism of action will, therefore, be referred to as chemical extinguishment. Because the speeds of chemical reactions can vary by many factors of ten, chemical extinguishing agents offer, at least in theory, the possibility of major advances in extinguishing ability and hence in fire fighting. It is for this reason that the Department of Defense has directed its efforts toward sponsorship of research in this area, and it is with this type of agent that the remainder of this discussion will be concerned.

There are, in general, two classes of materials that can be called chemical extinguishing agents, the covalent alkyl halides and dry inorganic salts. They will be discussed here in turn.

The Covalent Halides

Under the heading "covalent halides" we may include all compounds of carbon that contain members of the halogen group; *i.e.*, fluorine, chlorine, bromine, and iodine. These are liquids or gases and must be distinguished from compounds of metal and the halogen, such as sodium chloride, which are completely different chemically and would be called ionic halides. Carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), and the Freons (CF_2Br_2; CF_3Br), are common examples of covalent halides. Carbon tetrachloride has long been used as an extinguishing agent. During World War II, the Germans carried out tests on chlorobromomethane (CH_2ClBr) and were preparing to utilize it as the principal ingredient in fire-extinguishing agents on their military aircraft.

We may inquire first what evidence there is to show that materials of this class extinguish by a chemical rather than a physical mechanism. Figure 1 is a flammability-limit plot for the methane-air system. The region inside the curve represents the region of flammability, that exterior to it of nonflammability. Thus methane-air mixtures will not burn if there is less than 5.4 per cent or more than

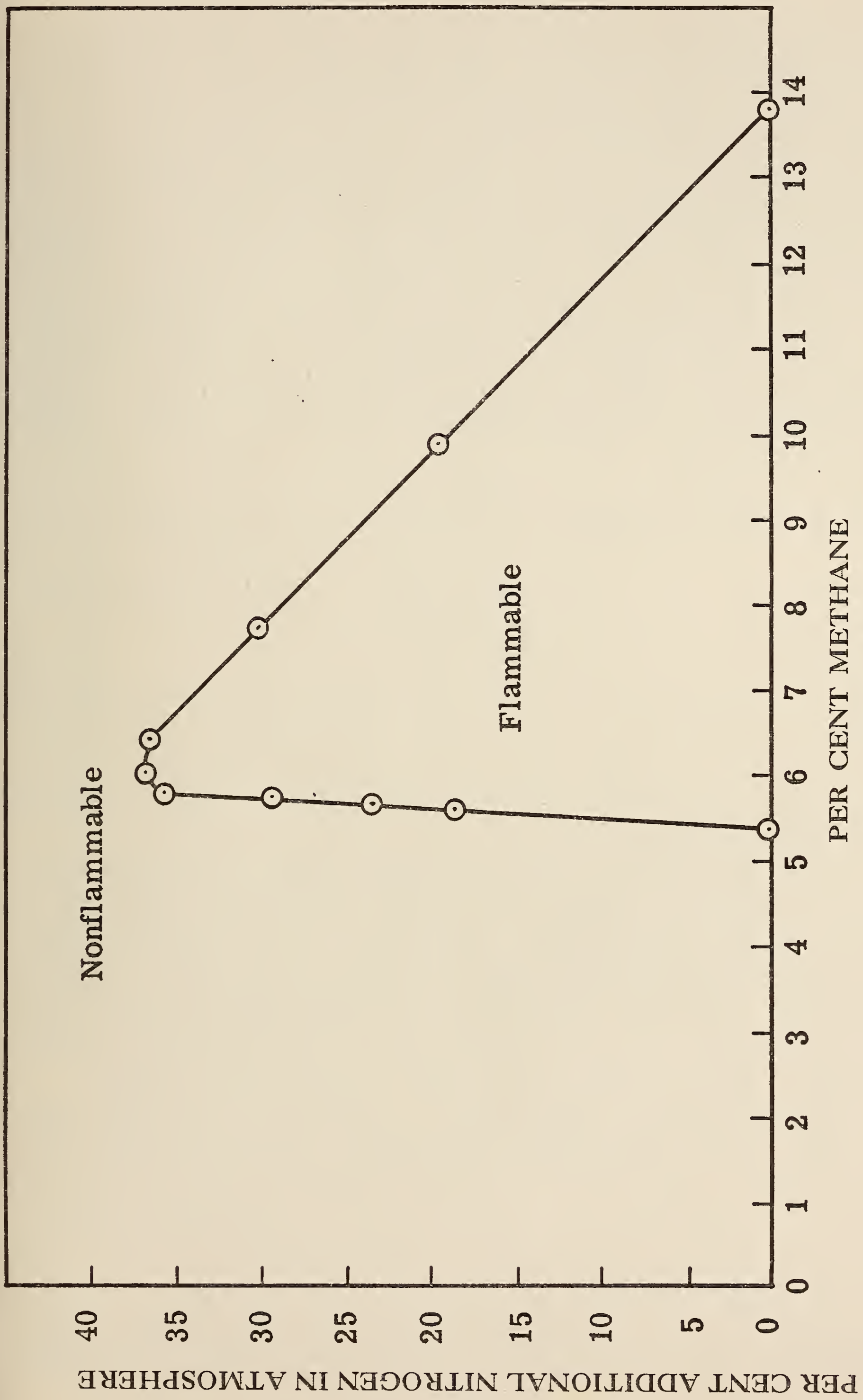

Figure 1

Flammability Limits of Methane - Air - Nitrogen Mixtures

13.8 per cent methane present. If excess nitrogen is added the flammability limits shrink until, when 38 per cent excess nitrogen is present, no methane-air mixture will burn, whatever the proportions. This percentage of nitrogen is called the peak percentage. It can readily be interpreted in terms of the cooling effect of the inert nitrogen. Carbon dioxide, which has a higher heat capacity than nitrogen and hence soaks up more heat per molecule, has a peak percentage of 25 per cent for the methane-air system. The compound methyl bromide (CH_3Br), on the other hand, has a peak percentage of 4.7 per cent. This amount is far too small to be interpreted by a cooling mechanism and it follows that methyl bromide must be extinguishing the flame by some other mechanism which can only be chemical in nature. Table I shows data taken from the work of J. H. Burgoyne and his co-workers at the Imperial College of Science and Technology, London [6] which lists further examples of the relative extinguishing powers of methyl bromide. It is clear that its extraordinary extinguishing power is a general phenomenon for flames in air. Rosser and Wise[18] at the Stanford Research Institute, under sponsorship of Wright Air Development Center, have recently found that covalent halides are not effective in flames where nitrogen dioxide is the oxidizer. This work awaits further elucidation.

TABLE I

Comparison of the Extinguishing Power of Methyl Bromide, Nitrogen, and Carbon Dioxide

Combustible (In Air)	Peak Percentage		
	Methyl Bromide	Nitrogen	Carbon Dioxide
Hydrogen	13.7	75	61
Carbon Monoxide	6.2	68	52
Ethylene	11.65	50	41
Methane	4.7	38	25
n-Hexane	7.05	42	29
Benzene	7.75	44	31

Evidence of this type is the basic evidence for the chemical extinguishing effect of methyl bromide. In addition, flame temperatures have been calculated by Burdon, Burgoyne and Weinberg [5] for mixtures of hydrogen-air-methyl bromide and carbon-monoxide-air-methyl bromide where the amounts of methyl bromide were just below those required to render the mixtures nonflammable. These temperatures have been found to be several hundred degrees above those corresponding for extinction by addition of a cooling diluent. The existence of a chemical extinguishing mechanism rather than a cooling mechanism is thus supported.

A few years ago the Corps of Engineers of the U.S. Army sponsored a research project at Purdue University [17] in which fifty-six covalent halides were evaluated as fire-extinguishing agents using n-heptane (C_7H_{16})-air mixtures. The general procedure was to fill a glass tube with n-heptane-air-covalent halide mixtures of known composition and to ignite the mixture at one end of the tube. If ignition propagated, *i.e.,* if a flame travelled up the tube, the mixture was flammable and other mixtures were tested until the flammability curve, similar to that of Figure 1, could be plotted.

It was found that alkyl bromides in general were effective agents. Alkyl iodides were about as effective as bromides while alkyl chlorides were markedly less effective. Alkyl fluorides were comparatively ineffective. Simmons and Wolfhard[21] at the Royal Aircraft Establishment, Westcott, England, studied the effect of methyl bromide (CH_3Br) and of bromine (Br_2) on methane- or ethane-air flames. Their results indicated that bromine was about twice as effective as methyl bromide, *i.e.,* the number of bromine atoms introduced is the decisive factor. Rosser, Wise, and Miller,[20] of Stanford Research Institute, in a project sponsored by the Engineer Research and Development Laboratories, U.S. Army, measured the effectiveness of halogen-containing agents on methane-air flames by measuring the decrease in flame speed brought about by the addition of small amounts of agent. They studied bromoform ($CHBr_3$) as well as mono and dibromides and concluded likewise that it was the number of bromine atoms that was important.

Various workers have attempted to explain the effect of these agents.[2, 5, 19, 23] All the explanations are based on interactions in the flame zone. We have mentioned earlier that the flame zone is a very hot region of the flame (~1500–3000°C). At temperatures of this order we expect large concentrations of very reactive species. At about 2500°C, for example, water is largely dissociated into hydrogen atoms (H) and hydroxyl radicals (OH). Various other such species, such as methyl (CH_3), ethyl (C_2H_5), etc., are present in flames of hydrocarbons. These species are capable of very fast reaction by a chain-reaction mechanism. In a hydrogen-oxygen flame, for example, the processes occurring in the flame zone are generally considered to be of the type

$$H+O_2 \rightarrow OH+O \qquad \text{(I)}$$

$$OH+H_2 \rightarrow H_2O+H \qquad \text{(II)}$$

$$O+H_2 \rightarrow OH+H \qquad \text{(III)}$$

In each reaction an active species, H, OH, or O is used up, but one or more new active species are formed. Thus H is used up in (I) but produced in (II) and (III). In the course of this, hydrogen and oxygen are converted to water. Once an H (or OH or O) is formed, it can then start a series or chain of reactions of the above type. If one of the active species in the chain (called a chain carrier) is destroyed by something which is introduced, this prevents the occurrence of the whole chain of reactions that would have followed, and this chain-length may vary from a few to many thousands. Thus, breaking a chain can exert a powerfully retarding effect on chain reactions; covalent halides are believed to extinguish flames by acting as efficient chain breakers. The order of activity wherein bromine and iodine compounds are more effective than those of chlorine, which are in turn more effective than those of fluorine, is in harmony with this mechanism. There is ample chemical evidence that this is the order found in reactions of halogen compounds with active species of the above type.

Complete proof of this mechanism is most difficult because of the experimental difficulties encountered in the study of flame reactions. It is, however, a most plausible mechanism. Whether it will be possible to find even more potent chain breakers than the covalent halides, only further research can decide.

The Inorganic Salts

The fact that salts of the alkali metals affect various aspects of combustion processes has been known for a long time.[1] In the operation of blast furnaces it has been observed that the gases formed burn regularly only after the potassium salts held in suspension are removed. The hazard of igniting combustible coal-mine atmospheres by setting off explosive charges has long been minimized by the incorporation of salts in the explosive either as a sheathing material or as an intimate mixture. The salts are thus present in the explosion products and are effective in preventing ignition of combustible gases in the atmosphere. The use of sodium and potassium salts in suppressing muzzle flash in gun firings has also been known for some time.

Commercial fire extinguishers in which dry salts are the extinguishing agents have been available for many years. The fact that bicarbonate or carbonate salts have generally been principal ingredients in these dry salt agents has suggested the possibility that the extinguishing action arose from the evolution of carbon dioxide as a result of the heat of the flame. Although the evolution of carbon dioxide would have an effect on the flame, it may be pointed out that:

a) Studies have shown that most of the salt is recovered unchanged, *i.e.,* that the carbon dioxide is evolved in only small amounts.[16]

b) Salts which cannot evolve carbon dioxide are effective to the same degree as are carbonates.[22]

The effects of salts on combustion have been studied scientifically by direct application of salts to test fires, by observing the effects of dispersing them in the finely divided state in combustible gases, and by applying them as coatings to container walls and observing their effects on ignition.

The results obtained from such experimentation are typified by the careful measurements of Dolan and Dempster [7, 8] in Scotland, or Laffitte and coworkers [3,14] in France, who studied the ability of flames to propagate through combustible gaseous mixtures containing suspended dust particles of various materials and particle sizes. Two important things have been learned from these studies: (I) The finer the particle size, the more effective is the dust, as long as it is effectively dispersed. In some cases the surface area per unit weight of dust has been shown to be inversely proportional to the weight required for extinction of a unit volume of gas. (II) When different solids of the same particle size are compared, tremendous differences in effectiveness are found, which appears to prove that the effect must involve chemistry, even though physical factors may also be involved.

The idea of the importance of chemical effects is also supported by the experiments of chemical kineticists [13, 24] who have found the explosion limits of gas mixtures in glass vessels are drastically changed by coating the walls with certain salts, notably potassium chloride.

Research has not been carried far enough to reveal the details of what happens when a powder is introduced into a flame. The dependence of effectiveness on surface area could be explained by assuming any of the following: (A) gaseous diffusion of flame species to the particles, followed by surface reactions which destroy chain carriers; (B) partial evaporation of the powder to form gaseous species which inhibit the combustion, the rate of evaporation being proportional to surface area; (C) in cases where the flame is burning over a liquid, radiation from the flame to the fuel source is blocked to a degree dependent upon state of subdivision of the powder.

Noting that Dolan and Dempster [7, 8] had found powdered aluminum chloride to be one of the most effective substances they studied, and further noting that this salt may be relatively easily vaporized, Levy and Friedman [12, 15] at Atlantic Research Corporation carried out vapor-phase studies of burning velocity of the system methane-air-aluminum chloride at 200°C, under sponsorship of Wright

Air Development Center. They measured the rate of decrease of burning velocity with increasing inhibitor concentration, and compared with published results of the effectiveness of carbon tetrachloride and elemental chlorine. They concluded that the results could be generally accounted for by the assumption that the inhibiting effectiveness per atom of chlorine is essentially independent of the nature of the chlorine carrier. Further, they found that aluminum chloride vapor was apparently not quite as effective an inhibitor as Dolan and Dempster's results indicated for the powder. They attributed this to the more favorable conditions for stable burning present with their burner as compared to Dolan and Dempster's combustion tube and spark source. This study suggests that the inhibiting behavior of at least one solid salt may be accounted for by the hypothesis that it vaporizes and is effective in the vapor phase.

It is interesting to note that dispersed solids have been found [4, 14] to extinguish detonations propagating through a tube containing a combustible gas mixture, but the order of effectiveness of various solids is entirely different than for extinguishment of ordinary flames. Specifically, silica powder was far better for extinguishing detonations than for extinguishing ordinary flames, potassium oxalate being used as a standard for comparison. No explanation for this behavior is known.

Conclusions

Throughout the world, scientists are interested in understanding how chemical additives interact with flames to cause their extinguishment. This interest is motivated partly by scientific curiosity, but mainly by the hope of finding more effective ways for controlling fires. Scientific progress is very slow because flames are extremely complicated and only partially understood. The high temperatures and short times involved in combustion of a given molecule of fuel make direct experimental studies very difficult. It may also be said that, while isolated scientists are working on the problem, often intermittently, particularly in the United States, England, France, Russia, and Japan, the over-all level of effort devoted to the problem is quite small. The rate of further progress will probably depend in large measure on the degree of continuing support available.

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Subject Headings: ***Extinguishment, action of chemical agents; Flame, chemical agents for extinguishment of.***

ABSTRACTS

I. Ignition Phenomena

Gross, D. and Robertson, A. F. (National Bureau of Standards, Washington, D.C.) "Self-Ignition Temperatures of Materials from Kinetic Reaction Data," *Journal of Research of the National Bureau of Standards,* 61, 413–417 (1958) *

The self-ignition of materials placed in long-period storage is attributed to a self-heating reaction within the material generating heat in excess of that lost at the surface to the surroundings. Prior to self-ignition a critical steady-state heat balance exists wherein the heat generated equals the heat lost. In this condition a slight increase in either the "critical" bulk size of the material or the "critical" ambient temperature (ignition temperature) results in self-ignition.

This work deals with a technique for obtaining kinetic reaction data which can be used to predict critical surface and ambient temperatures as a function of size and shape of the following materials: wood fiberboard, cotton linters, sugar pine, cork, crepe rubber, GRS, foam rubber (100 per cent natural, 100 per cent synthetic, blended with and without additive), oils (raw linseed, cottonseed, rapeseed, sperm, olive, castor, and neatsfoot), ammonium perchlorate, nitrocellulose plastic. The analysis considers three different geometrical shapes, sphere ($m=2$), cylinder ($m=1$), and semi-infinite slab ($m=0$). It is assumed that heat is generated according to the first order reaction law ($A \exp\text{-}E/RT$) and transferred by conduction to the surface or, stated analytically

$$k\left[\frac{d^2T}{dx^2}+\frac{m}{x}\frac{dT}{dx}\right]+Ae^{-E/RT}=0 \tag{1}$$

$k =$ thermal conductivity
$A =$ heat generation coefficient
$E =$ activation energy

Two solutions of equation (1) are used. The one by Thomas † involves the assumption that temperature differences within the material are small compared to the temperature. The other by Enig *et. al.,*‡ a numerical solution presented as tables of center (T_o) and surface temperatures (T_B), does not give the corresponding ambient temperatures (T_A); but is more general, not being subject to Thomas' restrictive assumption. The authors evaluate the ambient temperature from the data given by Enig *et.al.* from the equation

$$T_A=T_B-\frac{A\ B_c}{3\ h}e^{-\frac{E}{RT_m}} \tag{2}$$

$h =$ surface film coefficient
$B_c =$ critical radius (half thickness)

which was obtained by assuming heat generated is lost at the surface according to Newton's law of cooling ($T_m=T_o-T_A/2$).

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* A comment on this paper appears on page 143

† Thomas, P. H., "On the Thermal Conduction Equation for Self-heating Materials with Surface Cooling," *Transactions Faraday Society,* 54, 60 (1958)

‡ Enig, J. W., Shanks, D., and Southward, R. W., "The Numerical Solution of the Heat Conduction Equation Occurring in the Theory of Thermal Explosions," *NAVORD rep.* 4377 (1956)

Inasmuch as the general problem of self-heating depicted above is difficult to duplicate in the laboratory (*i.e.,* fixed ambient temperature, etc.) the kinetic reaction constants (A and E) are determined under self-heating conditions involving negligible loss of heat from the specimen. The constants are thus evaluated quite readily from

$$\rho c\frac{dT}{dt}=Ae^{-\frac{E}{RT}} \tag{3}$$

In particular the specimen is placed in an "adiabatic" furnace equipped with a servo-controller which maintains the temperature of the surrounding air very close to the mean temperature of the specimen over a range of 30 to 300°C.

The computed values of self-ignition temperature for various sizes of wood fiberboard and cotton linters appear to agree well with corresponding experimental determinations. Whether this agreement exists for the other materials tested is not indicated and until verified it is questionable whether the first order reaction hypothesis is the correct mechanism for all materials. However, the experimental technique presented in this paper for determining kinetic data for reactions of this type is certainly worthwhile.

Subject Headings: ***Ignition, temperatures, from kinetic reaction data.***

P. A. Ross

Toong, T. Y. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "Ignition and Combustion in a Laminar Boundary Layer Over a Hot Surface," *Sixth Symposium* (*International*) *on Combustion,* New York, Reinhold Publishing Corporation, 532–539 (1957)

The author reports on a theoretical and experimental study of the problem of ignition of a steady stream of combustible mixture in the laminar boundary layer over an isothermal flat plate. The study is an effort to further the basic understanding of the effects of reaction rate and transfer of momentum, heat, and mass on ignition. The advantage of utilizing a flat plate over that of immersing the igniter in the stream is that the flow pattern, both theoretical and experimental, is one which may be accurately described and analyzed by the use of boundary-layer theory. The theoretical results obtained in the first phase of the project are presented, as well as a qualitative comparison of the theoretical predictions of the conditions for incipient ignition with experimental results.

Preliminary tests consisted of the study of the effects of velocity, density, and temperature of the free-stream of a stoichiometric mixture of ethyl alcohol and air on the surface temperature required for ignition. The experiments were conducted in a ½ in. i.d. Nichrome test section, 2 in. in length. The free-stream velocity was varied over the range from 25 to 90 ft/sec and the ratio of the wall temperature to the free-stream temperature from 3.4 to 4.0. Free-stream temperatures ranged from 634 to 704° R. Comparison of the theoretical and experimental results verifies the qualitative predictions, namely: (1) for a mixture of given composition and a flat plate of given length, ignition occurs at the same value of the surface temperature ratio if the free-stream velocity varies directly with the free-stream density; (2) for a given value of the dimensionless activation energy, the exponential term increases as the surface temperature increases; hence, as the free-stream velocity increases, the surface temperature ratio required for incipient ignition increases; (3) in order to ignite a given mixture at the same surface temperature ratio but at a higher free-stream velocity, the free-stream temperature must increase.

Computer solutions of the boundary-layer equations are presented, subject to the usual boundary-layer approximations. It is assumed that the reaction occurs in a single step and is of second order and Arrhenius type, the fluid being a perfect gas with constant molecular weight, specific heats, and Prandtl and Schmidt numbers. The viscosity is presumed to vary directly with the absolute temperature. The velocity, temperature, concentration, and reaction rate profiles across the laminar boundary layer are presented at various distances downstream of the leading edge of the heated plate for a value of the ratio of wall temperature to free-stream temperature of 3.9. The Prandtl and Schmidt number values were chosen as 0.65, the dimensionless activation energy and enthalpy of combustion as 57.5 and 6.64 respectively. The development of combustion in the physical plane is presented for the same values. The thermal and velocity boundary layer growths are shown with and without chemical reaction, and various streamlines are plotted. The velocity, temperature, concentration, and reaction rate at two downstream stations are presented. Variation of the temperature, concentration, and reaction rate along the individual streamlines are shown. The proximity of a streamline to the heated surface determines the relative importance of the reaction rate.

Subject Headings: ***Ignition, and combustion, in laminar boundary layer; Ignition, surface, in a laminar boundary layer; Boundary layer, ignition and combustion.***

L. A. Povinelli

Swarts, D. E. and Frank, C. E. (University of Cincinnati, Cincinnati, Ohio) "Effect of Hydrocarbon Structure on Reaction Processes Leading to Spontaneous Ignition," *National Advisory Committee for Aeronautics Technical Note 3384* (July 1955)

Several hydrocarbons were oxidized in a flow system and product analyses made. The reactor was a small glass tube (1/16″ or 1/4″ diameter) and contact times varied from 0.04 to 0.16 seconds; the temperature was varied from 350 to 550°C. The product stream was led through a series of cold traps (−70°C) and finally through a 2,4 dinitrophenylhydrazone scrubbing solution. The analytical procedure resulted in data on total peroxides, H_2O_2, total carbonyl compounds, total olefins, total aldehydes and total acids. The hydrocarbons investigated were 2,2,5 trimethylhexane, 2,2 dimethylbutane, 2,3 dimethylbutane, n-heptane, isobutane, 3 heptene and isobutene.

Within the experimental accuracy, the comparable data led to the following order of stability for oxidative attack isobutane $\geqq$ isobutene $>$ iso-octane $>$ 2,2,5 trimethylhexane $>$ 3 heptene $>$ n-heptane. The branched hexanes were not studied under comparable temperature conditions, hence cannot be included in this ordering. 2,3 dimethylbutane is less readily oxidized than the 2,2 isomer.

The authors briefly discuss generalizations based on their data. Generally speaking, the ease of attack on hydrogens at various positions in a hydrocarbon molecule is tertiary $>$ secondary $>$ primary. Thus, adding a methylene group to iso-octane results in lower stability of 2,2,5 trimethylhexane. The importance of steric effects however, is clearly indicated in the case of the isomeric hexanes, where this effect is probably responsible for the observed results. Hydrogen abstraction from a hydrocarbon molecule yields a radical. In the case of 3 heptene, this radical can be stabilized by resonance, whereas the radical formed from n-heptane cannot be stabilized in this way. Both the lower reactivity of the more stable radical, and its relatively unfavorable thermochemistry point in the direction indicated by experiment, namely, that 3 heptene is more stable than n-heptane. Even these cursory remarks illustrate the complexity of the oxidative process.

The small diameters of the furnaces employed in this work were deliberately chosen to push the conditions beyond the normal auto-ignition limit. As such, the comparative data on the 1/16″ and 1/4″ diameter furnaces might be useful in design of catalytic burners to avoid explosions. The high surface-to-volume ratio also magnifies the wall effects considerably, and the data on product analyses await kinetic interpretation when the wall reactions in hydrocarbon oxidation are identified. The product distribution curves are not unexpected.

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

P. R. Ryason

O'Neal, C., Jr. (National Advisory Committee for Aeronautics, Cleveland, Ohio) "Effect of Pressure on the Spontaneous Ignition Temperature of Liquid Fuels," *National Advisory Committee for Aeronautics Technical Note 3829* (October 1956)

The variation with pressure of the spontaneous ignition temperatures was determined for several fuels in air. The fuels were n-heptane, iso-octane, benzene, JP-4 aviation fuel and JP-5 aviation fuel. A pressure range of 1 to 9 atmospheres was investigated. A 125cc. Erlenmeyer flask, in a cast iron pressure chamber served as the ignition vessel. The flask was heated by an electrical mantle. A Bosch pump was used to inject fuel into the vessel as a liquid stream. The ignition delay was taken as the time interval between fuel injection and the first appearance of a visible flame. Ignition delays of 3 to 4 minutes were used to define the spontaneous ignition temperature. The high temperature of the ignition flask assured essentially complete evaporation of the liquid fuel. Thus, ignition occurred in a fuel-rich fuel-air mixture, since the air in the pressure chamber was stagnant. The mixture was probably not homogeneous, hence the data refer to ignition of mixtures of unknown fuel-air ratios.

In all cases, the measured spontaneous ignition temperatures decreased with increasing pressure. The principal decrease occurred, in every instance, between 1 and 4 atmospheres. Increasing the pressure from 1 to 9 atmospheres resulted in the following decreases in spontaneous ignition temperature: benzene, 626 to 350°C; iso-octane, 467 to 231°C; n-heptane, 250 to 191°C; JP-4 fuel, 272 to 210°C; JP-5 fuel, 247 to 206°C.

A constant 20°C difference was noted between the spontaneous ignition temperatures of two samples of JP-4 fuel. To remove possible inhibitors, such as metallo-organic or amine compounds, both fuels were percolated through silica gel. This lowered the difference to about 10°C. While the treatment would also lower the aromatics level in both fuels, as well as the additive level in both cases, it is not evident what one should expect in an unknown mixture as regards the spontaneous ignition temperature.

Increasing the pressure tends to reduce differences in spontaneous ignition temperatures. Thus, the spontaneous ignition temperature determined at low pressures may not be used to compare with another fuel at a high pressure. The differences become smaller at higher pressures.

It was found necessary to season the flask to obtain reproducible data for the spontaneous ignition temperature of benzene. Also, an apparent break in the spontaneous ignition temperature pressure curve was noticed for benzene. This has not been reported previously for this compound.

From a plot of heptane ignition lag data *vs.* reciprocal temperature, an activation energy for ignition was derived ($\triangle E \approx 22$ kcal/mole). This is in fair agreement with previous values. In general there is good agreement with previous data for the pure compounds. The ignition temperatures, and the total decreases of spontaneous ignition temperature with pressure are ranked aromatic>branched chain paraffin>straight chain paraffin.

The data in this paper will be useful in evaluating permissible residence times of fuel-air mixtures in regions of hot walls and pressures above atmospheric. Potential fire hazards can be more readily and accurately assessed when information such as given in this paper is readily available.

Subject Headings: *Ignition, temperatures, effect of pressure on.*

P. R. Ryason

Frank, C. E., Blackham, A. U., and Swarts, D. E. (University of Cincinnati, Cincinnati, Ohio) "Investigation of Spontaneous Ignition Temperatures of Organic Compounds with Particular Emphasis on Lubricants," *National Advisory Committee for Aeronautics Technical Note 2848* (December 1952)

Spontaneous ignition temperatures of a number of organic compounds have been determined with particular emphasis on lubricants used in aircraft engines. A spray injector method has been developed which allows ignition temperatures of the more viscous materials (300 to 600 Universal Saybolt seconds at 37.8°C) to be determined. Previous studies had indicated that ignition temperatures of viscous materials as determined by the conventional dropwise-addition method was in error due to the slow rate of vaporization of the droplet. By spraying the fuel into the heated cup in the form of a fine mist, lower and more consistent results were obtained. A comparison of the two methods using conventional fuels showed the results to be comparable. Of the lubricants studied, the polyisobutylenes were the only ones which gave consistently high ignition temperatures (above 400°C) using both methods.

Efforts to raise the ignition temperature by the use of halogen-containing compounds were quite ineffective, although these compounds are quite effective as fire extinguishing agents. Tetraethyl lead was the most effective additive tried, followed by the aromatic amines. In the low temperature range (~235°C) iodine was the only additive effective in raising the spontaneous ignition temperature.

Mixtures of dodecane and 1,1-dineopentylethane and of cetane and di(2-ethylhexyl) adipate mixtures showed the usual ignition peninsula in the low temperature region and a zone of nonignition above this when the ignition boundary is plotted as a function of fuel mixture. Di-p-tolylamine, tetraethyl lead, and dilauryl selenide were all effective in raising considerably the spontaneous ignition temperature of these mixtures.

Although previous work had shown various surfaces to have little effect on the ignition temperature, the present study showed variations of as much as 44°C at air flows of 125 cc/min and 65°C at zero air flow. Apparently, the higher the ignition temperature the greater the effect of surfaces.

Subject Headings: *Ignition, temperatures, of lubricants; Lubricants, ignition temperatures of; Additives, effect on ignition of lubricants.*

I. R. King

Klinkenberg, A. (N. V. Bataafsche Petroleum Maatschappij) and **Poulston, B. V.** ("Shell" Research Ltd.) "Antistatic Additives in the Petroleum Industry," *Journal of the Institute of Petroleum,* 44, 379–393 (1958)

Based on the fact that during operations in handling petroleum products, electrostatic charges can be sufficiently accumulated to cause explosions, the authors surveyed 46 accidents attributed to this cause and explained that the generation of electricity is associated with the movement of one liquid relative to another or to surrounding walls, and also that safe operation can be achieved if the accumulated charges can be dissipated at a desirable rate to the walls of the container through the liquid itself.

Experimental work was carried out on the measurements of conductivities of oil products and the field strength along the vertical axes of oil tanks during various operational conditions. Investigations showed satisfactorily that on increasing the specific conductivity of the product by means of an antistatic additive, the field strength can be reduced to the required safety level, but explosions were not produced without the aid of a spark gap in critical fields and the absence of additives.

It was found that refined volatile products have the lowest conductivities and are especially prone to the hazards due to static electricity. It was concluded that the safety level of conductivity for all oil products is in the region of 10–9 reciprocal ohm/m, which allows a comfortable margin of safety. Considerations were given to the choice of additives for raising conductivities of products to this level and to their side effects.

An additive, which in a very low concentration (2kg/1000m^3) is sufficient to attain the desired conductivity for all oil products, is a chromium salt of mono and dialkyl salicylic acid mixed with a calcium salt of a substituted succinic acid.

Subject Headings: *Additives, antistatic, in petroleum; Petroleum, use of antistatic additives.*

A. S. C. Ma

II. Thermal Decomposition

Laible, R. C. (Quartermaster Research and Engineering Center, U.S. Army, Natick, Massachusetts) "Recent Work on the Mechanism of the Thermal Degradation of Cellulose," *American Dyestuff Reporter,* 46, 173–178 (1958)

Due to the need for textile fabrics which offer improved protection against flame and thermal hazards, considerable effort has been spent to determine the mechanism of thermal degradation of cellulose, cellulose derivatives, and of cellulose treated with flame retardant compounds.

Fabrics that were treated with various inhibitors were found to produce much smaller quantities of tars upon pyrolysis. A second difference in the degradation of treated and untreated fabrics was noted in the gas phase. The CO/CO_2 ratio of gases evolved upon heating the material at 550°C was found to increase 40-fold in the case of treatment with sodium tetraphosphate. The latter is a glow-retardant and apparently is effective in preventing the complete oxidation of carbon to carbon dioxide.

Several approaches have been taken in applying these flame retardants to the fabric. One method was to incorporate the retardant in a binder which could be applied to the cloth. A second method involved the attachment of the flame retardant groups to the cellulose molecule itself. A third method involved the application of phosphorus polymers to the cloth. The latter procedure tended to produce more tars than the inorganic compounds used in previous methods. This was successfully combated by the incorporation of halogen derivatives of these polymers or development of various phosphorus compounds such as Phoresin III and THPC.

Although much evidence exists for the flame retardance of various materials an effort was made to determine their action on a theoretical basis. Three distinct explanations have been offered. One, the degradation proceeds by dehydration of the fiber to water and carbon via a carbonium ion mechanism. Evidence exists for this in that many effective flame retardants liberate electron-donating catalysts at the flaming temperatures. These incorporate, in general, those Lewis acids such as $ZnCl_2$, Al_2Br_6, $TiCl_4$, and $TiCl_3$.

Two, treated fabrics decompose at a much more rapid rate than untreated fabrics. The volatile products are liberated in such a concentrated form that they are not flammable. Also, the temperature of evolution of these volatiles from flame-retardant materials occurs at a lower value which may be below the ignition point.

The third and most persuasive theory is based upon the importance of an intermediate and final product of the degradation of cellulose, levoglucosan. This compound is a pyrolysis product of pure cellulose and when degraded in the presence of certain flame retardants, larger amounts of tars and volatiles were produced than when pyrolyzed alone. This suggested that it would be desirable to modify the cellulose molecule to prevent the formation of this principal source of combustible products. The primary hydroxy group was then carboxylated with N_2O_4. It was found that the percentage of levoglucosan decreased from 12 per cent to 5 per cent when a 50 per cent oxidation had been effected. The amount of tars decreased by an order of magnitude. Other investigations included attempts to identify early products of the thermal decomposition of cellulose. Actual modification of the cellulose unit using methane sulfonyl chloride in the presence of pyridine and subsequent halogenation of the mesyloxy group resulted in a fiber with vastly improved flammability and glow resistance without any serious influence on the fabric. Lack of practicability in any industry-wide application of these techniques resulted in a more straightforward phosphorylation reaction. This method again resulted in producing a flame-retardant fabric. This method has only been attempted on a laboratory scale.

Much work remains to be done in answering questions such as the exact role halogens play in flame inhibition and the nature of the tars and chars produced from flame retardant-treated cellulose.

Subject Headings: *Cellulose, thermal degradation; Cellulose, thermal decomposition; Thermal degradation, of cellulose; Thermal decomposition, of cellulose.*

P. Breisacher

Pakhomor, A. M. (N. D. Zelinskii Institute of Organic Chemistry, Moscow, U.S.S.R.) "Radical Mechanism of Thermal Decomposition of Cellulose and Formation of Levoglucosan," *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,* 1497–1499 (1957)

By analogy with mechanisms proposed for the breakdown of organic polymers (rubber) it is suggested that the thermal formation of levoglucosan from cellulose does not require the intermediary formation of glucose but proceeds by way of free radical steps. The most likely breaking point of the cellulose chain is at the 1,4-glucoside linkage forming large radicals which can break down further in two ways. There may be intraradical transposition of atoms in the terminal structural unit carrying the free bond with simultaneous break-away of the radical, mutual saturation of free valences, and formation of the stable levoglucosan molecule. The other path postulates initial break-away of the terminal structural unit, formation of a di-radical and its further isomerization into levoglucosan.

The article contains no new experimental material and merely applies a plausible reaction scheme suggested by regularities observed in the breakdown of large molecules to the case of cellulose.

Subject Headings: *Cellulose, thermal decomposition; Thermal decomposition, of cellulose.*

W. G. Berl

Friedrich, M. (Research Division for Technique of Extinguishing Fires, Karlsruhe Polytechnical Institute, Germany) "Plastics in Fires," *VFDB-Zeitschrift Forschung und Technik im Brandschutz,* 4, 176–181 (1958)

The chemistry of 23 plastics is reviewed, with statements about the nature of the combustion of these materials and the composition of the reaction products. In view of the complexity and variability of the combustion process of such materials the available information is only qualitative in character. The article emphasizes the existence of physiologically objectionable combustion products from polyurethane, halogenated polyethylenes, and cellulose nitrates.

Subject Headings: *Plastics, fire behavior of; Fires, of plastics.*

W. G. Berl

III. Heat and Material Transfer

Jain, S. C. (University of Leeds, Leeds, England) "Simple Solutions of the Partial Differential Equation for Diffusion (or Heat Conduction)," *Proceedings of the Royal Society*, A **243**, 359–374 (1958)

The article deals with the solution of the well-known differential equation

$$\frac{1}{D}\frac{\partial c}{\partial t}=\frac{\partial^2 c}{\partial x^2} \tag{1}$$

which is applicable to problems in diffusion as well as to problems in heat conduction. In the former case the variable "c" refers to the concentration of the diffusing material and in the latter "c" should be regarded as the temperature. In the following discussion the variable "c" will be called the concentration, but it is understood that "c" can also signify temperature. Similarly the constant "D" should be interpreted as the diffusion constant in the first instance, and as the thermal diffusivity in the second.

Several problems are considered regarding diffusion in solids of different shapes. In all examples it is assumed that the diffusing substance is initially distributed uniformly throughout the solid at a concentration c_i. It is further assumed that the concentration at the surface is then suddenly lowered to zero and maintained at this value. The subsequent concentration distribution is to be described.

As a first example a rod of length "a" is being analyzed, taking the distribution over each cross section to be uniform. The exact solution to the problem can be obtained in terms of a Fourier series. It is pointed out, however, that for small values of the time "t," this solution does not converge rapidly and is inconvenient to use. It is then recalled that for a semi-infinite bar the solution can be written in terms of the error function as follows

$$1-\frac{c}{c_i}=\operatorname{erfc}\frac{x}{2\sqrt{Dt}} \tag{2}$$

where "x" is the distance from the surface and $\operatorname{erfc} u=1-\operatorname{erf} u$. Superimposing two of the solutions by considering alternately each one of the ends of the bar as being the surface of a semi-infinite bar, one obtains the expression

$$1-\frac{c}{c_i}=\operatorname{erfc}\frac{x}{2\sqrt{Dt}}+\operatorname{erfc}\frac{(a-x)}{2\sqrt{Dt}} \tag{3}$$

It is shown that this expression gives the concentration at any point to an accuracy of better than 1 per cent of c_i as long as

$$\frac{a}{2\sqrt{Dt}}<0.08 \tag{4}$$

The average concentration as well as the amount of material removed from the bar is given to an even better accuracy. It is interesting to note that within the interval corresponding to $\frac{a}{2\sqrt{Dt}}=0.08$ the average concentration has decreased to about 40 per cent of the original value, so that the error function expression is applicable over a large portion of the diffusion process.

The same approach is then used for approximating the concentration in a rectangular parallelepiped with edges of length a, b, and h respectively. The complete solution for this problem may be written as

$$\frac{c}{c_i} = \frac{c_a}{c_i} \frac{c_b}{c_i} \frac{c_h}{c_i} \qquad (5)$$

where c_a is the concentration of a bar of length "a" and c_b and c_h are the corresponding solutions for bars of length "b" and "h." The expressions c_a, c_b, and c_h may now again be approximated by the error function solution given in Eq. (3).

For the special case a=b=h (a cube) the average concentration is given to an accuracy of about 1 per cent as long as $\frac{a}{2\sqrt{Dt}} < 0.1$. Furthermore, the concentration at the time given by $\frac{a}{2\sqrt{Dt}} = 0.1$ will have decreased to about 3 per cent of the initial concentration, so that the time period involved essentially accounts for the complete diffusion process. The analysis for a sphere leads to a very similar result.

In summarizing, it may be said that the paper presents an approximate solution to the diffusion equation for certain cases. The solution presented is sufficiently accurate for many applications. Numerical values can be obtained more quickly than from the complete solution in the form of Fourier series. It must, however, be pointed out that the results of the Fourier solutions have been computed for many examples and are widely available in graphical or tabular form.

Subject Headings: ***Diffusion, solution of differential equations of; Heat conduction, solution of differential equations of.***

R. H. Sabersky

Spalding, D. B. (Imperial College, London, England) "Heat Transfer from Surfaces of Non-Uniform Temperature," *Journal of Fluid Mechanics,* 4, 22–32 (1958)

Spalding seeks to improve Lighthill's approximate method of calculating heat transfer across a laminar incompressible boundary layer for arbitrary distribution of main-stream velocity and of wall temperature. Lighthill's method is powerful and has been exploited for various applications. For example, extension of Lighthill's formula to the calculation of heat transfer at high Mach numbers frequently is possible and yields accurate results. On the other hand, heat transfer may be calculated for the difficult case of large temperature difference and variable fluid properties if certain similarity requirements are met, and transformation is possible to an equivalent incompressible flow to which the formula can be applied directly. Finally, the formula may even be applied to some turbulent boundary layer flows. Evidently, Lighthill's method of computing heat transfer is very useful, but it is an approximate method and several attempts have been made to improve its accuracy.

Lighthill assumed a linear velocity profile in the region close to the surface that is important to the heat-transfer process. This assumption is valid when the thermal boundary layer is much thinner than the velocity layer, e.g., when the Prandtl number is large or when the thermal layer starts far downstream from the origin of the velocity layer. The assumption is justified even for moderate Prandtl numbers when the pressure gradient along the surface is zero. In other cases, however, the assumption leads to appreciable errors in calculated heat-transfer rates. Spalding proposes a correction to Lighthill's formula which accounts for departures from linearity of the velocity profile occurring within the thermal boundary layer. The correction is tested for isothermal wedge flows, *i.e.,* flows for which the main-stream speed is proportional to a power of the distance from the forward stagnation point. For these flows, solutions are known which serve well as tests for the validity of any method of calculating heat transfer. In fact, Lighthill's uncorrected formula yields results that differ from the known solution by less than 20 per cent when the pressure gradient is not extreme. Spalding's correction reduces the error in heat flux to less than 2.5 per cent, exactly the error found by Lighthill for the flat plate. Spalding says that this figure represents the maximum error in heat flux to be expected from his formula, particularly when the heated section starts well back from the leading edge, a case for which other proposed corrections are inaccurate.

Subject Headings: *Heat transfer, from surfaces of non-uniform temperature.*

F. H. Wright

Hottel, H. C. and Williams, C. C., III (Massachusetts Institute of Technology, Cambridge, Massachusetts) "Transient Heat Flow in Organic Materials Exposed to High Intensity Thermal Radiation," *Industrial and Engineering Chemistry,* 47, 1136-1143 (1955)

This paper is concerned with an analytical description of the temperature rise occurring in plastic and wood samples exposed to high intensity radiation for short periods of time. Experimental results are presented and compared to the analytic predictions. Radiation intensities of up to 6cal/cm^{2}sec were employed in the experimental phase.

In the mathematical analysis, the slab thickness, the sample diathermancy (transparency to heat radiation), convective and reradiative losses from the irradiated surface, and chemical change prior to ignition were considered. In the analysis the specimens were assumed to be one-dimensional, constant in properties and thickness throughout exposure, irradiated uniformly, and homogeneous and isotropic. The radiation (monochromatic) was assumed to obey a Lambert's law decay as it passed through the slab. Work of other investigators justified the ignoring of pre-ignition chemical change by the authors. The equation formulated and the appropriate boundary conditions were resolved by Laplace transform technique for the case of monochromatic radiation. The analysis was extended to the case of chromatic radiant flux by treating the temperature rise due to each spectral region, *i.e.,* wave lengths with identical absorption coefficient, as independent, and summing the effect arithmetically.

The experimental phase employed as radiant sources a solar reflecting device capable of concentrating solar radiation to an intensity of 5.7cal/cm^{2}sec, and a 2000°K graphite resistance furnace. This latter unit provided radiation intensities from 0.26 to 3.5cal/cm^{2}sec with a uniformity of 15 per cent on a one inch target. For the main portion of the work, the resistance furnace was employed.

The samples tested were a polyester plastic, a Ponderosa pine, and a sapwood birch. Wood samples were oven-dried at 105°C for 24 hours and stored in a desiccator prior to use. Temperature measurements were made by casting lap-welded noble metal thermocouples at known depths in the plastic samples and placing butt welded iron-constantan thermocouples in holes drilled parallel to the irradiated surface in the wood sample.

The experimental temperature profiles from the plastic samples obtained in the 2000°K furnace are presented in dimensionless form and compared with the mathematical results. The experimental results exhibit the characteristics of a diathermanous material in that the experimental points cut across the analytic curve for opaque materials. An improved fit of the data was obtained by partitioning the incident radiant flux and assigning a smaller absorption coefficient in the Lambert decay law to a part (about 15 per cent) of the flux. The data from all depths exhibit a trend to fall below the predicted temperature at large time increments. No explanation is presented other than the possibility of polymerization in the sample. The agreement between experiment and analysis with variation of transparency to different wave length ranges taken into account is satisfactory.

Tests on the wood samples in the 2000°K furnace showed that in the first few seconds of exposure the temperature fields of the samples were essentially independent of the flux intensity over the flux range, 0.26 to 3.5cal/cm^{2}sec. Satisfactory correlation (standard deviation 30 per cent) of the results is obtained with the theoretical curve for an opaque solid. This is true for both the birch and pine sample. However, the results obtained on the pine specimen with radiation from the solar source, while meager, show a data trend characteristic of a diathermanous material. These data are suggestive that the specimen is transparent to short wave radiation, but opaque to the relatively long wave radiation of the 2000°K source.

In view of the reasonable agreement between the experimental and analytical work performed by the authors, relations between the ratio (dimensionless) of unreflected energy impulse to temperature rise versus a time-depth parameter (dimensionless) are presented. The curve for an opaque solid on this type of plot suffices to correlate the "depths of char" data obtained by the authors and that from previous work at the Naval Material Laboratory. These latter data were on maple samples. This correlation should prove useful to workers studying damage initiation from high intensity radiation of various duration.

Subject Headings: ***Radiation, transient heat flow due to.***

H. N. McManus, Jr.

Robertson, A. F. and Gross, D. (National Bureau of Standards, Washington, D. C.) "An Electrical-Analog Method for Transient Heat-Flow Analysis," *Journal of Research of the National Bureau of Standards,* 61, 105–115 (1958)

The prediction of the fire performance of structures which have not been tested is a difficult task. The authors point out that while useful data are available, in some cases, the actual estimate of the fire performance depends to a great extent on the experience and judgment of the person making the estimate. Hence, the work reported in this paper was undertaken in order to provide a more exact basis for making these estimates. Since fire resistance tests are usually performed only on parts of buildings, and since the thermal transmission seems to be the most important factor in determining the fire resistance, it was possible to formulate a relatively simple one-dimensional transient heat flow problem which contained all the necessary mechanisms found in an actual test. These mechanisms include a time varying temperature function at one surface, representing a standard fire exposure, conduction through a slab of material, and convection and radiation losses at the other surface. It was noted that the method of solution presented may be extended to two- or three-dimensional problems.

In general, this paper deals with the design, construction and evaluation of an electronic instrument, to obtain the variation of temperature with time at given locations. The design is based on the direct analogy which exists between corresponding thermal and electrical systems, and the resulting instrument is of the so-called "fast time" type wherein the solution time is of the order of 10^{-6} of the real problem time. The physically continuous material is represented by twenty lumped sections consisting of a number of resistances representing the inverse of the conductivity of the test material and capacitors representing the heat capacity of the test material. The section networks are of the so-called L type. The varying surface temperature at the hot boundary is given by an arbitrary function generator of the photoformer type while the radiation and conductive losses at the cool boundary are replaced by a varistor together with series and parallel resistors at the termination of the electrical circuit. Measuring circuits for obtaining readings at any section point within the electrical model complete the instrument itself. A discussion of the electrical characteristics of the separate components is included, as well as a list of the actual components and instruments used.

An analysis of the possible errors incurred with this method of solution is given. They are divided into errors due to "lumping" and those due to experimental sources. The "lumping" errors are greatest at the first section and attenuate very rapidly as more sections are included. The experimental errors, other than those associated with the values of the thermal properties of the material are estimated to be within 2 per cent of full scale.

A solution was found for a 4 in. concrete floor slab, and the resulting plot of temperature rise versus time at the center of the slab was compared with experimental results for two values of specific heat. The agreement was quite good for a specific heat of 2.09 joules/g°C(0.5 BTU/lb°F), and illustrated that this method might be useful for determining average thermal properties in those cases where direct measurement is not feasible. Although variable thermal properties cannot be employed in this instrument, it is possible to use different average values for each network section if the approximate temperature range to be covered by each section is known. However, as the authors point out, there is enough uncertainty in the values themselves, that their variation with temperature is a refinement which does not seem to be justified at the present time.

Subject Headings: ***Heat flow, analysis, by electrical analog methods.***

T. C. Adamson, Jr.

Chen, N. Y. and Jensen, W. P. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "Heat Transfer to Skin Through Thermally-Irradiated Dry Cloth," *Office of Naval Research Contract Nonr-1841 (37), Technical Report No. 6* (July 8, 1958)

This paper is concerned with the problem of heat transfer through dry cloth (opaque or diathermanous) to skin. The skin and cloth are separated by an air space, and the heat is transported to the cloth surface by high intensity thermal radiation.

An exact analysis is performed on the cloth-air gap-skin system with the following assumptions made: heat flow is one-dimensional and the radiation intensity constant; for cloths with finite transmittance, penetration is assumed to follow a Beer-Lambert Law; no change in the cloth properties occur during irradiation; effects due to moisture and chemical reaction are negligible; convective and reradiative losses from the outer cloth surface are characterized by a single over-all heat transfer coefficient; heat transfer from the inner cloth surface to the skin (or experimental skin simulant) is also characterized by an over-all coefficient, and the skin (simulant) is a homogeneous opaque solid of infinite depth. The analysis and assumptions lead to a pair of partial differential equations of the one-dimensional time-dependent type. The appropriate boundary conditions are nonlinear, hence, the exact solution of the system is impossible.

To effect an approximate solution, the system is expressed in equivalent finite difference form; to obtain generality, the finite difference equations are brought into dimensionless form by suitable substitution. Solution of the finite difference equations is obtained by employing the so-called Schmidt method suitably modified. A two-slab and six-slab solution have been effected and compared, with the finding that serious uncertainty occurs in the two-slab solution for short time intervals. Little improved accuracy is to be expected with slab numbers exceeding six. To reduce the number of calculations a combination six-two slab solution is used. The solutions for opaque and diathermanous materials are demonstrated. A simplified method is presented for use with diathermanous materials. The necessary graphs are included.

Experimental results have been obtained from a cloth-air gap-skin simulant system and these results have been compared with analytical predictions. The agreement between experiment and analysis is satisfactory. The curves presented are deemed sufficient for calculating heat transfer in systems of this type for exposure times of up to 30 seconds.

Subject Headings: *Heat transfer, to skin through cloth.*

H. N. McManus, Jr.

Wise, H. and Ablow, C. M. (Stanford Research Institute, Menlo Park, California) "Burning of a Liquid Droplet. III. Conductive Heat Transfer within the Condensed Phase During Combustion," *Journal of Chemical Physics,* **27,** 389-393 (1957)

The mechanism of combustion of liquid fuel droplets can be divided into three parts. Initially, the droplet is preheated by radiation from the furnace walls and by conduction, convection, and radiation from the surrounding gases until ignition occurs. Then the second stage commences, and the rate of vaporization increases. The heat transfer from the flame surrounding the droplet augments the heating processes in stage one. Lastly, any carbon residue formed in the first two stages is consumed.

Most of the theoretical studies at the present time assume that there is no change of temperature within the droplet during the burning stage. This is justifiable for fast burning droplets but not for relatively slow burning ones. The authors have attempted to calculate the magnitude of such internal heating during the second stage of combustion.

It is thought that generally an internal rise in temperature will have little effect on the steady burning rate, but it is possible that physical or chemical instability, *i.e.,* disruptive boiling or thermal cracking, could result in certain fuel-oxidant systems.

The problem is resolved into one in which heat is passed into a sphere, causing vaporization, and hence change of diameter with time.

The analysis is based on the following assumptions.

1) The system is spherically symmetric.
2) Conduction is the only means of heating the interior of the droplet.
3) The burning rate is constant during combustion.
4) It is permissible to use average values of the physical properties of the liquid, taken at a suitably chosen temperature.
5) The temperature distribution is uniform until ignition occurs.
6) At ignition, the surface temperature has reached a constant value.

If the mass burning rate of the droplet, $\dot{m}$, is proportional to the droplet radius, R, then

$$\dot{m}=\epsilon' R$$

and the surface area will decrease linearly with time, t,

$$R^2=\epsilon t_f\left[1-\frac{t}{t_f}\right]$$

t_f = droplet burning time
ϵ = a burning rate coefficient
$\epsilon=\frac{\epsilon'}{2\pi\rho}$ where ρ = liquid density

Heat transfer can be considered to take place between two concentric spheres, according to the differential equation

$$\frac{\partial T}{\partial t}=k\left(\frac{\partial^2 T}{\partial r^2}+\frac{2}{r}\cdot\frac{\partial T}{\partial r}\right)$$

T = liquid temperature at time t and at a radial distance r from center
k = thermal diffusivity

The following boundary conditions apply

1) No temperature gradient at the center

$$\left(\frac{\partial T}{\partial r}\right)_{o,\,t}=0$$

2) Surface temperature is constant

$$T_{R,\,t}=T_s$$

3) Initially, temperature of the droplet is uniform

$$T_{r,\,o}=T_i$$

The equation is made dimensionless by

a temperature ratio $\phi=\frac{T-T_i}{T_s-T_i}$

a time parameter $u=\frac{1}{2}\log\frac{1}{1-\frac{t}{t_f}}$

a distance parameter $x=b\,\frac{r}{R}$

where $b=\sqrt{\frac{\epsilon}{2k}}$

and is solved analytically by means of a Laplace transform or by a finite difference method. The solution has been evaluated to give temperature distributions with respect to time for values of b ranging from 1 to 3. This range includes most of the common fuel oxidant systems.

The most interesting conclusions are derived from a plot of ϕ at the droplet center against $\frac{t}{t_f}$. The half life of the droplet corresponds to $\frac{t}{t_f}=0.5$. When $b=1$, the droplet attains 90 per cent of the surface temperature during its half life, but when $b=2$, only 12 per cent of the surface temperature during this period.

The duration and level of the center temperature in the droplet may lead to the instability mentioned above.

Subject Headings: *Droplet, burning of; Heat transfer, during combustion of liquid droplets.*

P. L. Start

Gambill, W. R. (Carbide and Carbon Chemicals Company, South Charleston, West Virginia) "Best Methods for Prandtl Number," *Chemical Engineering,* **65,** 121–124 (1958)

One of the dimensionless parameters which is important in fixing heat transfer rates in gases and liquids is the Prandtl number. This parameter is defined as $Pr = Cp\ \mu/k$, where Cp is the specific heat at constant pressure, μ, the dynamic viscosity, and k, the thermal conductivity. In this paper the literature is reviewed concerning values of the Prandtl number for gases and liquids in the temperature range between 200 and 1200°K and, in addition, the usefulness of several general and semitheoretical calculations which relate the Prandtl number for gases to the molar specific heat at constant pressure is discussed. An excellent summary of recently published material is presented.

The principal difficulty in obtaining accurate estimates of the Prandtl numbers for gases is that values of the thermal conductivity are not accurately known at high temperatures. For example, although recommended values of Prandtl number for such a well studied substance as air differ by less than 3 per cent in the temperature range, 200 to 500°K, the variation is over 13 per cent at 1200°K.

The semitheoretical relations, which are generally of the form $Pr=[Cp_m/(a\ Cp_m + b)]$, where Cp_m is molar heat capacity, and a and b are constants, are discussed and are shown to have maximum errors of the order of ± 15 per cent. The author suggests that a more satisfactory result is obtained by classifying gases according to the nature of their interatomic bonds and by picking a constant value of the Prandtl number for the whole temperature range for each classification group. Such constants are suggested by the author.

A brief discussion is also included concerning the calculation of Prandtl numbers for nonreacting gas mixtures, reacting gas mixtures, and for gases at pressures different from one atmosphere.

When discussing the Prandtl numbers for liquids, the author finds no general relationship which is accurate and suggests that use be made of the various empirical estimates for Cp, μ, and k.

In closing, the author briefly discusses the calculation of values of the Schmidt number.

Subject Headings: *Prandtl number.*

E. E. Zukoski

Godridge, A. M., Thurlow, G. G., and Wallis J. (British Coal Utilization Research Association, Leatherhead, England) "A Method of Studying the Influence of Flame Characteristics on Heat Transfer in Furnaces," *Journal of the Institute of Fuel,* 31, 491-505 (1958)

A vertical cylindrical combustion chamber 40 in. high and 5 in. in diameter was designed primarily to study heat transfer properties of flames from gaseous fuels. Insulating refractory and lining were selected to give temperatures comparable to those of industrial furnaces. Heat flow through the wall was measured across machined refractory rods located at eight positions; flame temperatures were measured using a suction pyrometer. Measurements were made of the radiation from the flame backed by both a water-cooled target and the high temperature wall, and from the hot wall alone. Estimates of flame emissivities were then calculated using the modified Schmidt method.

The experiments were designed to study (1) the effect of momentum of the gas leaving the burner and the air/gas ratio on laminar and turbulent diffusion flames, (2) the differences in diffusion and premixed flames produced at the same gas rate, and (3) the heat transferred from town gas and methane at the same heat release rate.

The laminar flames were produced from town gas at a gas rate of 21 cu ft/hr using 3⁄16 in. and 3⁄8 in. nozzles and air/gas ratios of 5.0 and 6.5. Results are shown as graphs in which flame temperature and emissivity, rate of heat absorbed (Btu/hr/ft^2), radiation from the flame (ergs/sq cm sec), and total heat transferred to the wall are given at various distances above the nozzle. Carbon dioxide concentration and rate of combustion expressed as (local CO_2/CO_2 maximum) are also given along the flame axis. Similar graphs are given for turbulent diffusion flames produced from town gas at a gas rate of 60 cu ft/hr at air/gas ratios of 5.0 and 6.5. In the second series of tests, diffusion and premixed flames, both laminar and turbulent, are compared. The distance from the burner is plotted against gas temperature, per cent maximum carbon dioxide, heat absorbed per unit area, radiation from flame, and, for the turbulent flames, total heat received at walls. Results of the third series of tests are given in two graphs showing the relation of heat absorbed per unit area to distance above burner for methane and town gas at two comparable calorific values.

Values of the measured heat absorbed were compared with radiation calculations, and discrepancies between measured and calculated values are great. For example, at 20.5 in. above the burner using a 3⁄8 in. nozzle and an air/fuel ratio of 5.0, the calculated radiation is given as -4250 Btu/hr/ft^2; the measured heat absorbed is given as $+3100$ Btu/hr/ft^2. The authors plan further calculations to take into account other factors, particularly heat exchange in the vertical direction, which may be more significant than was first assumed.

The lengths of the laminar diffusion flames were estimated from emissivity data and from the peak carbon dioxide value determined on the flame axis. Values from 20 to 30 in. were found, compared with 23 in. quoted by Hottel and Hawthorne* for the flame length of effectively free jets produced under similar conditions. For the turbulent flames, lengths were estimated using calculations by Thring and Newby † and also from the intersection of the curve of carbon dioxide

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* Hottel, H. C. and Hawthorne, W. R. "Diffusion in Laminar Flame Jets," *Third Symposium on Combustion, Williams and Wilkins Co.,* 254–265 (1949)

† Thring, M. W. and Newby, M. P. "Combustion Length of Enclosed Turbulent Jet Flames," *Fourth Symposium on Combustion, Williams and Wilkins Co.,* 789–795 (1953)

concentration on the flame axis with the curve of maximum carbon dioxide on a cross section.

Estimates were made of the carbon particle concentration in the flame, and the two values given in this paper compare well with those given for oil flames by Holliday and Thring*. An increase in total air rate of 13 per cent caused the heat liberated in the furnace to fall by 10 per cent for laminar flames, 24 per cent for turbulent flames. The authors emphasize the similarity shown in total radiation between diffusion and premixed flames in spite of differences in the temperature and emissivity curves for the two.

Subject Headings: *Heat transfer, influence of flame characteristics on; Flame, characteristics, influence on heat transfer.*

C. R. Orr

IV. Diffusion Flames

Kimura, I. and Kumagai, S. (University of Tokyo Bunkyo-ku, Tokyo, Japan) "Diffusion Flames," *Proceedings of the Gas Dynamics Symposium on Aerothermochemistry, Evanston, Illinois,* 199-203 (1956)

The diffusion flame obtained when a fuel gas discharges into quiescent air from a circular nozzle has been studied by a number of investigators. Kimura and Kumagai have been studying the effect of eddy diffusion between the fuel gas and the air when flowing in the same direction. They determined lengths of diffusion flames, using laminar fuel flows, from circular nozzles burning in a flowing turbulent air stream. The air flow was sufficient to ensure complete combustion.

They injected the fuel coaxially into the center of a flowing air stream having varying amounts of turbulence. Experimentally, the diffusion flame was stabilized at the opening of the "city gas" tube with a ring stabilizer. This combustion process is treated analytically, assuming that molecular diffusion is the controlling factor.

An equation is derived to predict the distance where a specified degree of mixing of air and fuel is obtained along the center line of the coaxial system. When the air velocity is set equal to zero in the derived equation, it reduces to the well-known relation for a laminar diffusion flame in quiescent air. Their experimental data for the ratio of flame length in a laminar air stream to the flame length in quiescent air agree rather well with the theoretical calculations.

Kimura and Kumagai have shown that the length of the laminar diffusion flame decreases with increasing air velocity. In addition, the length of the flame of laminar "city gas" decreases with increasing eddy diffusivity of the air stream, but the amount of decrease is not too large in the range of turbulence employed in this experiment.

Subject Headings: *Flame, diffusion, length of; Diffusion flames, length of; Turbulence, effect of, on diffusion flames.*

L. E. Bollinger

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* Holliday, D. K. and Thring, M. W. "The Radiation from Flames in a Small-scale Oil-fired Furnace," *Journal of Institute of Fuel,* 30, 127 (1957)

Kunugi, M. and Jinno, H. (Kyoto University, Kyoto, Japan) "Turbulent Diffusion Flames," *Sixth Symposium (International) on Combustion,* New York, Reinhold Publishing Corporation, 311-316 (1957)

This paper describes an experimental investigation of turbulent diffusion flames. The main objective of the research was to obtain information on the gross structure of turbulent diffusion flames, and to estimate the influence of constraining walls and the recirculation of exhaust gases.

The experiments were carried out in a rectangular combustion chamber with cross section dimensions of 2 by 7cm. and a length of 30 cm. City gas and air were introduced from the bottom through two parallel rectangular ports placed 2 mm. apart. The ports were 2 cm. long and about 2 mm. wide.

Measurements taken on the diffusion flames which appeared at the interface between the fuel and air streams included composition, temperature and velocity. These measurements were made at five levels above the ports.

Concentration profiles of carbon dioxide, hydrogen, and oxygen clearly show the progressive consumption of hydrogen and oxygen with increasing distance above the ports. Maximum carbon dioxide concentration occurs at the interface between the streams, but there is a considerable concentration of carbon dioxide in the region between the ports and the chamber walls due to recirculation of the burnt gases.

Concentration measurements were also made on nonburning jets of fuel and air. The concentration profile of hydrogen generally corresponded to the hydrogen profile in the burning jet, and the authors suggest that the course of combustion in diffusion flames can therefore be predicted from a study of the mixing process of nonburning models. Velocity profiles in the hot and cold jets were also quite similar, indicating that the influence of the flame on the turbulence and mixing process in the case of the burning jets was minor.

The authors conclude with the statement that the mixing process and the gas recirculation have an important effect on the combustion process. This is essentially the statement made at the beginning of the paper. The primary value of this research lies in the clear picture of the time-average flame structure afforded by the composition, temperature, and velocity measurements.

Subject Headings: *Diffusion flames, turbulent; Flame, diffusion, turbulent.*

G. S. Sutherland

V. Combustion Principles

Jones, H. (Imperial College, London, England) "Accelerated Flames and Detonation in Gases," *Proceedings of The Royal Society,* A **248,** 333–349 (1958)

One of the least well understood processes in the combustion field is that concerning the transition between deflagration and detonation processes. In the present paper, this transition is investigated by means of a greatly simplified analytic model. The purpose of the investigation is to determine the general features of the process and, in particular, to determine whether the reaction rates, or the heat release and dynamic properties of the reacting gas are the most important parameters in fixing the characteristics of the transition.

The critical assumptions made in the analysis are that: (a) the acceleration of the flame front is uniform or increases uniformly with time, and (b) that the velocity of gas just preceeding the flame front is linearly proportional to the velocity of the flame front in the laboratory coordinate system. Thus, the problem is reduced to the determination of the flows in front and behind a piston which also acts as a mass sink or source. The solutions for the flow before and behind the flame front or piston are found as a function of position and time, and the two solutions are matched at the flame front by use of the conservation laws. These laws also make possible the calculation of the heat release rate required to drive the acceleration.

Thus, a complete "solution" of the flow can be determined up to the time at which a shock wave first appears. The properties of the flow such as pressure, temperature, velocity, and density are obtained as functions of time and position, and two parameters. The unknown parameters are those fixing the acceleration of the flame and the proportionality constant for assumption (b) above. They are not determined as eigen values of the solution and hence, the time and distances scales for the transition can not be fixed by the present calculation.

The curve along which a shock wave may develop in the flow upstream from the flame can be obtained from the solution; however, a further assumption concerning the position or time of shock formation must be made to fix the actual position and time. In the detailed calculation discussed in the paper, the assumption is made that the shock is formed at the sound wave front.

The calculations are extended to cover the period immediately after the shock formation by neglecting the entropy change across the shock wave. In addition, the velocity of the shock wave thrown back by the detonation wave is discussed.

The solution obtained is only useful as a qualitative description of transition since, for example, the acceleration and propagation rate of the flame front must be arbitrarily specified, and the heat release by the flame cannot be arbitrarily specified. However, the features of the early part of the transition phenomena are shown in a general manner, and comparison with experimental results shows good qualitative agreement. The author concludes that the reaction rates are not important in fixing many of the essential features of the transition phenomena.

Subject Headings: *Flame, accelerated; Flame, detonation in gases; Detonation, accelerated flames.*

E. E. Zukoski

Martin, F. J. (General Electric Research Laboratories, Schenectady, New York) "Transition from Slow Burning to Detonation in Gaseous Explosions," *Physics of Fluids,* **1**, 399-407 (1958)

One of the earliest explanations for the transition of slow burning to detonation (such as might occur in coal mine fires) was the onset of turbulence. But this mechanism alone has since been shown to be inadequate to produce the detonation velocities which have been measured. In presenting his now well-known "hot gas piston" model, Zeldovich proposed that the hot gas behind the flame distorts its shape (because of wall friction) so that the central portion is accelerated to the point that a shock wave is developed ahead of the flame, heating the unburned gas by compression, and increasing the burning rate. This process is repeated until the unburned gas reaches the auto-ignition point, and detonation results. All of the previous situation assumes laminar flame propagation.

The author of the present paper presents an experimental arrangement whereby the Zeldovich hot gas piston model does not provide a complete explanation.

The gas mixture used was acetylene-oxygen at 50 mm. of mercury absolute pressure, in a 5 cm. i.d. tube 2.4 m. long. The ignition spark was gentle enough so that no initial shock wave was formed. Within 20-30 cm. of the ignition source, the flame reached a steady velocity of about 800 m/sec, preceded by a shock wave several centimeters ahead of it. This situation continued for another 50-60 cm. in the tube, whereas the Zeldovich model would have predicted the rapid development of detonation. But instead, bumps appeared in the otherwise dome-shaped flame surface, and finally, right before detonation occurred, tongues of flame developed along the boundary near the wall, giving the flame a scoop-shape. There was never any indication of auto-ignition.

The explanation offered is that a turbulent boundary layer developed in the region between the main shock wave and the flame front, as evidenced by a value of Reynolds number (10^7) in excess of the critical value required for such development. In this (unstable) boundary layer, spots of turbulence occurred, in which the burning velocity was so high that secondary shocks developed. In the case of this scoop-shaped flame, higher flame velocities were observed in the region of the wall than were observed at the center, a situation just the reverse of the original steady-state case and that described by the Zeldovich model.

But the final stages of detonation development appeared to be the same, by whatever model. The unburned gas ahead of the flame became sufficiently heated and compressed to sustain a steady detonation with a velocity (in the present case) of 2950 m/sec. (This implies, of course, that the burning velocity has positive pressure and/or temperature exponents.) It is not claimed that this turbulent boundary layer development is valid for any other experimental configuration, but it seems worthwhile to investigate other situations which affect in particular such development.

Subject Headings: *Explosions, gaseous, transition from slow burning to detonation; Detonation, transition to, in gaseous explosions.*

J. K. Richmond

van Tiggelen, A. and Deckers, J. (University of Louvain, Louvain, Belgium) "Chain Branching and Flame Propagation," *Sixth Symposium International) on Combustion,* New York, Reinhold Publishing Corporation, 61–65 (1957)

In this paper flame kinetics for stationary premixed flames are interpreted on the basis of collision theory. To avoid difficulties due to the variation of the relevant parameters across the flame front mean values are utilized, and the flame front is treated as a homogeneous region of constant temperature.

By considering the two types of collision which may occur in the flame front in the evolution of the final product [*i.e.,* (a) a primary reaction analogous to that which occurs in slow combustion, or (b) an effective collision with a chain carrier] relationships are derived giving a number of effective collisions. For case (a) this number is found to be much less than one, thus illustrating the impossibility of pure thermal explosion. For case (b) it is shown that the number of effective collisions may be greater than one provided a sufficient mean radical concentration is maintained in the flame front.

The mechanism of a chain reaction is discussed in general terms and illustrated for a stoichiometric methane-oxygen mixture. An equation is derived for the probability (v) for a radical to undergo a branching reaction (the corresponding probability for chain termination being denoted by β).

By considering the diffusion of particles an equation is derived for the steady state burning velocity (V_0):

$$V_0=\frac{4T_0}{\pi}\sqrt{\frac{2R(v-\beta)}{3MT}}$$

where T_0 = initial flame temperature,
T = mean temperature in flame front,
R = gas constant,
M = mean molecular weight of chain carriers.

This basic expression explains flammability limits when $v=\beta$. The authors state that many different laminar flames have been successfully tested on the basis of the expression. By further manipulation the equation is simplified to

$$\frac{V_0}{\sqrt{T}}=\frac{3\cdot 9\times 10^{-2}}{\sqrt{M}\cdot x_0}$$

where x_0 = flame front thickness. If M is assumed to be constant, this expression represents a straight line giving $V_0/\sqrt{T}$ as a function of $1/x_0$. Many different flammable mixtures are found to obey this relationship remarkably well, the slope of the experimental line having exactly the expected value.

The authors have produced a simplified theory by considering the individual molecule, radical or free atom in the flame reaction zone, and by defining for each species some kind of "mean molecule" whose behavior is "most likely." This approach leads to a number of relationships which are generally applicable, simple to use, and which compare very well with practice.

Subject Headings: *Flame, propagation by chain branching; Chain branching, on flame propagation.*

R. G. Siddall

Michelsen, W. R. and Ernstein, N. E. (National Advisory Committee for Aeronautics, Cleveland, Ohio) "Growth Rates of Turbulent Free Flames," *Sixth Symposium (International) on Combustion,* New York, Reinhold Publishing Corporation, 325–333 (1957)

Measurement of the velocity of propagation of a flame front provides a convenient method for comparing the reactivity of various fuel-oxidant mixtures. Furthermore, flame velocities determined in the laboratory can be checked against theoretical predictions to test the propriety of different theoretical analyses of combustion. For these reasons there has been considerable interest in developing reliable laboratory techniques for measuring flame velocities.

This paper is concerned with determining flame velocities in the presence of turbulence (velocity fluctuations) in the unburned gas. The work reported is limited to a gaseous premixed fuel-oxidant mixture, but the techniques developed may be extendable to liquid fuels and to diffusion flames.

Measuring turbulent flame velocities is more complicated than measuring laminar flame velocities because turbulence is a statistical phenomenon, and thus so are turbulent flame velocities. Whereas under a given set of conditions a unique value exists for the laminar flame velocity, one obtains for apparently identical testing conditions a statistical spread in the turbulent flame velocity. The authors emphasize this statistical nature, and as a consequence they have run each data point hundreds of times and have employed statistical concepts to analyze the data.

The method used to measure turbulent flame velocities is relatively new, having been developed in the past five years. The experiment involves the spark ignition of a flame globule in a combustible mixture which is itself in motion. The gas is swept past the point of ignition, and as it flows downstream the radius of the flame globule increases. This rate of increase can be directly related to the flame speed. By placing various wire screens upstream of the ignition point and by varying the flow velocity, the spreading flame globule can be subjected to different conditions of ambient turbulence. The growth rate of the flame globule was observed by three independent methods: direct photography, ionization probes, and photomultipliers. The principle variables in the experiment were the turbulence intensity, the scale of the turbulence, and the fuel-air ratio of the gas stream.

Sufficient supporting tests were conducted by the authors to show that the measured flame velocities are substantially unaffected by extraneous influences such as the energy of the spark discharge, the velocity of the flowstream, etc. On the whole, the data are very convincing.

The results show that the turbulent flame velocity has a statistical spread that encompasses the laminar flame velocity for the same fuel-air ratio. On the average, turbulent flame velocities are somewhat higher than laminar ones, particularly near the stoichiometric mixture. For example, at the stoichiometric fuel-air ratio for propane-air, the laminar flame speed is about 1.3 fps., whereas at a turbulence intensity of 1.7 fps. the turbulent flame speed varies from about 1.25 fps. to about 2.0 fps.

The data further show that the mean turbulent flame speed increases with increasing turbulence intensity. However, the rate of increase is not nearly so rapid as that reported in most earlier theoretical and experimental studies. In fact, the present study, which must be considered one of the most authoritative to date, indicates that turbulence does not have the effect on flame speed that once was anticipated. In the cases reported, the average turbulent flame speed is usually less than 50 per cent greater than the corresponding laminar flame speed.

Other tests show that large scale turbulence has substantially more effect in increasing the flame speed than does small scale turbulence. Moreover, the maximum turbulent flame speed occurs at a fuel-air ratio about 10 per cent greater than stoichiometric, similar to the behavior of the laminar flame speed and the blowout velocity of a flame stabilized on a flameholder at high speeds.

Subject Headings: *Flame, turbulent free, growth rate of.*

A. B. Schaffer

Gross, D. and Loftus, J. J. (National Bureau of Standards, Washington, D. C.) "Flame Spread Properties of Building Finish Materials," *American Society for Testing Materials, ASTM Bulletin No. 230,* 56–60 (May 1958)

The spread of flame across the surface of a wide variety of building finish materials was measured, using the National Bureau of Standards radiant panel method.* Representative samples of liquid coatings, films, sheets, panels, and plastics were applied to plywood, fiberboard, and gypsum board wall base materials, air dried for at least 72 hours, and aged for at least one week in an environment of 75°F and 50 per cent relative humidity. The test samples, measuring 6 by 18 in., were uniformly oriented at a 30 degree inclination to a 12 by 18 in. gas heated refractory panel having a radiant energy output corresponding to black body emission at 670°C. The top edge of each sample was ignited with a pilot flame, and the rate of flame spread downward over the sample surface was timed to 0.01 sec. over 3 in. increments along the entire length of the specimen.

The combustion data were correlated in terms of a flame spread index, I_s, which was defined in terms of the measured rate of flame spread, and the measured temperature rise of the combustion products relative to a standard sample and a calibration burner. An empirical constant was adjusted to yield a flame spread index of 100 for red oak samples, to bring the numerical values in line with other systems of flame spread classification (e.g., the Underwriters' Laboratory Flame Spread Factor).

A statistical evaluation of the reliability of the combustion data indicated that variations due to testing order in the day, or day-to-day effects were not significant compared with differences between specimens. The reliability of the measurements was expressed as a coefficient of variation calculated for each reported flame spread index; this is the standard deviation divided by the mean flame spread index, and multiplied by 100.

Flame spread indexes, coefficients of variation, and smoke deposit data were given for forty-seven finish materials. Values of the flame spread index ranged from low values of around 1.0, such as for aluminum foil on plywood (coefficient of variation 73.3 per cent) to a high value of 832 for shellac on plywood (coefficient of variation 35.3 per cent).

Both the base material and the surface finish material were considered to contribute to the magnitude of the flame spread index, but in ever varying amounts, depending on the nature and thickness of the surface coating. Paints and thin coverings showed low values of I_s, even lower than obtained with the bare base materials. Coatings on gypsum board base showed the lowest values of I_s, and fiberboard the highest; however the effect of the base material decreased as the coating thickness increased.

The relationship between the flame spread index and the actual fire hazard represented by specific materials was not determined.

Subject Headings: ***Flame, building materials, spreading properties of.***

B. Greifer

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* A. F. Robertson, D. Gross, and J. Loftus "A Method for Measuring Surface Flammability of Materials Using a Radiant Energy Source," *Proceedings American Society Testing Materials,* 56, 1437–1453 (1956)

Coffin, K. P. and Brokaw, R. S. (National Advisory Committee for Aeronautics, Cleveland, Ohio) "A General System for Calculating Burning Rates of Particles and Drops and Comparison of Calculated Rates for Carbon, Boron, Magnesium, and Iso-octane," *National Advisory Committee for Aeronautics Technical Note 3239* (February 1957)

A system of simultaneous equations, numbering one more than twice the number of molecular species present, is set up for direct determination of the temperature dependence of partial pressures in the combustion of small particles burning as diffusion flames. The present method is superior to previous analyses in that the effects of diffusion and dissociation are introduced in rigorous fashion. Numerical results are obtained either by a complicated process of numerical integration or by a less complicated and less rigorous analytical solution involving stepwise iteration in the temperature domain. Readily obtained by-products of the directly determined partial pressures are the burning rates and flame structure.

For a system containing n molecular species and s atomic species, the equations include s continuity equations, $n-1$ diffusion equations, a total pressure equation, $n-s$ equilibrium equations, and an energy equation. The dependent variables include $n+1$ flow rates (one for each molecular species, one for total fuel flow rate) and n partial pressures. For the simplified solution, the nonlinear terms of the diffusion equations are neglected as of second order and the partial pressures for the s atomic species may be obtained directly by solution of a series of simultaneous linear equations. The remaining partial pressures can then be calculated from the equilibrium equations, and the mutual dependence of pressures and temperatures is then determined by a straightforward iteration procedure.

The method of calculation is applied to specific cases of the combustion of carbon, boron, iso-octane, and magnesium. The combustion of carbon was analyzed both in terms of an exact numerical integration and in terms of the simpler analytical solution involving certain average values. Since the boron system involved a more complex series of equilibria than that of the carbon system, only the analytical solution was undertaken. However, the complete flame structure was determined for each case. For the magnesium and iso-octane cases, the general equations were reduced to the previously presented simpler equations. The only resultant information available on the flame structures was the location of the high temperature zone for magnesium and the flame front location for iso-octane.

For carbon, the results of the numerical integration and the iterative procedure do not differ significantly. In the oxygen-rich region below 2100°F, where the diffusion of oxygen and carbon dioxide is actually equimolar counter-diffusion, the numerical integration and the analytical solution give identical plots of partial pressures against temperature. In the fuel-rich region, the partial-pressure *vs.* temperature curves diverge for the two cases; two molecules of carbon monoxide pass out for each molecule of carbon dioxide going in. The burning rates for the two carbon calculations agree well. This is an indication that the considerably less difficult analytical solution does not introduce significant variations in the results.

The partial-pressure *vs.* temperature curve and the flame structure for boron burning in air are plotted from the analytical solution. For boron, the analytical solution involving the iterative procedure is applied to four separate boundary conditions. These results together with two curves representing boundary conditions for the condensed oxide, yield boron burning rates for a wide range of ambient temperature and oxygen concentration.

The numerical results of the calculations described yield burning rates, evaporation constants, and particle lifetimes which are listed in Table I.

The results can be summarized as follows:

1. Burning rates of liquid hydrocarbons and relative rates for magnesium ribbons have been predicted in satisfactory agreement with experiment from a model in which heat- and mass-transfer processes are assumed rate determining.
2. The equations which determine the steady-state burning of liquids or solids can be set down in a general form. From these general equations, together with appropriate simplifying assumptions, the explicit burning-rate equations which have been used previously for hydrocarbons and magnesium may be derived.
3. If dissociation is considered in the calculations, more realistic temperature and composition profiles are obtained for the combustion zone. However, such considerations do not change burning rates greatly from those calculated from highly simplified models.
4. Calculations indicate that heat-release rates are in the order: liquid hydrocarbons >magnesium>boron ≅ carbon.
5. The burning-rate calculations (which apply only to steady-state burning) do not in themselves explain the extreme difficulty of burning elemental boron.

TABLE I

COMPUTED BURNING RATES OF VARIOUS SUBSTANCES

[Temperature, 300°K; air at 1 atmosphere.]

	Burning rate, W_f			Evaporation constant, β', $\frac{\text{sq microns}}{\text{sec}}$	Lifetime of 1-micron particle, t_7, sec
	$\frac{\text{moles}}{(\text{cm})(\text{sec})}$	$\frac{\text{gm}}{(\text{cm})(\text{sec})}$	$\frac{\text{cal}}{(\text{cm})(\text{sec})}$		
Iso-octane [a]	0.86×10^{-5}	99×10^{-5}	10.5	1.11×10^{6}	0.90×10^{-6}
Magnesium [a]	3.97	97	5.7	.444	2.25
Boron					
[a]Case A	1.31	14.2	1.98	.0492	20.3
[a]Case B	1.79	19.4	2.70	.0673	14.8
Analytical	1.27	13.7	1.92	.0477	21.0
Carbon					
Numerical	1.05	12.7	1.02	.0505	19.8
Analytical	1.10	13.2	1.07	.053	18.9

[a] Simplified calculation.

Subject Headings: *Burning rates, calculation of, for particles and droplets; Droplets, burning rates of.*

C. C. Miesse

Browning, J. A., Tyler, T. L., and Krall, W. G. (Dartmouth College, Hanover, New Hampshire) "Effect of Particle Size on Combustion of Uniform Suspensions," *Industrial and Engineering Chemistry,* 49, 142-147 (1957)

The combustion of simulated uniform sprays was studied by igniting a suspension of very small solid particles which were held in suspension by continuous circulation about a loop. Acceptable simulation of a liquid spray was achieved by choosing methylene bis-stearamide ("Armowax"), a solid hydrocarbon which has a low melting point and combustion characteristics similar to the more common liquid fuels. In the course of the experimental program it was hypothesized—and qualitatively confirmed—that optimum conditions for combustion occurred when the upward stream velocity past a vaporizing wire ignition source balanced the terminal settling velocity of the particles.

Data included the lean limit of flammability and pressure-concentration curves. Maximum pressure was found to vary inversely with particle size, while larger particle sizes were found to sustain high pressures over a greater range of fuel concentration than the smaller particles. Both phenomena were attributed to the greater surface-to-volume ratios of smaller particles, in that the greater surface area leads to more rapid vaporization and combustion, and the gaseous fuel/air ratio lags the ratio computed for the solid pellets by a greater amount for larger particles and hence tends to a flattening of the curve.

The particle size was found to exert an appreciable effect on the lean limit of flammability, with the 60 micron size permitting the leanest air/fuel ratio. This was attributed to the influence of two opposing trends: the tendency to burn as a gaseous fuel where mixing is adequate, and the diffusion-type combustion in the vicinity of a particle. Large particle diffusion flames require more available fuel combustion to proceed, and for particles in the 10 micron range, combustion occurs in the gaseous state. The ability of the 60 micron size suspension to burn at the leanest air-fuel ratios is apparently the result of a balance between the rate of vapor production and the ability of the flame to progress from droplet to droplet. Observed experimental trends agreed well with liquid spray data previously reported by Burgoyne and Cohen, and Anson.

Subject Headings: ***Suspensions, effect of particle size on combustion of.***

C. C. Miesse

Deckers, J. and van Tiggelen, A. (University of Louvain, Louvain, Belgium) "Extraction of Ions from a Flame," *Combustion and Flame* 1, 281-286 (1957)

Ion extraction from a flame and the concentration of the ions in a flame by a new sampling technique are given. The ions and burned gases from a flame are brought into a low pressure vacuum system where, after separating the burned gases, the ions are accelerated by an electrostatic field and collected on a target. If the ion collector is replaced by the entrance slit of a mass spectrometer, the identification of the ions may be accomplished. However, no mass spectrometer data are reported.

The paper describes the equipment for the extraction of the ions from a flame, a procedure for reducing the data, and some preliminary data on stoichiometric ethylene-oxygen flames at different dilution with nitrogen, and a few qualitative experiments with flames of low ion concentration such as nitrous oxide-oxgyen flames.

The equipment consists of three chambers, a combustion chamber where a flat flame is burning at 3 to 10 cm. of mercury, an intermediate chamber at 10^{-2} mm. of mercury where the ions are separated from the burned gases, and a low pressure chamber at 10^{-4} mm. where the ions are focussed and collected. The combustion chamber is separated from the intermediate chamber by a rotating disc seal. A 2 mm. hole in the rotating disc becomes coaxial with a 2 mm. hole in the side of the combustion chamber six times a second and the communication lasts for 1/220 of a second. During this time ions and burned gases are removed from the flame to the intermediate chamber. In the intermediate region there is a focussing electrode which is used to collimate the beam of ions which is now focussed on a 2 mm. hole separating this region from the low pressure region. In the low pressure region there are two focussing electrodes and a shielded collector target. The rotating disc and focussing electrodes are connected through resistors to a potentiometer by means of which it is possible to adjust the field distribution. The position of the ion collector is adjustable and permits measurement of the dispersion of the beam.

It is interesting to note that the flow through the 2 mm. holes is not critical flow but proportional to the pressure difference and hence the number of ions passing in unit time through the hole is proportional to the square of the area. From the constants of the system the total amount of gas withdrawn from the flame can be calculated.

Data for a stoichiometric ethylene-oxygen flame at different dilutions with nitrogen are given. For 60 per cent nitrogen, a flame velocity of 182 cm/sec and a flame temperature of 2570°K, the ratio of the number of ions per cubic centimeter is 0.5×10^{10}. A few experiments have been made on flames which could be expected to have a low concentration of ions. The sensitivity of this equipment was not sufficient to measure the concentration of ions in a nitrous oxide-oxygen flame where the value certainly does not exceed 10^9 ions/cm^3 most probably reaches the order of magnitude of 10^8 for a stoichiometric flame with 35 per cent nitrogen.

The order of magnitude of the results reported in this paper should be compared with the work of Calcote and King* who obtained data by means of the Langmuir probe on flames burning at atmospheric pressure.

Subject Headings: *Ions, extraction from flames; Flame, extraction of ions from.*

W. C. Johnston

Line, L. E., Clark, W. J., and Rahman, J. C. (Experiment, Incorporated, Richmond, Virginia) "An Apparatus for Studying the Burning of Dust Clouds," *Sixth Symposium (International) on Combustion,* New York, Reinhold Publishing Corporation, 779-786 (1957)

A detailed description is given of an apparatus for generating a flowing nonturbulent dust cloud in the form of a 1 in. diameter vertically downward moving stream. The dust cloud can be produced in either a wall free condition when it is surrounded by an annular stream of gas or in a wall confined condition where the cloud fills the burning tube completely. Satisfactory wall free dust columns of charcoal, boron dust, lycopodium, and atomized magnesium have been produced. Provision is made for varying the percentage of oxygen in an oxygen-diluent gas mixture used as the carrier gas continuously from 0 to 100 per cent and also for varying the dust concentration and spark ignition energy over wide limits. Instantaneous measurements of the concentration of the dust cloud can be made by a light absorption method. The apparatus is so designed that experiments can be made with an initial pressure up to 100 psi. Two types of dust cloud generators are described, their use being dependent on the flowing characteristics of the dust powder.

Initial experiments at atmospheric pressure using lycopodium powder with a linear flow velocity of 30 cm/sec and dust concentration of 180 mg/l have been carried out to determine the critical oxygen concentration with a fixed spark energy and critical spark energy with a fixed oxygen concentration. These ex-

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* Calcote, H. F. and King, I. R. *Fifth Symposium (International) on Combustion,* New York, Reinhold Publishing Corporation, 423 (1955)

periments also test the precision of the apparatus and the importance of certain apparatus parameters. An arbitrary definition of ignition requires a flame propagation of 4 in. or more along the dust column. The results indicate that the critical oxygen concentration or condenser energy for spark ignition of dust clouds is not sharply defined but there is a certain region over which ignition appears to be statistical and results are presented as ignition frequency, usually based on 10 trials, against other parameters. The ignition frequency *vs.* oxygen concentration curve for a wall free dust column goes through a maximum at about 30 per cent oxygen concentration. A similar maximum is found for the condenser energy. Further work is to be carried out to determine if this is a real property of the dust cloud or a function of the apparatus.

With a nitrogen diluent and a wall-confined dust column the ignition frequency rises sharply with per cent oxygen or ignition energy whereas with the wall-free colum the rise is initially more gradual; with a helium diluent these differences are less pronounced. Data have been obtained relating a decrease in condenser energy with an increase in oxygen concentration and a minimum dust concentration for a given oxygen concentration. Both dust concentration and minimum condenser energy for ignition are very sensitive to oxygen concentration at low oxygen concentration.

An optimum spark gap distance of 6 mm. is indicated and a study of the inductance of the spark ignition circuit shows a significant decrease in the condenser energy required for ignition when an inductance of 13μh is introduced into the circuit.

Subject Headings: *Dusts, burning of.*

G. L. Isles

VI. Radiation

Fraser, A. R. (Atomic Weapons Research Establishment, Aldermaston, Berks, England) "Radiation Fronts," *Proceedings of The Royal Society,* **A 245,** 536–545 (1958)

A radiation front may be formed when very intense thermal radiation penetrates a cold, absorbing, compressible fluid. Radiant energy which is absorbed heats the cold medium causing it to radiate and in turn heat the cold fluid in the path of the advancing front. If the cold medium were transparent to the radiation, there would not be a radiation front. Absorption of radiation sets the fluid in motion due to heating effects and to the fact that the absorbed radiation has momentum which is transferred to the fluid. Hydrodynamic shocks (a shock in which radiation plays no part) may run ahead of the radiation front, or the front may be supersonic relative to the cold gas. In a front radiation decays over a narrow region; in this region the gradients of temperature, pressure, and velocity are very large.

It is possible to obtain the restrictions on the radiation fronts by using the conservation laws (mass, momentum, and energy) and the second law of thermodynamics. These differ from the ordinary compressible fluid relations by including in the energy both the internal energy of the fluid and the radiant energy, in the pressure the hydrostatic plus the radiation pressure, and in the energy flux an additional term for radiation. Steady state is assumed. Viscous effects are included in the formulation; however, heat conduction is considered negligible.

Generalized forms for the Rankine-Hugoniot relations across a front follow from the analysis.

Considering the fluid, associated radiation, and radiation sources and sinks as a thermodynamic system, an inequality is given which expresses the fact that the entropy of an isolated system cannot decrease. By assuming that the radiant flux ahead of the front is negligible and that viscous effects are negligible both ahead and behind the front, the inequality can be expressed as a function of pressure P and specific volume V. The inequality divides the PV plane into accessible and inaccessible regions. Figures are presented for two limiting cases: pure radiation only, and a perfect gas only. The accessible part of the PV plane is further divided into four regions; the basis for the division is provided by the properties of a "normal" mixture of radiation and fluid. A normal mixture possesses the usual thermodynamic properties such as a positive coefficient of thermal expansion.

Two of the four regions seem to be of little importance. The other two regions involve radiation fronts with properties similar to detonation and deflagration and, hence, are called "radiation shocks" and "radiation flames." A radiation flame is subsonic relative to the cold fluid and is rarefactive. The front is followed by a positive flux of radiation, *i.e.,* a flux moving in the same direction as the front. A radiation flame may be preceded by hydrodynamic shock.

A radiative shock is supersonic relative to the cold gas and is compressive. As in the case of a radiative flame, there is a positive flux of energy in the hot fluid behind the front.

In addition to the radiation flames and shocks there can exist an isothermal shock which is primarily a viscous shock followed closely by gas which is being rapidly cooled by radiation. An isothermal shock has a negative flux of radiant energy downstream of the viscous portion of the shock. The shock is isothermal in the sense that the fluid has the same temperature across the shock but higher temperatures within the shock. Using the isothermal speed of sound as a reference velocity, the isothermal shock is supersonic relative to the fluid ahead and subsonic relative to the fluid behind the shock.

In order to find the structure of the radiation front it is assumed that thermodynamic equilibrium exists everywhere within the front and that a simple viscosity coefficient applies within the front. Compared to a hydrodynamic shock, a radiation front is thick. The radiation mean free path is usually much greater than molecular mean free paths. The equilibrium assumption may not be invalid for the radiation fronts, except for isothermal shocks. If viscosity has little influence, then P varies linearly with V within the front. If viscosity is important, a complex path in the PV plane describes the structure of the radiation front; this path may be in the form of an open loop. Viscous radiation shocks give subsonic flow (using again isothermal speed of sound as reference) in the hot fluid whereas nonviscous fronts give supersonic flow. Viscous radiation shocks correspond to strong detonations and nonviscous to weak detonations.

Subject Headings: *Radiation, fronts; Radiation, shock.*

A. E. Fuhs

Lubny-Gertsyk, A. L. (I. I. Polzunov Boiler and Turbine Institute, Moscow, U.S.S.R.) "Certain New Methods of Approximate Calculation of Radiative Heat Transfer," *Soviet Physics, Technical Physics,* 2, 1255–1268 (1957)

A number of problems of heat transfer between fixed solid walls and an enclosed radiating gas which may be either stationary or moving are discussed by the author. The primary field of application of these problems is in steam boiler technology.

The first problem considers either a cubical, spherical, or cylindrical volume of gray radiating gas in which heat is generated at a constant rate. The effective emissivity between the gas and the enclosing solid surface is calculated by several methods: (1) an approximate method derived from an exact treatment by Syrinov using integral equations; (2) a solution of the differential equations of radiation in a gas; (3) an empirical generalization of the well-known exponential expression for the emissivity of an isothermal gas; (4) a calculation based on graphs of emissivity of an isothermal gas. A comparison of the results obtained shows reasonably good agreement between methods (1), (2), and (3). Method (4) gives results that are seriously in error for high values of the absorption coefficient.

A solution of the differential equations is also given for the case of a cubical, spherical, or cylindrical volume of gas with constant generation of heat, surrounded by inert gas, and the whole enclosed by a solid surface of the same shape.

The problem of calculating the radiation from a non-isothermal selectively absorbing gas is discussed, and a method of solution based on the use of a function giving the probability of all absorption coefficients is outlined.

Next, an approximate calculation is given for a gray gas in a cylindrical enclosure, the gas being traversed in all directions by thin heat absorbing tubes. The two cases worked out are for a constant gas temperature and for a constant density of heat emission by the gas.

The last two problems consider a gray radiating gas which is in motion. In the first of these, the gas is moving along a tube. Mixing and convective heat transfer are neglected. The velocity distribution across the tube cross section is assumed to be uniform. A radial temperature distribution function is assumed and taken to be similar at any cross section. The mean temperature along the tube is then calculated by integration of the radiation from individual gas volume elements. It was found that the results were very insensitive to the particular form of the assumed temperature distribution.

The other problem of a radiating gas in motion is the case of a gas flow normal to an infinite screen which is partly reflecting The flow originates at infinity on one side of the screen and continues to infinity on the other side. Calculated results are shown for the radiant heat transfer between gas and screen.

The usefulness of the paper is somewhat impaired by the lack of a list of symbols and by the rather sketchy presentation of the steps leading to the calculated results.

Subject Headings: *Heat transfer, radiative, calculation of; Radiation, heat transfer, calculation of.*

W. Y. Pong

Gardon, R. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "Temperatures Attained in Wood Exposed to High Intensity Thermal Radiation," *Office of Naval Research Contract N5-ori-07851, Technical Report No. 3* (April 20, 1953)

The investigation, which arose from the hazard of atomic weapons, was designed to develop and verify experimentally an analytical treatment of the early stages of irradiation of such solids as wood and Masonite in order to predict thresholds of damage. The possibility of quantitative analysis of later stages, when decomposition alters the composition and properties of the material and evolves or consumes energy, appears remote.

In the early stages of irradiation the energy absorbed by the solid goes wholly to raise its sensible heat. The rate and distribution of its temperature rise $\triangle T$ then depends on the conditions of irradiation, the shape of the solid, and its reflectance, volumetric specific heat $c\rho$ (product of specific heat and density), thermal conductivity k, and effective absorption coefficient γ, taking account of possible scatter of radiation within the material. The radiation is characterized by its intensity I, duration t, and spectral composition, the last of which affects the reflectance and absorptivity of the material. The rate and distribution of temperature rise were analyzed for opaque solids in slabs of finite thickness L, for opaque semi-infinite solids, and for diathermanous (transparent to heat radiation) semi-infinite solids.

The analysis led to equations involving independent dimensionless groups of the physical variables. The groups are: (1) dimensionless temperature rise $\theta_L = \triangle T \cdot k / I_0 \cdot L$ (opaque finite slabs), $\theta_x = \triangle T \cdot k / I_0 \cdot x$ (opaque semi-infinite solids), or $\phi = \triangle T \sqrt{kc\rho} / I_0 \sqrt{t}$ (diathermanous solids); (2) dimensionless time $Z_L = \alpha \cdot t / L^2$ (opaque finite slabs), $Z_x = \alpha \cdot t / x^2$ (opaque semi-infinite solids), or $\phi = x \sqrt{\alpha t}$ (diathermanous solids); (3) dimensionless position $r = x/L$ (opaque finite slabs); (4) $\xi = \gamma \sqrt{\alpha t}$ (diathermanous solids). I_0 is the intensity of unreflected radiation, α the diffusivity (equal to $k/c\rho$), and x the distance from the irradiated surface. Plots of the dimensionless groups serve to represent visually the relations among the physical variables for any one of the three cases of solids considered and also for comparison of the three cases with one another.

Opaque slabs may be considered semi-infinite solids above moderate limits of the parameters x/L and $\alpha t/L^2$. The surface temperature rise of an opaque slab is within 5 per cent of that of a semi-infinite solid when $\alpha t/L^2$ does not exceed 0.5. A slab of wood 1 cm. thick remains within that limit for 4 min. whereas the limit comes at 0.3 sec. for a 1 cm. slab of silver. For a 1-second exposure, a slice of wood only 0.07 cm. thick may be considered semi-infinite.

Diathermancy retards the temperature rise at the irradiated surface but hastens the rise in deeper layers of the material. The significance of diathermancy, however, diminishes as the time of irradiation increases so that the solid may be considered opaque when $\gamma\sqrt{\alpha t}$ exceeds 6, in which case $\triangle T$ for diathermanous and opaque semi-infinite solids are within 10 per cent of each other. For wood γ varies from 10 cm^{-1} upward. When $\gamma = 10$ cm^{-1} diathermancy becomes unimportant after 160 secs. and when $\gamma = 100$ cm^{-1} it is unimportant after 1.6 secs. Scattering within diathermanous materials such as wood can be allowed for by taking $\gamma = \sqrt{(\gamma_A + \gamma_S)^2 - \gamma_S{}^2}$, in which γ_A is the true absorption coefficient and γ_S is the scatter coefficient.

For the experiments, relatively short wave length radiation of intensity from 3.6 to 5.35 $cal/cm^2 \cdot sec$ was obtained from a segmented mirror solar furnace described in this and a previous publication.* The intensity was uniform within 5 per cent over an area of target 1½ in. in diameter, which was large enough for the sample to be treated as one-dimensional with negligible edge effects. To measure the intensity of radiation during an exposure (the impulse, $I \cdot t$), a silver disc calorimeter patterned after Abbot's pyrheliometer † was used. To measure

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* See page 141

† Abbot, C. G. "The Silver Disc Pyrheliometer," *Smithsonian Miscellaneous Collections,* 56, No. 19 (1912)

intensity directly when it varied rapidly with time, circular foil radiometers described in this and a previous publication * were used. Record was kept of the intensity of solar radiation with an Eppley pyrheliometer connected to a potentiometer-recorder.

Wood specimens for test were 2½ in. square about ½ in. thick, thick enough to be considered semi-infinite. They were irradiated over a circle 2¼ in. in diameter. The woods were sugar pine and birch, in edge-grain, in flat-grain, and in end-grain orientations, and usually dry (desiccated) but in several different levels of moisture content for some tests. Woods were exposed both with natural surface and with the surface blackened with India ink. Masonite specimens ¼ in. thick, natural and blackened, were tested also.

Temperature at the surface of specimens was measured with chromel P-alumel thermocouples 0.0025 cm. in diameter. Temperature at points within specimens was measured with thermocouples 0.032 cm. in diameter embedded at distances from the irradiated surface that varied from as little as 0.08 mm. to as much as 4.58 mm. Usually three positions were observed for each specimen. Outputs of thermocouples, radiometers, and calorimeter were recorded on an oscillograph recording camera.

Wood irradiated by 5 cal/cm^2 begins to evolve smoke almost at once but does not begin to char until 3 secs. have elapsed. The smoke alters both the intensity and the spectral composition of the radiation reaching the wood by scattering, absorbing, and reradiating part of the radiant flux. The effect of the smoke was observed by mounting one radiometer in the surface of the wood and a second radiometer in a plane normal to the wood surface and just outside the region of specular reflection from the surface.

Masonite, which is dark brown in color, and blackened wood behave as opaque materials. Wood in its natural color behaves as a diathermanous material but the effect of diathermancy decreases with time of irradiation as predicted by theory. After 2 secs. of exposure, even before charring is observable, the surface may be considered opaque. Diathermancy may be particularly important for short exposures of thin slices of wood in which the radiation scattered back from the interior is reduced.

The effects of diathermancy of wood are most pronounced for wave lengths from 0.8 to 2μ where reflection is also greatest. This reflection, however, comes from the diathermancy which permits more internally scattered radiation to reach the surface again. Radiation from sources having black body temperatures of 2000°C should be suitable for studying the diathermancy of wood.

Prediction of the absorbed fraction of high-intensity radiation is still uncertain and needs further study. Approximately, the absorptivity for intense radiation of the spectral composition of sunlight might be taken as 0.5 for all but thin slices of wood regardless of the color of the surface. Once the effective absorptivity is known, temperatures attained prior to damage in dry painted wood or in wood of natural color exposed for 2 secs. or longer should be readily predictable. Prediction for shorter exposures of wood in natural color is complicated by the different effects of radiation of different wave lengths and by sparsity of data on coefficients of absorption and scatter.

Subject Headings: *Radiation, effects, on wood; Wood, temperatures in, by high intensity thermal radiation.*

F. L. Browne

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* See page 140

Ho Leong, E. and Williams, M. E. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "Surface Temperatures in a Two-Layer Air-Spaced Slab System Irradiated from One Side," *Office of Naval Research Contract N5-ori-07851, Technical Report No. 4* (January 30, 1956)

A mathematical and experimental analysis was made of the utility of clothing materials in protecting the skin from high intensity radiant heat fluxes such as are liberated by an atomic explosion.

A simple two-layer model consisting of a thin layer of material (cotton sateen) at various distances from a semi-infinite solid body (polyethylene block) was used. The mathematical analysis was carried out for unsteady state heat conduction for different spacings of the two-layer system and for different thermal conductivity/volumetric heat capacity ratios. A system of simultaneous partial differential equations with nonlinear boundary conditions was set up and solved by the Schmidt method of finite difference approximations.

The mathematical relationships were tested experimentally by irradiating the model from a solar furnace, impinging the heat pulse on the surface of the clothing material. The solar furnace was able to give high intensity thermal radiation, ranging up to 6.89 cal/cm^{2}sec. Four hundred mirrors (3″ x 3″) reflected the direct radiation from the sun to a secondary mirror system which in turn reflected the radiation to the target area. The cloth contained two thermocouples, one on each surface; a third thermocouple was located at the surface of the polyethylene block. In a later development the polyethylene skin simulant was replaced by a copper-fin skin simulant, consisting of 0.005 in. copper fins attached to a 0.002 in. copper sheet with 0.125 in. air spaces between the fins.

A comparison of predicted and experimental curves revealed much discrepancy for the cloth top and under surface, but good correlation for the polyethylene surface. Heat absorption by the inherent moisture content of the cloth top surface apparently increased the conductivity of the air gap between the cloth and polyethylene in a complicated manner. This moisture effect was large enough to prevent reproducible experimental results. The simple treatment of heat conductivity through a two-layer system without correction for the presence of steam was thus inadequate in describing the actual heat transfer process. The results clearly indicate, however, that lighter shade fabrics give better protection from radiation damage than dark ones over the first two seconds after exposure.

The experience gained in this study will no doubt be useful in a future attempt. Several recommendations were made for future work, including the necessity for constant humidity and for comparison of skin simulant performance with data of other investigations.

Subject Headings: *Clothing, protection of skin from radiation; Radiation, protection of skin by clothing.*

J. M. Singer

Ho Leong, E. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "Notes on Temperatures Attained by Bare and Covered Semi-Infinite Solids When Heated by a Thermal Radiant Impulse," *Office of Naval Research Contract N5-ori-07851* (June 1, 1954)

The work reported in this preliminary note was part of an extensive research project to study the effect of thermal radiation on organic materials. The author sought to develop an analytical method for evaluating the protective effect of clothing of such materials by calculating their temperature-time histories with a simplified model.

To establish the reasonableness of this approach, the calculations incorporated data from radiation experiments carried out at the University of Rochester. These experiments determined the exposure time required at a given radiation intensity to produce 2+ burns on bare and covered pig skins. They also explored the feasibility of using polyethylene as a skin simulant and finally equated a 42°C rise in surface temperature of cloth-covered polyethylene to a 2+ burn in pig skin.

The simplified model assumes that the main body is semi-infinite and that an air gap separates it from the cover. The numerical method of finite difference approximations was used to calculate the temperatures. Three graphs present the calculated temperature-time histories of bare pig skin and cloth covered polyethylene irradiated for 1, 2 and 5 sec. with air gaps of 0, 0.1 and 0.5 mm. under the covering. The measured and calculated temperature rises for polyethylene are not far apart especially with a 0.1 mm. air gap. However, the bare skin gets considerably hotter than when covered by polyethylene during irradiation but its temperature drops faster once irradiation ceases. This may explain the fact that for exposure times up to 5 sec., less intense heat pulses are required to produce a 2+ burn on a covered pig skin than on a bare one. If polyethylene is to be used as a skin simulant, the extent of surface temperature rise is not a good measure of damage. It was concluded that an integral analysis evaluating the duration of temperature experience would be better.

Subject Headings: *Radiation, effects, on bare and covered solids.*

G. M. Steffan

VII. Suppression of Combustion

Spalding, D. B. (Imperial College, London, England) "A Theory of Inflammability Limits and Flame-Quenching," *Proceedings of The Royal Society,* **A 240,** 83–100 (1957)

This paper is a genuine effort to give a theoretical foundation to one of the first established problems in combustion science. The inflammability limit of combustible mixtures has been determined for a number of years using many diversified techniques, and many experimental papers on the subject have been published. Another paper on this subject was published independently by E. Mayer.* Radiative heat loss downstream of the flame is the primary consideration of both theories.

The author begins with a mathematical argument based on a one-step reaction where fuel and oxidant yields a single product. A steady stream of the reactants is assumed to be flowing at a given mass rate in a positive x-direction through a flame where they are consumed and product produced. Far downstream of the reaction zone only the product and excess oxidant remain. The temperature is low in the unburnt mixture and high in the flame, but a gradual falling off of the temperature occurs downstream as a result of heat transfer to the surroundings. Variations of stream properties normal to the x-axis are absent, and therefore the theory treats a one-dimensional flame.

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* See page 125

The conservation equations are written for energy, fuel, and oxidant; and the stoichiometric relation between fuel and oxidant is given. Kinetic energy is excluded from the energy equation, all gases are assumed to be perfect, and the base of enthalpy is taken at absolute zero for the components downstream of the flame.

With several assumptions and mathematical manipulations, the equations are put into dimensionless form incorporating an eigenvalue. From these emerge two differential equations involving the temperature gradient and fuel concentration gradient, both with respect to a "distorted space variable." As a mathematical convenience the space variable is given the value of unity and the fuel concentration is set equal to zero at the maximum temperature in the reaction zone. Physically, this corresponds to placing an adiabatic porous catalyst plug at the point where the space variable equals unity and fuel concentration is reduced to zero. At the plug the dimensionless temperature has a value of unity, and generally, finite gradients exist at its surface.

Solutions of the equations are obtained by assuming; (1) no heat losses to the surroundings, (2) heat losses are present. The former case is identical to flame propagation theories put forth prior to the present paper. In this instance fuel concentration and temperature profiles in a flame are similar, and the sum of the dimensionless quantities is unity. For this case the author presents an analytical solution for calculation of flame speed. In the second case when heat losses are taken into account, the profiles of temperature and concentration are not similar. Here both equations have to be solved. The porous catalyst plug is retained for this case also since it serves to separate the region where reaction rate is dominant from the region where heat losses are dominant.

General methods of solution are briefly described. The author introduces these to assure the reader that the numerous assumptions and approximations to follow are not necessary but merely are expedient. An approximate solution for a class of reactions (hydrocarbon-air flames) is presented. The dependence of reaction rate on temperature is expressed as a power function of the dimensionless temperature. A heat-loss term has the same exponential dependence on temperature, and the exponent is said to vary between 1 and 5. The exact value depends on whether the heat losses are predominantly by conduction or radiation. From this point the problem is solved in two parts; the portion of the combustion zone upstream of the porous catalyst plug where chemical reaction is dominant, and the region downstream of the plug where heat losses are dominant.

An example is worked out for hydrocarbon-air flames and the result yields a plot of the heat-loss parameter versus an eigenvalue from which the burning velocity is determined. This curve clearly shows the two-valued character of the burning velocity at the inflammability limit. The heat-loss parameter represents the ratio of heat loss rate to chemical reaction rate. For each value of this parameter two eigenvalues (burning velocities) are read from the curve. Only the lower of the two is of real significance.

The theory is extended to quenching of flames by cold walls. Here a Peclet number is derived based on flame speed of the mixture, quenching diameter, and thermal conductivity of unburnt gas. The value given is 60.5 and is compared with a single experimental value of 46 taken from the literature. Since the derived value was obtained regarding the flame as one-dimensional, the comparison is considered very good. The theory predicts a value of 1.2 cm/sec for the burning velocity at the inflammability limit. The author believes this is too low since velocities have not been measured below 3 cm/sec. However, only nonluminous radiation was considered in the theory; Spalding feels that chemiluminescence and conductive heat loss would be present to some extent which might account for the discrepancy.

The author closes with a discussion of other mechanisms proposed to explain the existence of inflammability limits. In his opinion, none of these serve their intended purpose. In particular, Spalding disagrees with the "small disturbance from the steady state" hypothesis; and argues that a stable steady flame, even with large disturbances introduced, will re-establish itself in an unlimited one-dimensional system in the absence of heat losses.

This reviewer believes that the experimental evidence to confirm or deny this theory would be quite valuable. One such experiment might be the following: Stop the heat losses downstream of the flame in some manner (heated plate, etc.); and note whether destruction of the temperature gradient in the reaction zone would enable flame to continue to propagate beyond the primary zone, even with the fuel concentration so greatly reduced.

Subject Headings: *Flammability limit, theory of; Flame, quenching, theory of.*

C. O'Neal, Jr.

Mayer, E. (Arde Associates, Newark, New Jersey) "A Theory of Flame Propagation Limits Due to Heat Loss," *Combustion and Flame,* **1**, 438–452 (1957)

This theoretical paper is concerned with the limitations imposed by heat losses on the propagation of premixed flames. The lost heat may be transferred from the flame to its surroundings by convection or by radiation. In general, convective and radiative losses occur together but in the two limiting cases of all one and none of the other, each is considered as giving rise to characteristic phenomena—convective heat losses to quenching limits and radiative heat losses to flammability limits. Each kind of limit is treated separately.

The quenching of premixed flames by solid surfaces is the observable consequence of a series of interactions involving gas flow, chemical reaction, and heat loss. Mayer idealizes this complicated situation by considering only one-dimensional flames. Accordingly, the composition and temperature of a burning mixture may vary with distance through the flame but not with distance parallel to the flame. The essential features of such a flame are mathematically represented by three equations. The first of these relates flame speed to the maximum temperature attained by the combustion products. The second expresses the rate of convective heat loss in terms of flame speed and a characteristic dimension which in the case of tubes is the tube diameter. The third and final expression is an over-all heat balance.

Consideration of these three mathematical relations reveals that they are compatible only under certain conditions. In particular, for quenching by tubes and for a given combustible mixture, the equations are only compatible for tube diameters greater than a certain critical size, the quenching diameter. The critical condition is presented in simple mathematical form and used to calculate quenching Peclet numbers for hydrocarbon-air flames. The Peclet number is given by $\mathrm{Pe} = \frac{SQ}{\alpha}$ where S is flame speed, Q is quenching diameter, and α is the thermal diffusivity of the mixture. For hydrocarbon-air flames $\mathrm{Pe} \approx 40$. Agreement with experiment is obtained by adjustment of a constant "the flame configuration factor" which appears in the equation to describe the rate of convective heat loss.

The outstanding virtue of this treatment of quenching is its simplicity. Within the limitations imposed by the original idealization of a flame, the argument is convincing. The major defect is the idealization itself.

The mathematical approach already described in connection with quenching limits has also been applied by Mayer to the problem of flammability limits. In this case heat loss is by radiation and not by convection. Limiting conditions are again found to exist and are used to calculate the flammability limits for hydrogen-air and for propane-air. While the agreement with experiment is satisfactory, the author does not consider nor discuss the possibility that convective and conductive heat transfer may be involved in the experimental determination of "flammability limits." Flammability limits may indeed exist because of radiative heat losses, but they need not be the limits actually observed.

Subject Headings: ***Flame, propagation limit theory; Flammability limit, theory of.***

W. A. Rosser, Jr.

Belles, F. E. and Berlad, A. L. (National Advisory Committee for Aeronautics, Cleveland, Ohio) "Chain Breaking and Branching in the Active-Particle Diffusion Concept of Quenching," *National Advisory Committee for Aeronautics Technical Note 3409* (February 1955)

This article represents one of a series of theoretical and experimental investigations by A. L. Berlad and his co-workers concerning the quenching mechanism of propane-oxygen-nitrogen flames. In this theoretical analysis an attempt is made to correlate all available experimental data concerning quenching distances for lean and stoichiometric propane-oxygen-nitrogen mixtures.

Assuming that a flame approaches a homogeneous combustible gas mixture contained between two parallel plates, the authors predict the minimum plate separation which will permit flame propagation when quenching is controlled by the diffusion of active reaction intermediaries to the wall where recombination occurs preferentially. The active-particle diffusion concept hypothesizes that the rate-determining reaction is between fuel molecules and active particles, and invokes the criterion that a flame cannot propagate unless the total number of effective collisions of active particles before they are destroyed at the wall exceeds a minimum fraction of the total number of gas molecules. Neglecting convective transport effects, quenching distance equations are derived for chemical source terms representing:

(a) active particle production, predominantly chain-branching gaseous reactions of active particles, and an arbitrary chain-breaking efficiency of the walls.

(b) active particle production, predominantly chain-breaking gaseous reactions of active particles, and an arbitrary chain-breaking efficiency of the walls.

(c) active particle production, no chain-breaking or chain-branching in the gas phase, and an arbitrary chain-breaking efficiency of the walls.

(d) active particle production, no chain-breaking or chain-branching in the gas phase, and complete destruction of all active particles at the walls.

The resulting expressions for the quenching distance depend upon the properties of the initial combustible mixture, the average temperature and active-particle concentrations in a "preflame" zone, the (inaccurately known) average rate constant for the reaction between active particles and fuel, the (unknown) average chain-branching or chain-breaking coefficient (models (a) and (b) only), the (unknown) chain-breaking efficiency of the walls (models (a), (b) and (c) only), and the (unknown) fraction of fuel molecules which must react for continued flame propagation. The temperature and active-particle concentrations in the "preflame" zone are arbitrarily assumed to equal 0.7 times their equilibrium values for an adiabatic flame, which can be calculated by standard thermodynamic methods. It is shown from the form of the quenching-distance equation that the effect of the chain-branching and chain-breaking coefficients upon the quenching distance is greater for dilute mixtures than for vigorous mixtures; but because these coefficients are unknown, models (a) and (b) are not used for numerical correlation of the quenching-distance data. Assuming the wall chain-breaking efficiency to be 0.7 in model (c), it is shown that model (c) correlates the experimental data much less effectively than model (d). In these calculations the fraction of fuel molecules which must react for continued flame propagation is assigned a reasonable temperature dependence and adjusted in magnitude to provide the best correlation.

Experimental quenching-distance data for lean propane-oxygen-nitrogen mixtures including a wide range of initial temperatures, pressures, and concentrations are correlated quite satisfactorily by model (d). It is therefore concluded that chain-branching, chain-breaking, and incomplete destruction of active particles at the wall may be neglected in treating quenching data for these systems; a straight chain reaction with 100 per cent wall chain-breaking efficiency appears most probable. Since the similarity between diffusion and heat conduction processes indicates that an equally good correlation could be obtained by assuming a thermal quenching mechanism, the authors correctly conclude that their results are valid only within the framework of the active-particle diffusion model of quenching, and that this model is neither supported nor weakened by their results. Although the concept of flame quenching by heat transfer to the walls has been found more fruitful than the reaction-intermediary diffusion concept and has been adopted in nearly all of the more recent investigations, nevertheless it is of interest to determine the consequences of the diffusion model, which has not yet been unambiguously refuted.

Subject Headings: *Quenching, chain breaking and branching in; Diffusion, of active particles in flame quenching.*

F. A. Williams

Bouchet, R. and Laffitte, P. (Sorbonne, Paris, France) "The Extinguishing of Detonating Waves by Powdered Materials," *Comptes Rendus,* **246,** 1858–1861 (1958)

The extinction of detonations in gaseous mixtures at atmospheric pressure and room temperature by means of powdered materials is studied. The powder is introduced about ⅔ of the way up a vertical glass tube 16.4 mm. internal diameter and 1.4 meters long containing the gaseous mixture, and the detonation is initiated at the bottom. The quantities of powder required for extinction are larger than for deflagrations. For detonations in $CH_4+2O_2+N_2$ (velocity 1850 meters/sec) quantitative data are given both on a weight and on a surface area basis for 10–20 μ diameter particles of potassium bitartrate, silica, potassium bicarbonate, potassium oxalate, sodium bitartrate and potassium chloride. Except for KCl, rather less than 1 gm. of material was required. The above is also the order of efficiency on a weight basis. The effect of potassium bitartrate on detonations of several hydrogen+oxygen and propane+oxygen mixtures are also given, and determinations for methane, isobutane, acetylene and diethyl ether are mentioned (but without quantitative results). In all cases the maximum quantity of bitartrate was required when dealing with the stoichiometric mixtures, and not when dealing with the most rapid detonations.

Subject Headings: *Extinguishment, of detonations by powders; Detonation, extinguishment by powders; Powders, extinguishing of detonations by.*

G. Dixon-Lewis

Hartmann, I., Nagy, J., Barnes, R. W., and Murphy, E. M. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Studies with High-Expansion Foams for Controlling Experimental Coal-Mine Fires," *Bureau of Mines Report of Investigations 5419* (1958)

High expansion foams and foam plug techniques for controlling coal-mine fires were tested in the Experimental Coal Mine of the U. S. Bureau of Mines. The results of these studies constitute a preliminary progress report and are part of a continuous investigation of coal-mine fire control methods at the Bureau of Mines.

In a preliminary study in the laboratory, approximately 35 foaming agents and 20 stabilizers and additives were investigated in a 26 ft. long metal duct. The effects of concentration and temperature of solutions, speed of air, and additives were measured. Generally, foams produced with compounds of the lauryl sulfate type had a higher stability and lower rate of liquid loss than those produced with other types of compounds. A high-substitution carboxy methyl cellulose additive increased the stability and reduced the rate of liquid loss of the foam.

In transport tests in the Coal Mine, eight foam compounds were studied, most of them containing active ingredients of either alkyl aryl sulfonate or lauryl sulfate. The object of these transport tests was (1) to study the variables governing the formation and movement of foam plugs through the mine entries, and (2) to find or develop foams that could be transported at low water gage over long distances and still retain enough moisture to control fires. Foam compounds in the final spray liquid were in concentrations of 0.7 to 2.2 per cent; the proportions of active agents in the compounds were of the order of 30 to 40 per cent by weight. The spray solution was applied by means of a fire hose nozzle to a foam generating cotton net at rates of 35 to 75 gal/min. A light weight foam plug was produced that quickly filled the cross section of the mine entry. The foam was driven by a mine-ventilating system into an elliptical tunnel and mine entries having vertical cross-sectional areas of approximately 65 square feet. As in the laboratory tests, the lauryl sulfate detergent gave foams of higher stability, lower rate of liquid drainage, and higher liquid content than the alkyl aryl sulfonate compounds. The foam plugs lost moisture with time and distance of travel; occasionally a very long plug was useless in quenching a fire. The average forward speed of the foam varied from 30 to 70 feet per minute, depending on the driving air pressure and the extent of cross cuts into the mine.

Fire control tests were performed in the mine. Foam plugs were generated successfully at distances varying from 155 to 1010 feet upwind of fires set up in a 15 foot long section of the elliptical tunnel of the mine. Nine fire tests in all were made, one of 1100 pounds of rough wood and eight of bituminous coal of floor, floor-rib, and floor-rib-roof types. The experiments indicated that coal fires of moderate size and intensity could be brought under effective control by relatively moist foam plugs that contained 5 cc. or more of water per cubic foot of foam. The important factors in achieving control of the fire were moisture control of the foam reaching the fire and tightness of foam plug in the mine entry. Flaming combustion was stopped or suppressed by three effects: (a) a blanketing effect of foam excluding air; (b) a blanketing effect because of a decrease in oxygen concentration due to water vapor formed by evaporation of the moisture in the walls of the foam bubbles; and (c) a cooling effect on the fire because of the latent heat of vaporization. It was concluded that foam plugs were not likely to completely quench rapidly advancing deep-seated fires. The procedure would probably be useful in suppressing the combustion so that fires could be approached more closely and extinguished by other standard procedures.

Subject Headings: *Foams, for control of coal–mine fires; Fires, coal-mine, use of foams in control of.*

J. M. Singer

Walker, E. J., Aidun, A. R., and Grove, C. S., Jr. (Syracuse University Research Institute) "Additives to Improve the Fire-Fighting Characteristics of Water," *Bureau of Yards and Docks, Department of the Navy Contract NBy 13027, Quarterly Progress Report No. 5* (October 1958)

The report is the fifth in a series describing progress of work on the use of suitable viscosity and opacity additives to improve the fire-fighting properties of water. One phase of this work consisted in the study of the transfer of radiant energy. Using the light transmission apparatus described previously,* a series of experiments aimed at determining the effects of particle size and powder concentration were made with aluminum powder treated to float on the water surface. Light transmission was measured through the cell before and after admission of the powder and results were expressed as the ratio I/I_0 where I_0 is the transmission through pure water.

An equation was derived expressing the relationship between per cent transmission and the parameters studied. Neglecting the diffraction of light at the particle-water interface, the authors established that the ratio I/I_0 should be proportional to the fraction of the water surface which is free of powder:

$$\frac{I}{I_0}=\frac{A_t-A_c}{A_t} \qquad (1)$$

where A_t is the total surface of the water in the cell and A_c the portion of the water surface covered with the powder. A_c is equal to the product of the number n of aluminum platelets of diameter d by their surface in contact with the water:

$$A_c=\frac{n\pi d^2}{4} \qquad (2)$$

and the weight of powder used is in turn equal to:

$$W=n\rho\frac{\pi d^2 t}{4} \qquad (3)$$

where ρ is the density of aluminum and t the average thickness of the metal platelets.

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* *Fire Research Abstracts and Reviews,* Vol. I, No. 1, p. 18 (1958)

Solving equation (3) for d^2 and substituting in equation (2), it is found that:

$$A_c = \frac{W}{\rho t} \tag{4}$$

and equation (1), solved for t, becomes:

$$t = \frac{W}{A_t \rho} \cdot \frac{1}{(1 - I/I_0)} \tag{5}$$

Assuming that all platelets, irrespective of size, are similar in shape, then:

$$d = kt$$

or

$$d = \frac{kW}{A_t \rho} \cdot \frac{1}{(1 - I/I_0)} \tag{6}$$

The linear relationship between diameter of particles and light absorption as expressed in equation (6) was verified by the results of tests on the effect of particle size at constant weight of powder.

By rearrangement of equation (6):

$$\frac{W}{A_t} = \frac{d\rho}{k}(1 - I/I_0)$$

which shows that, when particle diameter is kept constant, the weight of powder per unit area of the water surface is directly proportional to the obscuration. Transmission measurements with varying amounts of powder also verify this equation up to a weight per unit area where total coverage is obtained forcing particles to pile up. This results in a sudden increase of the slope of the curve.

A new, but simpler, transmission apparatus equipped with a monochromatic light source is being constructed to test other reflective metal powders.

Fire tests, aimed at correlating laboratory results with field observations, have been continued. The addition of Acrysol ASE-60 to the water in sufficient amount (1 per cent) to increase the viscosity to 10 centipoises more than doubles the extinguishing power of the solution. A further addition of aluminum powder (0.05 per cent) increases this power by another factor of 10, superior performance being obtained when the aluminum powder is suspended in the solution rather than made to float on the surface which is contrary to the indications obtained in previous tests.* A logical explanation for the action of the metal powder is that the energy transferred from the flaming zone back to the surface of the fuel is mainly by radiation and, when the water contains aluminum powder, the aluminum forms a reflective blanket in the intermediate zone which reflects a large quantity of the radiant heat away from the fuel, with the water still having the same cooling effect. This combined action cuts down the supply of combustible gases to the flaming zone which results in a marked reduction in the extinguishing time.

In order to ensure that no other factors could in part account for the increased extinguishing power, an investigation is being made of the effects of the additives on spray distribution. The apparatus consists of an inclined pan with graduated cylinders (to collect the fluid) disposed at fixed distances from a point directly below the nozzle. After a run, the liquid level in each graduate is tabulated and plotted as a function of distance from the nozzle centerline. By integra-

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* *Fire Research Abstracts and Reviews,* Vol. I, No. 2, p. 58 (1959)

tion, one can determine the precentage of the total spray falling on the fire proper. Partial results indicate that Acrysol-water and Acrysol-water-detergent formulations have no effect on the spray distribution and merely decrease by a small amount the quanty of fluid over the fire area.

Subject Headings: *Additives, fire-fighting improvement; Water, improvement by additives.*

R. Jutras

Greenstein, L. M. and Richman, S. I. (Francis Earle Laboratories, Inc., Peekskill, New York) "A Study of Magnesium Fire Extinguishment Agents," *Wright Air Development Center Contract No. AF33(616)355, WADC Technical Report 55–170* (May 1955)

The present report summarizes the status of extinguishment of magnesium fires and describes experiments on standard fires. Previous agents used can be divided into solids such as pitch or mixtures of inorganic salts, that form fusible coatings on the magnesium and in so doing prevent combustion by preventing access of air, and liquids that vaporize and cool the magnesium below its ignition point.

All the work in this report deals with liquid solvents and solutions. Experiments were carried out with small, 200 gm. magnesium fires and with large, 15 and 50 lb., fires. Two criteria of effectiveness were chosen. One was the rapidity with which the temperature of the magnesium was lowered to 600°C, a figure taken as below the ignition point. The other was the amount of unburned magnesium left.

The importance of the cooling effect of the liquid and the formation of protective coatings as a result of the application of the extinguishing agent was confirmed. The cooling effect was responsible for actually putting out the fire while the coating effect prevented reignition while the mass cooled to below the ignition temperature. Liquids with high heats of vaporization, e.g., ethyl alcohol, or high boiling points, e.g. phthalate di-esters, were efficient coolants. The cooling efficiency of agents of this type could, in fact, be predicted fairly accurately from heat capacity and heat of vaporization data. A 50 per cent solution of di-isodecyl phthalate in chlorobromomethane solvent, for example, was an excellent extinguisher. The use of chlorobromomethane solvent had the double advantage that magnesium halide coatings were formed by the reaction of magnesium with the halogen of the solvent and the secondary fires resulting were easily extinguished with excess agent. Solutions of metal halides in a chlorobromomethane ethyl alcohol solvent were efficient in the small scale tests, but less so in the large scale tests, apparently because such thick coatings were formed that heat transfer from the magnesium to the agent was poor.

The report represents a thorough examination of the extinguishment of magnesium fires and should be of interest to those interested in the practical aspects of this problem.

Subject Headings: *Extinguishment, of magnesium fires; Fires, magnesium, extinguishment of; Magnesium, fires, extinguishment of.*

J. B. Levy

Belles, F. E. and O'Neal, C., Jr. (National Advisory Committee for Aeronautics, Cleveland, Ohio) "Effects of Halogenated Extinguishing Agents on Flame Quenching and a Chemical Interpretation of Their Action," *Sixth Symposium (International) on Combustion,* New York, Reinhold Publishing Corporation, 806–813 (1957)

To understand the chemical processes of flame extinction and to assist in the rating of halogenated extinguishing agents, the authors undertook the study of several halogenated agents on flame quenching. Unlike the usual flammability tests for rating the effectiveness of an extinguishing agent, flame quenching experiments permit the calculation of rate constants treating the mechanism of flame extinction as due to gas-phase chain-breaking similar to the wall-quenching of laminar flames by the destruction of active articles.

Pressure limits of flame propagation were measured for propane-air mixtures in the presence of small quantities of each of the following agents: CH_3Br, CCl_4, CH_2BrCl, CH_3I, CBr_2F_2, and $CBrF_2CBrF_2$ by the NACA tube method. This method gives the pressure at which the flame tube diameter equals the quenching distance which is in turn proportional to the parallel plate quenching distance. The higher the minimum pressure limit, the higher the rate constant, and the more effective the extinguishing agent. Rated in this manner from best extinguishing agents to poor, the agents tested as follows: (1) CBr_2F_2 (2) CH_2BrCl (3) CH_3I (4) $CBrF_2CBrF_2$ (5) CH_3Br (6) CCl_4. Thus, a qualitative comparison with the work of Friedrich * is in substantial agreement, but correlations between minimum pressure limit and flammability peaks were not conclusive.

Calculation of rate constants for the agent-active particle reaction yielded two groups: *poor* extinguishing agents, CH_3Br and CCl_4 whose rate constant values were of the order of $10^{-14}cm^3molecule^{-1}sec^{-1}$ and *good* agents, CH_2BrCl, CH_3I, CBr_2F_2 and $CBrF_2CBrF_2$ with values of the order of $10^{-13}cm^3molecule^{-1}sec^{-1}$. On the basis of these kinetic considerations the authors also predict that a halogenated extinguishing agent markedly superior to those already tested is highly unlikely.

The value of this paper lies in the pioneering attempt to include quantitative evaluations of flame extinguishing species as part of the growing body of flame theory.

Subject Headings: ***Flame, quenching, effects of halogenated compounds on; Quenching, of flame, by halogenated compounds; Halogenated hydrocarbons, quenching of flame by.***

D. Dembrow

Friedrich, M. (Research Division for Technique of Extinguishing Fires, Karlsruhe Polytechnical Institute, Germany) "On the Extinguishing Effect of Halogenated Hydrocarbons," *Erdöl und Kohle,* **11,** 248–252 (1958)

This article is a continuation of earlier discussions * on halogenated hydrocarbons as fire extinguishing agents. The author reviews previously reported findings and conclusions. Further test results are reported on flame inhibition with gaseous halogenated hydrocarbons (CH_3Br, CF_2Cl_2), carbon dioxide, and nitrogen. In the test, the extinguishing agent and fuel gas were mixed in a small chamber and fed to a gas bunsen burner. The rates of fuel and extinguisher fed to the

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* *Fire Research Abstracts and Reviews,* Vol. I, No. 1, p. 21 (1958) and Vol. I, No. 2, p. 60 (1959)

burner system were measured, and the minimum agent rate for various fuel rates to inhibit burner combustion were recorded. Plots were presented in which the order of effectiveness was indicated as follows: CH_3Br, most effective; CF_2Cl_2; CO_2; and N_2 least effective.

In this paper, the discussion of halogenated hydrocarbons is broadened to include consideration of corrosive and toxic effects, which were only briefly considered in the previous papers.

Data are presented covering corrosive effects of chlorobromomethane on iron, brass, aluminum, zinc and lead samples evaluated pursuant to DIN5850 (German Industrial Standard).

Data on the toxic effect on rats of chlorobromomethane, commercial grade chlorobromomethane, and dibromotetrafluoroethane are noted. In experiments involving caged rats and 1 cc. respectively of each of the above agents, rats died within three weeks after initial exposure to the respective compounds. Precise conditions for the experiments were not given.

In summation, the author concludes that as a class the halogenated hydrocarbons and/or their products of thermal decomposition were of such noteworthy toxic effect that thorough toxicological evaluation of any individual compound is indicated prior to general application as a fire extinguishing agent. He further concludes that the type of fire hazard must be considered prior to determining whether or not a halogenated hydrocarbon should be used for the fire extinguishing agent and concurred with Zablodil * in the conclusion that toxicity of individual halogen bearing compounds might preclude their use, even though they might be more effective than other agents.

Subject Headings: *Halogenated hydrocarbons, extinguishing effect; Extinguishment, by halogenated hydrocarbons.*

J. E. Malcolm

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* Zablodil, R. J. "Evaluation of Halogenated Hydrocarbon and Alkali-Earth-Metal-Salt Fire Extinguishing Agents for Low Temperatures," *Project NY 030 019–1. Technical Memorandum M-108, U.S. Naval Civil Engineering Research and Evaluation Laboratory, Port Hueneme, California* (November 1955)

VIII. Model Studies and Scaling Laws

Robin, A. G. (Bureau of Meteorology, Canberra, A.C.T., Australia) "The Association Between the Occurrence of Major Fires and a Synthetic Soil Moisture Index," *Australian Meteorological Magazine,* **17**, 1–7 (1957)

Fire danger and the outbreak of serious fires in southeastern Australia is closely associated with two seasonal or long-term factors, namely, the abundance of vegetative growth (mostly grass) and its degree of curing. These factors set the stage for serious fires which may then be precipitated by short-term factors consisting of various combinations of the current and recent meteorological conditions.

This paper is concerned with the long-term factors and presents the development of a synthetic soil moisture index for indicating the time of curing of fuels. The author states that no conclusions can yet be drawn from the index regarding the amount of fuel, which depends in considerable part on the rainfall during the growing season preceding the fire season.

The synthetic soil moisture index is in effect a method of "keeping books" on the soil moisture budget. The index is the difference between the actual and the effective monthly rainfall accumulated month by month. However, it is not accumulated indefinitely, but only up to a maximum value which represents the water-holding capacity of the upper zone of soil occupied by the roots of the grass vegetation.

The monthly effective rainfall P is a computed quantity which is assumed to be the amount of rainfall necessary to start and maintain growth after the break of a drought. It is computed from the monthly tank evaporation E by means of the formula

$$P/E^{0.7}=0.54$$

in which both P and E are in inches of water per month.

Subject Headings: *Fires, occurrence of and synthetic soil moisture index; Moisture index, association with fires.*

G. M. Byram

Hildenbrand, D. L. and Reid, W. P. (U.S. Naval Ordnance Test Station, China Lake, California) "Burning Rate Studies. III. Correlation of Experimental Results With the Thermal Model," *Jet Propulsion* **28**, 194–196 (1958)

Burning rate theories have been based on both thermal and mass diffusion mechanisms. The analysis cited in this paper is based on the thermal model, applied to the region where heat release from reaction is not important. Data, obtained from droplets burning around a thermocouple, are presented on temperature as a function of position in the liquid phase of ethyl nitrate and metriol trinitrate flames. These data are described empirically by a least squares fit to an equation of the form suggested by the cited analysis. The empirical exponent in the equation determined by this method is related by the analysis to thermal diffusivity, from which thermal conductivity may be found. The value for both fuels agrees well with directly measured thermal conductivities. This agreement is indicative of the applicability of the thermal theory and of the negligible contribution of heat release from chemical reaction in the liquid phase region for these cases. The conclusion, unfortunately, may not be applicable to the gas phase situation. A similar procedure applied to combustion of a gaseous mixture should produce equally interesting and significant results for another important combustion situation.

Subject Headings: ***Diffusion flames, burning rates of.***

A. E. Noreen

Hartmann, I. and Nagy, J. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Venting Dust Explosions," *Industrial and Engineering Chemistry,* 49, 1734–1740 (1957)

Some of the undesirable effects of dust explosions in closed galleries can be avoided by connecting the chamber to the atmosphere by a vent of appropriate size. The determination of the vent area required in a given instance is not a problem which admits of a complete theoretical solution and the paper under review constitutes an experimental investigation into the factors which affect the vent area required in particular circumstances. The maximum pressure in the gallery is chosen as the characteristic of an explosion most representative of its ability to cause damage, and determinations of the vent area required to limit the explosion pressure to a given value under a variety of different circumstances are reported.

The object of the authors was not primarily to provide a body of useful design data, but, rather to advance knowledge of the factors which affect the vent area required in particular circumstances. Tests were made using dust clouds of different substances; aluminum (atomized or flaked), magnesium (milled), cocoa, cornstarch, sugar, soybean protein, bituminous coal dust, cork, wood flour, sodium lignosulphate, soap, cellulose acetate, phenolic resin and polystyrene copolymer. The tests were usually performed with dust clouds of such density as to cause explosions of the maximum possible violence, but there were exceptions to the rule which are not clearly specified. This is not of great importance since difficulties experienced in obtaining dust clouds of uniform dispersion mean that the results are only of semi-quantitative significance. The data presented enable conclusions to be drawn about the relative importance of a variety of factors in determining the vent area required in given circumstances.

The results reported reveal that over a wide range the peak pressure (P) attained in an explosion depends on the 'vent ratio' (r) according to $P = Ae^{-kr}$ where A and k are constants. The 'vent ratio' is defined by the relation r = vent area/chamber volume. For the three chambers of different sizes tested, the constants in the expression were closely similar, and though some doubt exists arising from the difficulties experienced in obtaining adequate dust dispersion, it would appear that the relation might be used to apply the results to the design of vents for chambers of sizes other than those tested.

The values of the constants A and k depend on the dust employed and on the characteristics of the vent. Of the substances tested aluminum and magnesium powder caused the most violent explosions and required the largest vent area to limit the explosion pressure to a given value. Soap powder was considerably less violent than anything else. Fine particles produce more violent explosions than coarse ones, and the introduction of inert powders into the explosive dust inhibits the violence of the explosion considerably.

The characteristics of the vent should be such as to promote the flow of gas through it when explosion occurs. The shape of the vent is not significant, but the profile of the vent section should be such as to encourage streamline flow.

When possible the vent should communicate directly to atmosphere rather than through a duct as the inertia of the gas in the duct and friction effects tend to increase the peak explosion pressure. The use of diaphragms to exclude the weather causes an increase in peak explosion pressure, and it may be desirable to use more than one vent as the effectiveness of a vent diminishes as it becomes more remote from the source of the explosion. The paper forms a useful contribution to practical knowledge and establishes good ground for further work.

Subject Headings: ***Dust explosions, venting of; Explosions, of dusts, venting of.***

D. G. Martin

IX. Atomization of Liquids

Browning, J. A. (Dartmouth College, Hanover, New Hampshire) "Production and Measurement of Single Drops, Sprays, and Solid Suspensions," *Advances in Chemistry Series,* 20, 136–154 (1958)

This review represents an excellent survey of the literature (284 references), principally of experimental work on the production and size measurements of single drops and of sprays. The emphasis is primarily on applications to combustion devices, although valuable information on sprays for fire fighting is included. The following topics are discussed: Airstream Atomization (7 refs.); Pressure Atomization (27 refs.); Production of Aerosols (13 refs.); Single Drops and Streams of Uniform Drops (27 refs); Spinning Disk Atomization (9 refs.); Solid Suspensions (36 refs.); Aggregation of Particles (10 refs.); Diffraction Theory and Equipment (44 refs.); Size Distribution (9 refs.); Elutriation (4 refs.); Freezing of Drops (2 refs.); Jet Impactors (12 refs); Photographic Measurements (12 refs.); Sedimentation (8 refs.); Wax Method (2 refs.).

Subject Headings: ***Spray, production and measurement of; Droplets, production and measurement of.***

W. G. Berl

X. Meteorological Interactions

Dunskii, V. F. (Moscow Station for the Protection of Vegetation) "Paths of Hot Jets in the Layer of the Atmosphere Just Above the Ground," *Soviet Physics, J.E.T.P.,* 2, 962–968 (1958)

In this paper, the author presents experimental data to confirm the analytical predictions of a previous paper * concerning the paths of hot and cold jets in the layer of the atmosphere just above the ground. The main parameter of the earlier work, which is confirmed experimentally in the present paper, is the trajectory of a hot jet under equilibrium conditions of the bottom layer of air.

The experimental arrangement consisted of expelling high temperature air from a nozzle 80 mm. in diameter and photographing the air trajectory. The air jet was made visible by the injection of small amounts of aerosol. The experimental data consist of 11 photographs of the high temperature jet trajectory under different conditions of wind speed and gas temperature. The gas temperatures range from 300 to 650°C and wind velocities range from 0 to 4.35 m/sec.

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* Dunskii, V. F. *Journal Technical Physics,* 25, 2501 (1955)

Superimposed on each trajectory photograph are trajectories calculated from the theory contained in the 1955 paper. The author concludes that "the experimental results are in satisfactory agreement with the theory. This is confirmation of the ideas about the mechanism of the gravitational bending of hot jets in the lowest layer of the atmosphere which were put forward in the preceding paper (1955)."

The present paper does not list the assumptions on which the theory of the earlier work is based and is therefore somewhat difficult to evaluate. It is suggested that the 1955 paper be considered together with the present paper for a more complete understanding of the trajectories of hot jets near the ground.

Subject Headings: *Jets, path of; Atmosphere, path of jets in.*

W. T. Snyder

Kazanskii, A. B. and Monin, A. S. (Institute of Physics of the Atmosphere, Academy of Sciences, U.S.S.R.) "The Form of Smoke Jets," *Izv. Akad. Nauk SSSR, ser. geofiz.* No. 8, 1020–1033 (1957)

During 1955 and 1956 an aerophysical expedition from the Institute of Physics of the Atmosphere of the Academy of Sciences, U.S.S.R. undertook an investigation of smoke ejections to study the form and vertical dimensions of a smoke jet under various atmospheric conditions. The expedition also studied the density of the smoke in various parts of the smoke jet.

A line source of smoke from a number of smoke boxes situated perpendicular to the direction of the wind was used. Each smoke jet was photographed, the gradient measurements of wind velocity and air temperature were made at various elevations, and samples of the smoke-laden air were taken. Time-lapse motion pictures were taken of the smoke ejections.

The motion pictures were analyzed in the following way. All frames containing photographs of each individual ejector were projected in turn on a screen. The visible smoke boundary for each photograph was drawn on the screen and the mean curve of the numerous lines thus obtained was constructed. In this way, a graphical picture of both the mean boundary of each jet and the character and boundaries of its oscillations was obtained. Unstable, neutral, and stable classes of atmospheric stratification were investigated.

The results of the experiments showed that near the smoke source the smoke rose fairly sharply as a result of being heated and was at the same time carried away by the wind. The boundaries of the smoke jets had the form of a curve which bulged upward. At a certain distance from the smoke source, the smoke cooled and ceased to rise owing to mixing with the surrounding air. The further spreading of the jet along the vertical was the result of turbulent mixing. The upper boundary of the jet, above an initial height had the form of a straight line inclined to the horizontal at some slight angle α. The height was taken as the effective height or "ascent height" to which the smoke rose as a result of heating.

The angle α was found to be a function of the thermal stratification parameter L (the scale of the "dynamic underlayer"). Results of the study of the influence of the wind on the angle α showed that angle α apparently was not a function of the wind velocity. The authors also showed that the ascent height was proportional to the friction velocity.

A single puff of smoke was investigated as an additional experiment. The maximum horizontal and vertical diameters of the smoke puff were determined at different periods of time. The vertical diameter was found to increase in proportion to time. The horizontal diameter of the puff was found to increase at a rate proportional to time, but in a degree greater than unity.

Samples of the continuous smoke jet taken 100 meters from the smoke source showed the maximum concentration was reached at ground level or at a low height. The smoke concentration gradually diminished with height within the boundary of the smoke jet. Equations were developed to describe the relationship between the smoke density and the height at which the particular density existed in the smoke jet.

Calculations were made on the form of the smoke jet. Since the calculations based on the use of "the usual diffusion equation of parabola type" do not permit a straightforward determination of the smoke jet boundary, the authors suggest a calculation which is based on direct computation of the terminal velocity of the dispersal of the smoke in the air.

Equations were developed by the authors to determine the mean position of the upper boundary of a smoke jet for cases of neutral, stable, and unstable stratification. The calculations based on these equations agreed well with the experimental data.

The authors concluded that the forms of smoke jets which were described with the help of the theory set forth in the report agreed fairly well with the experimental data. The authors suggest that in examining the processes of smoke diffusion in air, the action of turbulence should be studied separately from other factors, and that in order to exclude the influence of the bouyancy force it would be desirable to institute experiments with smoke of ambient temperature.

Subject Headings: *Smoke, form of jets.*

A. W. McMasters

XII. Instrumentation

Shaw, T. M., Truby, F. K., and Wood, W. R. (Southwest Research Institute, San Antonio, Texas) "Study of Explosive Vapor Detection," *Wright Air Development Center Contract AF33(616)2802, WADC Technical Report 56–293* (June 1956)

As a guide toward the development of instrumental methods of determining explosive vapor concentration in rocket aircraft, this report presents a comprehensive review of the literature pertaining to methods and instrumentation for gas analysis. In addition, it provides a compilation of physical and chemical properties of fuels and oxidizers including ammonia, gasoline, JP-4, dimethylhydrazine, nitric acid, and liquid oxygen.

The first section contains brief discussions of various physical principles. Mention is made of methods which run the gamut of the electromagnetic spectrum from microwave to X-rays, in addition to other physical methods. The two optimum methods, considered to be nondispersive infrared analysis and radio frequency mass spectrometry, are analyzed in greater detail in the second section, where the common types of commercial instruments are described and their possibilities for further development are indicated.

The third section describes tracer methods, which seem to offer the greatest promise in the fields of positive ion emission, mass spectroscopy, and infrared absorption spectroscopy. A fourth section discusses contact potentials, gas phase chromatography, glow discharge phenomena, ionization phenomena, microwave spectroscopy, and semi-conductor phenomena as worthy of experimental development.

The summaries of physical and chemical properties of various rocket propellant fuels and oxidizers contained in the appendix have been gathered from many sources including some relatively inaccessible report literature. There is a well indexed bibliography of more than one thousand items.

Although this report is directed toward the development of rocket aircraft instrumentation, its comprehensiveness is such that it would serve as an excellent starting point for anyone embarking on a program of research in explosive vapor detection.

Subject Headings: ***Detectors, for explosive vapors; Explosive vapors, detectors for.***

A. Strasser

Carlton, C., Gunkel, W., and Yuill, C. (Southwest Research Institute, San Antonio, Texas) "Study of Explosion and Fire Suppression of Aircraft Engine Sections," *Wright Air Development Center Contract AF33(616)3489, WADC Technical Report 57–300* (April 1957)

This report concerns a comprehensive study to determine whether explosion and fire suppression systems are feasible for turboprop and turbojet aircraft engine sections.

A statistical analysis of 408 accidents involving explosions or fires in engine sections of jet powered U.S. Air Force aircraft in the three-year period, 1953–1955 showed; (1) 84 per cent of these accidents resulted in major damage to the aircraft, (2) a majority of the accidents were caused by a malfunctioning in the fuel metering, compressor, and turbine sections, (3) the nature of most of the explosions could not be determined, (4) failure of materials is the major cause of accidents involving explosions or fires, (5) explosions and fires resulting from the ignition of combustible vapors is a secondary factor caused by mechanical failures, (6) approximately 15 per cent of the accidents involving explosions possibly could have been prevented had an effective explosion suppression system been installed; however, about 72 per cent of the accidents involving only fires could have been prevented, (7) a monetary savings of at least eight million dollars could have been achieved for the two-year period, 1954–1955, had an effective fire and explosion suppression system been available in the cases studied. The possible value of explosion and fire suppression systems with respect to the safety of aircraft personnel is not fully discussed.

A detection system or systems is required for (1) fires in combustible mechanical and electrical components, liquids, and vapors, (2) the presence of combustible vapors within the engine nacelle to determine the possibility of a fire or explosion before it occurs, and (3) the detection of explosions in very short times, in microseconds if possible, so that the suppression systems can be activated before damage is done.

The basic requirements that fire and explosion detectors must possess include reliability, simplicity, light weight, low power requirement, low cost, and repetitive operation for successive fires. It is a major problem to place the detectors so that the entire engine nacelle is under surveillance. A practical system will probably depend on placement of detectors in those areas most likely to be subjected to conditions leading to fires and explosions.

Many types of systems for detecting fires and explosions are described and evaluated. It is concluded that nondispersive infrared analysis and mass spectrometry offer the most promising methods of detection of combustible vapors in the engine nacelle. If infrared detectors are used, it is probable that three separate systems will be required, a vapor detector, a separate fire detector, and a separate explosion detector. Ultraviolet detectors can probably be developed to function as both fire and explosion detectors simultaneously.

The problem of suppressing explosions once they are detected is one of rate of response of the effective detecting and extinguishing systems. At the present time effective extinguishing systems are probably available but the required detecting systems are not. It is believed, however, that explosion detection and suppression systems are feasible provided detectors can be developed to operate at very high ambient temperatures (preferably 1100°F).

At the present time, it is not considered feasible to design a combined explosion and fire detection and suppression system.

Subject Headings: ***Explosions, suppression of, in aircraft engines; Fires, suppression of, in aircraft engines; Aircraft engines, suppression of fires and explosions.***

L. R. Griffith

Gardon, R. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "An Instrument for the Direct Measurement of Intense Thermal Radiation," *The Review of Scientific Instruments,* 24, 336–370 (1953)

A robust, direct-indicating radiometer has been designed which is suitable for measurement of thermal radiation flux intensity between 1–100 cal/cm²sec. It has a time constant in the range .01–.001 sec., and records unamplified signals without a spectral quality reference.

These characteristics, which are useful in studies of heat radiation effects on materials, are achieved by high conduction of energy from the absorbing surface to a large heat-sink.

A large copper block is soldered to the circumference of a thin, circular, blackened, constantan, foil. A fine copper wire is soldered perpendicular to the center of the foil, thus completing a copper-constantan thermocouple circuit which produces a emf proportional to the temperature difference across the disc.

The sensitivity of the circular foil radiometer is derived as

$$E/q = e \cdot \frac{\Delta}{q} \text{mv/cal/cm}^2\text{sec}$$

where E = emf output of thermocouple, mv
q = radiation intensity, cal/cm²sec
e = thermoelectric power coefficient, mv/°C
Δ = radial temperature difference across foil, °C

This simplifies to a linear relation for a constantan foil of radius, R and thickness, S of $E/q = .183\ R^2/S$ which is accurate to better than 5 per cent at 300°C.

Based on an exponential temperature rise rate model, the radiometer response is shown to have a time contanst, τ_0,

$$\tau_0 = c\varrho R^2/4k \text{ sec}$$

where c = foil specific heat, cal/gr°C
ϱ = foil density, gm/cm^3
k = foil thermal conductivity, cal/cm sec°C

Using properties of constantan at 70°C the time constant, τ_0, equals 3.7R^2 seconds.

A foil diameter of .034 cm. and .0001 in. thickness results in $\tau_0 = .001$ sec. and a high sensitivity of .21 mv/cal/cm^{2}sec. If 300°C melting point solder is used, an intensity up to 63 cal/cm^{2}sec can be measured.

Thicker foils result in less sensitivity but greater intensity range. Larger diameter foils increase the time constant and sensitivity, and are easier to make.

Experimental tests of three radiometers up to 185°C showed substantial agreement with the theoretically predicted characteristics.

Subject Headings: ***Radiation, instrument for direct measurement of.***

K. M. Foreman

Gardon, R. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "A Segmented-Mirror Solar Furnace for High-Intensity Thermal Radiation Studies," *The Review of Scientific Instruments,* **25**, 459–463 (1954)

The article describes a solar furnace used in a study of ignition of materials by thermal radiation. In order to simplify treatment of the heat transfer and the product gas flow problem, relatively large exposed surfaces are desired.

The flat segmented-mirror solar furnace is a source of short wave length thermal radiation for intensities up to 5.5 cal/cm^{2}sec over a 5 cm square area.

An array of 400 plane mirrors, each 3 in. square was calculated to meet requirements of the primary reflector. Each mirror is back-silvered window glass retained in a copper frame and mounted with a flexible attachment and inclination adjusting screws to a rigid ribbed steel plate. The reflected sunlight intersects in one plane with uniform intensity over a target area the size of the individual mirrors.

A trapezoidal, back-silvered, water-white plate glass secondary mirror deflects the reflected radiation to the sample which is mounted in the vertical plane, regardless of the sun's orientation. Also, by moving the secondary mirror from the path of the converging rays, the shutter in front of the target is protected from concentrated heat effects.

Two polished aluminum plates open or close a 6 in. square aperture in the shutter. Exposures of a few seconds are controlled by manual switches or a motor driven timer which activate the spring loaded plates through solenoid operated latches.

The furnace, mounted on a roof, is aimed by projection of the sun's image through a sight onto a screen grid. Furnace calibrations, employing a circular foil radiometer * and a silver disk calorimeter, relate the target area intensity to normal solar radiation. The expected over-all furnace efficiency is 66 per cent based on reflective efficiencies of the primary and secondary mirrors (82 per cent and 87.5 per cent respectively) and angle of incidence dispersion.

From initial measurements of efficiency in May 1952 (62 per cent) the furnace rapidly deteriorated to a level of 55 per cent efficiency for several months. Winter operation decreased efficiency to a final 41 per cent in March 1953.

* See page 140

Analyses of furnace performance showed uniform radiation distribution, within 5 per cent, over a 1½ in. diameter target contrasted to an expected 2½ in. square. However, the 7 ft. 6 in. focal length segmented reflector produced results comparable to a 35 ft. focal length continuous parabolic mirror.

Loss of operating efficiency was attributable to:

a. inadequate flatness of the mirrors which increased reflection divergence (6 per cent loss).
b. deterioration of silvering (pitting) which scattered solar radiation (3 per cent loss).
c. dust deposits on mirrors which increased radiation absorption and scatter (8 per cent loss).
d. wind induced vibrations causing mirror segment misalignment.

Experimental results are not discussed although an example is given of the value of large exposure areas in detecting the shielding effect of smoke from a wood specimen. Recommendations are given for modifications which may improve furnace performance.

Subject Headings: *Radiation, segmented-mirror solar furnace to produce; Solar furnace, for high-intensity radiation.*

K. M. Foreman

Reed, L. E. (Joint Fire Research Organization, Boreham Wood, England) "The Estimation of the Darkness of Smoke by Visual Methods," *Journal of The Institute of Fuel,* **32,** 3–9 (1959)

A standard basis of comparison for optical estimation of smoke darkness is the Ringelmann Chart, which shows five shades, numbered 1 to 5, corresponding to 20, 40, 60, 80, and 100 per cent solid black. The (English) Clean Air Act specifies No. 2 Ringelmann as the legal maximum shade. Because use of the chart is inconvenient and causes eye fatigue, a low-power telescope, called the "Telesmoke," was constructed containing a comparison disc with sectors of optical densities corresponding to Nos. 2 and 3 Ringelmann. Tests on standard smokes of various densities by experienced observers showed that

1) when plotted against ocular density determinations made simultaneously with a photo-electric smoke meter most observations fell within a band about one Ringelmann number wide, the scatter about the mean being about the same with Telesmoke as with the chart.
2) Telesmoke gave slightly better consistency among observers; Ringelmann Chart gave slightly better consistency among conditions of illumination.
3) in comparison with readings by the smoke meter, darkness estimates based on both Telesmoke and Ringelmann Chart rose with disproportionate rapidity to about No. 3 Ringelmann, then failed to keep up with increasing optical density.
4) estimates made by the unaided eye were slightly more consistent than those made with the help of a chart.

Apparently the Telesmoke is an acceptable substitute for the Ringelmann Chart for smoke inspection to the prescribed standard, but neither suffices for accurate estimation of the higher levels of ocular density.

Subject Headings: *Smoke, estimate of darkness of.*

G. R. Fahnestock

COMMENTS AND DISCUSSIONS

Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "On the Kinetics of the Ignition and Self-Heating of Cellulosic Materials."

The paper by Gross and Robertson * shows an agreement between data obtained from heating experiments in an adiabatic calorimeter and Mitchell's ignition data [1] on the basis of an application of thermal explosion theory in its simplest form, *i.e.,* a single reaction without loss of reactant. It is interesting to apply this calorimetric data to some results in Mitchell's paper for the maximum temperature reached when specimens of material were heated in a constant temperature oven at temperatures insufficient to produce ignition. One finds that the temperature rises measured by Mitchell, when these were small, are about ten times those calculated either from Gross and Robertson's data or from Mitchell's ignition data. This latter comparison has been made assuming a value for the theoretical critical ignition parameter δ † of about 3; the comparison with Gross and Robertson's data needs no assumption about the criterion for ignition or about the theoretical value of δ.

For example, at 161°C (322°F) the value of the rate of heat generation $Ae^{-\frac{E}{RT}}$ where A is constant, E is the activation energy, R the universal gas constant and T the absolute temperature is obtained from Gross and Robertson's data for wood fiberboard as

$$1.97\times10^{9}\exp\left\{\frac{-25{,}700}{1.99\times434}\right\}\textit{i.e.}\ 0.24\ \text{cal cm}^{-3}\text{sec}^{-1}$$

Conduction theory shows that for heat generated uniformly in a sphere of radius r, conductivity K and surface heat transfer coefficient H, the central temperature will rise above the ambient by

$$\Delta T=\frac{Ae^{-\frac{E}{RT}}r^{2}}{6K}\left(1+\frac{2K}{Hr}\right)$$

For wood fiberboard K is equal to 1.2×10^{-4} cgs. units and if H is taken as 4.4×10^{-4} cgs. units we obtain for a sphere of radius ½″ (1.27 cm) $\Delta T=0.8°C$ which is sufficiently small to justify assuming a uniform heat distribution in the above calculation. Mitchell used octagonal piles and we have estimated that this may make a 50 per cent increase in the above value, say 1½°C. For a 1 in. pile, however, at 322°F, Mitchell measured nearly 10°C. (Fig 8 in his paper.)

This discrepancy can be shown to be largely independent of the value of K and, because it is a discrepancy between rates of heating calculated from the two types of experiment conducted by Mitchell, it is not due to differences between types of wood fiberboard.

The theoretical values of δ obtained from thermal explosion theory assume a heat of reaction which is large, an assumption suitable for explosives. Information on the heat of reaction for wood products is scanty. Estimates [2] vary from less than 100 cal/gm to 400 cal/gm so that there is the possibility that δ is larger than its value calculated for a reaction with no loss of reactant.

It will be shown, however, in a paper shortly to be published,[3] that from the theoretical calculations of Todes and Melentiev [4] and Frank-Kamenetskii [5] it appears that a heat of reaction low enough to produce a tenfold increase in the

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* See page 89

† δ [dimensionless parameter] is equal to $Ar^{2}\,E/KRT^{2}\cdot e^{-\frac{E}{RT}}$

theoretical value of δ would be too low to produce the well defined ignitions found in practice. The explanation appears to be that more than one reaction is involved. Provided the first reaction does not produce volatiles which are lost from the bulk material before further exothermic reactions occur, this possibility can be consistent with there being no significant loss in weight in the specimen.

Bowes has heated 1 in. cubes of fiber insulating board in an oven at a constant temperature of 175°C and the temperature-time history shows that there is a rise in temperature of about 10°C in about ½ hour followed by relatively fast fall to about 1°C and then a long slow fall over many hours. The heat of reaction calculated from the initial rise and fall is relatively low and is less than the minimum estimate of 48 cal/gm obtained from the figures given by Gross and Robertson who allowed wood fiberboard of specific heat 0.33 to self-heat through 145°C. The total heat, including the heat liberated in the period when the temperature was less than 1°C, is about 150 cal/gm. It appears, therefore, that there are at least two reactions, the first mainly responsible for the relatively high self-heating temperature in the early stages of heating, and the second, with a high heat of reaction, being mainly responsible for self-heating in prolonged heating and for ignition.

Mitchell's ignition data or similar ignition experiments can be extrapolated to large sizes and low temperatures because δ is a constant although its value may differ from that given by the simple theory,[6] provided the specimens are large enough for the surface cooling parameter not to affect δ. It must also be assumed that the various rate constants and activation energies for the two or more reactions have values that permit an effective E to be employed which is the same throughout the range of extrapolation.

The use of kinetic constants obtained from calorimetric data to predict kinetic constants for behavior according to some other temperature-time history must also be based on a similar assumption that the reaction can be treated as effectively as a single reaction of zero order. Despite these reservations, agreement between the calorimetric data and Mitchell's ignition data for fiberboard is good and it is suggested that this is because the first reaction, being relatively fast, plays a secondary role in self-heating in the adiabatic calorimeter and in ignition.

However, complications in the kinetics may lead to difficulties in other cases. For example, there is a trend, which may be significant, for the ignition temperatures for cotton linters calculated from the calorimetric data to be increasingly greater as the size of the specimen increases than the values obtained by Mitchell.

It is worth noting that Mitchell's measurements of the induction times show that they are 60 times longer for cotton linters than for cane or wood fiberboard. The actual values for cane and wood fiberboard can be shown to be in reasonable accordance with theory; the large value for the cotton linters suggests the presence of reaction inhibitors or an autocatalytic reaction.

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Errata – Volume I Number 2

page 41 second footnote — A coefficient used in calculating Reynolds number is in error by a factor of 10

Line 4 from the bottom: should read 13.3 instead of 1.33

Similarly, numbers appearing in the next 3 lines should all be increased by a factor of 10

page 42 — The Reynolds-number scale appearing on the plot is in error by a factor of 10

The scale should run from 200 to 50,000 instead of 20 to 5,000

page 43 — The last equation should read:

$$\frac{q}{\pi d^2/4}=\frac{4k_1(T_F-T_B)}{d}+U(T_F-T_B)+\sigma F(T_F^4-T_B^4)(1-e^{-\kappa d})$$

page 59 third line next to last paragraph: effectiveness instead of exectiveness

page 67 third line next to last paragraph: nozzle instead of nozle

Volume I September 1959 Number 4

Fire Research Abstracts and Reviews

Committee on Fire Research
and
Fire Research Conference

Division of Engineering and Industrial Research
NATIONAL ACADEMY OF SCIENCES—NATIONAL RESEARCH COUNCIL
Washington, D. C.

FIRE RESEARCH ABSTRACTS AND REVIEWS is published three times a year by the Committee on Fire Research and the Fire Research Conference of the National Academy of Sciences — National Research Council, 2101 Constitution Avenue, Washington 25, D. C. It is supported by the Office of Civil and Defense Mobilization, the U. S. Department of Agriculture through the Forest Service, and the Department of Defense under Contract CD-SR-58-45. The opinions expressed by contributors are their own and are not necessarily those of the Committee on Fire Research and the Fire Research Conference.

Library of Congress Catalog Card Number 58–60075 rev

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COMMENTS AND DISCUSSIONS

FOREWORD

It is gratifying to announce that the First *International* Symposium on Fire Research, organized by the Committee on Fire Research of the National Academy of Sciences—National Research Council, will be held in Washington, D.C. on November 9 and 10, 1959. The topic of this two-day conference is "The Use of Models in Fire Research." A truly international participation is indicated with speakers from England, Japan, France, Germany, Canada, and the United States. An invitation extended to the Academy of Sciences of the USSR to participate, unfortunately, was not accepted.

The program for the meeting is as follows:

Sir Geoffrey Taylor Cambridge University (England)	Fire Under Influence of Natural Convection
H. C. Hottel Massachusetts Institute of Technology (U.S.A.)	Modeling Principles in Relation to Fire
P. H. Thomas Joint Fire Research Organization (England)	The Study of Fires in Buildings Using Models
Tosiro Kinbara University of Tokyo (Japan)	On the Self-Ignition of Wood Materials
Howard W. Emmons Harvard University (U.S.A.)	Some Observations on Pool Burning
J. S. Barrows U.S. Forest Service (U.S.A.)	Natural Phenomena Exhibited by Forest Fires
J. Faure National Hydraulic Laboratory (France)	Investigation of Convection Currents Caused by Widespread Fires
Sizuo Yokoi Building Research Institute (Japan)	Upward Convection Current from a Burning Building
J. G. Dawes Safety in Mines Research Establishment (England)	Preliminary Experiments with Model Mine Fires
W. L. Fons U.S. Forest Service (U.S.A.)	A Steady-State Technique for Studying Properties of Free-Burning Wood Fires
Gert Magnus Technische Hochschule Karlsruhe (Germany)	Test on Combustion Velocity of Liquid Fuel and Temperature Distribution in Flames and Beneath Surface of the Burning Liquid
David Burgess U.S. Bureau of Mines (U.S.A.)	Burning Rates of Liquid Fuels in Large and Small Open Trays
T. G. Lee National Bureau of Standards (U.S.A.)	Fire Extinction with Chemical Powders as Influenced by Size of Fire Models
G. W. Shorter National Research Council (Canada)	The St. Lawrence Burns
Raymond M. Hill City of Los Angeles Department of Fire (U.S.A.)	Operation School Burning

The full text of the papers and pertinent discussion will be published.

Your attention is drawn to the lead article in this issue by D. I. Lawson, Director of the British Joint Fire Research Organization, in which he discusses the manner in which fire research is carried out in England. One admires the ingenious arrangements by which a capable professional staff with adequate facilities is supported from both public and private funds. This scheme provides continuity of effort and flexibility; it fosters a long-range outlook on research and development programs that can only be solved by continuous and persistent effort. The results, as summarized in the 1958 Annual Report from that establishment, speak for themselves.

Walter G. Berl

REVIEWS

Fire Research in the United Kingdom

by

D. I. Lawson, M.Sc., M.I.E.E., F.Inst.P.*

INTRODUCTION

The first systematic inquiry into fire protection in the United Kingdom took place about sixty years ago following a particularly disastrous fire during 1897, in Cripplegate, a district of London. At that time Edwin O. Sachs, an architect of only 27 years of age, gathered together a number of influential people to study how to protect life and property from fire and formed the British Fire Prevention Committee. A fire testing station, a reading room and a reference library were started and six years later with Sachs as its Chairman, the Committee convened the First International Fire Congress which was attended by over 800 members. During the first seven years of its existence, the British Fire Prevention Committee conducted 79 fire-resistance tests and tests on fire equipment and issued 57 publications of test results and 22 other publications dealing with fire prevention and visits to fires. In 1919, at the age of only 49, this remarkable man, Edwin Sachs, died and after his death the British Fire Prevention Committee on which he had spent so much of his energy and private fortune, lapsed. By that time they had issued over 200 publications or "Red Books" as they came to be known, dealing with fire prevention and after the Committee had disbanded a further 46 books in this series were published from public funds.

The insurance companies had of course always been interested in reducing fire loss and in fact at one time operated the Fire Brigades. Nearly one hundred years ago, in 1868, an association of insurance companies was constituted as the Fire Offices' Committee for the purpose of transacting business and fixing insurance rates appropriate to risks. As time went on, the assessment of risks naturally involved a certain amount of technical investigation and therefore a station was opened in Manchester in 1905 for the purpose of testing sprinklers and other extinguishing apparatus. Later the Fire Offices' Committee erected a furnace for testing fire-resisting doors and shutters. As the work increased during the following quarter of a century, a new Testing Station had to be built. This was opened in 1935 at Boreham Wood, some 14 miles north of London and contained three large furnaces, in use at the present day, for testing walls, columns, and floors in addition to laboratories where sprinklers and other extinguishing apparatus could be examined. While the Fire Offices' Committee's own staff were responsible for tests on sprinklers and fire alarms, the new furnace equipment was operated by the staff of the Building Research Station of the Department of Scientific and Industrial Research working to a programme devised jointly by the Department of Scientific and Industrial Research and the Fire Offices' Committee.

In 1936, a Government Committee was set up under the Chairmanship of Lord Riverdale to inquire into the working of the Fire Services in the United King-

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dom and one of its recommendations was that the Government should carry out research on fire protection. This recommendation was due to be implemented on the 1st September, 1939, two days before war on Germany was declared and so the question of starting a Fire Research Station had to be shelved for the time being.

During the war it became rapidly apparent that the damage by fire was many times that caused by high explosives and very soon fire research programmes were started under the Ministry of Home Security at the Building Research Station, the Forest Products Research Laboratory, and also in universities to discover how the new problems of fire spread and the extinction of fire could be solved.

As the war drew to a close, discussions again took place on the establishment of a Station to carry out research into fire protection. By this time the Fire Offices' Committee were themselves also considering the starting of a Fire Research Station, as distinct from a Fire Testing Station and it was finally agreed that both they and the Department of Scientific and Industrial Research should join together in an equal partnership. So in 1946, the Joint Fire Research Organization was formed with Mr. S. H. Clarke appointed as its first Director in 1947.

Development of Joint Fire Organization

When the Joint Fire Research Organization came into being at the end of 1946, its laboratories had a total area of just over 10,000 sq. ft. By 1951 various temporary buildings had been acquired and the Station then occupied nearly 25,000 sq. ft. The next addition came in 1958 when a new Models Laboratory was provided by the Fire Service Research and Training Trust. This is a hall 150 ft. long, 50 ft. wide, and 40 ft. high. A section of the roof, 30 ft. wide, is movable by hydraulic motors and serves to release smoke and hot gases during experiments. A 12-ft. diameter fan driven by a 200 h.p. electric motor is let into one side of the building and is used to develop an air stream transversely across the laboratory; this is uniform over a working section 10 ft. wide, 15 ft. long, and 10 ft. high and is continuously variable up to 30 m.p.h.

From the early days of the Joint Fire Research Organization it was the intention to build a permanent station as soon as possible. This is now taking shape and should be complete in June, 1960. The building, with a total floor area of over 31,000 sq. ft., will just double the size of the Station and provide a very welcome addition to the accommodation which has become quite inadequate in recent years. The new building is a three-storied block and will house the sections dealing with (a) Ignition and Growth, (b) Extinguishing Materials and Equipment, (c) Chemistry and Chemical Engineering, and (d) Operational Research and Intelligence (the latter section has so far been partly situated in London because of lack of space) in addition to common services such as Library, Drawing Office, and General Office facilities. Three large spur laboratories, running at right angles to the main building, will be used for work on thermal radiation, fire extinction, and chemical engineering problems. The section dealing with Building Materials and Structures will be housed in the Large Furnace Hall and a single-storey building nearby. The rest of the present buildings will be used for Station services such as garage, workshops, stores, canteen, etc.

The new Station will be set in grounds having an area of about ten acres, and these will be broken up into a number of sites for experiments on fires and explosions which cannot be conveniently carried out in the laboratories.

When the Joint Fire Research Organization came into being in 1946 the staff was recruited from other stations in the Department of Scientific and Industrial Research (largely from the Building Research Station) and from the universities. By the end of 1949 the professional staff of the Station totalled 17. This figure should have increased to 50 by the end of this year when recruitment is complete. The junior technical, clerical, and industrial grades total 85 bringing the total staff of the Station to 135.

Fire Research is a subject covering a very wide field involving physics, engineering (mechanical and electrical), physical chemistry, mathematics, economics, and at times some aspects of medicine. In particular the work calls for a detailed knowledge of heat and mass transfer, the kinetics of chemical reaction, the theory of structures, and a working knowledge of statistical tests and the design of experiments.

RESEARCH PROGRAMMES

All fire research programmes must be designed to reduce the loss of life or property due to the action of fire. Sometimes if an answer is required quickly or if a problem is circumscribed it may be tackled directly and in a narrow way. Generally it is more profitable to analyse a group of problems, to pick out the common unknown factor and after carrying out experimental work, to apply the results to everyday practice.

In devising a research programme the items fall into two classes, those which deal with hazards already existing and those that concern the future. Future hazards come about largely through changes in design often brought about by economic pressures. Examples are the changes in the number or design of escape routes required in buildings and the use of curtain walling to replace masonry for the outer walls of buildings. Items affecting future design follow from innovations introduced by other government departments or industry. Naturally a number of topics for research are suggested by the staff in the course of their work.

Fire Statistics

A watch is kept over existing hazards by the work of the Operational Research and Intelligence Section who receive standardized reports on the 120,000 or so fires attended by Fire Brigades in the United Kingdom every year. These annual statistics also show the changes in the fire pattern and consequently where research is needed. Examples of this would be the growth in the number of fires due to electricity and oil. In the former the fire risk, measured in terms of the electrical energy consumed, is sensibly constant while in the latter case the risk, as a function of number of fires per unit consumption of oil, is increasing as well as the gross number of fires.

Of course it is not practicable to collect from the annual statistical data all the information necessary for detailed inquiries into the hazards of equipment. Frequently it is necessary to ask the Fire Brigades throughout the country, or more often in a few selected areas, to fill in detailed questionnaires about incidents relating to specific hazards. Other inquiries in hand relate to fires in departmental and retail stores and information about these is being collected from a number of large retail firms. Quite apart from the direct information gained on the performance of sprinklers and fire alarms in restricting the spread of fire it will be possible to ascertain with precision the causes of fires in this type of risk, as the fires are often trivial and nearly always detected in the very early stages by the staff or customers. The cause should be independent of the size of the fire but is often more difficult to determine when a fire has become sufficiently important to merit the attention of the Brigade. The effect of fire cover on fire losses is also being studied; fire cover for this purpose being measured by the type of attendance and time of arrival of the Brigade.

Ignition and Growth

Much attention has been given in the past in a number of countries to the circumstances under which materials ignite. The effort on this work at the Fire Research Station has now fallen to a considerably lower level than in the last few years since as far as the ignition of plane surfaces is concerned, enough information has been obtained to specify the levels of heating necessary for ignition. This enables such quantities as the separation between buildings to be worked out. At present a small amount of work is in hand on the dynamics of self-heating, but generally it may be said that the real drive is on the growth of fire and particularly on the use of modelling techniques.

By far the greatest number of fires attended by the Brigades occur in single compartments, such as factories, warehouses, and fires in dwellings confined to the room of origin. It is hoped by the use of models to find the part played by ventilation, fuel (amount, size, and dispersion), shape and size of compartment, and wind. Good progress has been made in some sections of the work. For example the size of flames and rate of burning of fuel seems to be amenable to scaling. These factors are in themselves important because they lead to an assessment of the spread of fire over the facade of a building. While the modelling of fires was considered to be a rather intractable subject a few years ago, it now seems fairly certain that using this method it should be possible before very long to specify the time/temperature curves for fires in compartments of different shapes and sizes. A start will be made next year however on the growth of fires in areas of brushwood in the open under different humidity conditions and wind velocities and this may have an application to the early stages of fires in large single compartments. The results of this experimental work should also be applicable to the movement of gases in conflagrations in cities.

Models are also being used to study the venting of industrial fires by openings in the roof. It has been shown that simple scaling laws hold for the release of heat from fixed sources by roof vents and the work has now been extended to the study of fires to see how rates of burning are affected by roof venting. Experiments with different sizes of building have been made and scaling laws have been developed. The problem of shape and spacial growth of fire has yet to be investigated.

Building Materials and Structures

Since the Station opened, the volume of sponsored fire tests on building materials and structures has increased by a factor of 12. These are required in the main by firms who are seeking to satisfy some building regulations or who are desiring to improve the performance of their products. The work of testing has now become so onerous that it is threatening research work on structures. One way of counteracting this is to ensure that as far as possible new test methods use apparatus which can be purchased or manufactured by industry.

Furnace tests involving the large-scale testing of structures are costly and time consuming. Since 1952 it has been possible to calculate approximately the thermal transmission of structures by using an analogue computer and this has been a great help in giving advice to manufacturers on the sort of structures worth testing. It is not yet possible to predict from first principles the mechanical failure of structures in fire tests, though the fire performance of smaller-sectioned structures can be estimated with a fair degree of confidence, once that of a similar larger structure is known. Any future advance in the prediction of fire resistance will require more information on spalling and this is an item of research which will receive emphasis during the next few years.

Closer attention than ever before is now being given to structural economies. In the past rolled steel joist columns were designed on the assumption that the steel supported all the load and the concrete cladding was regarded as purely thermal insulation. The load that is borne by the concrete is now allowed for in the design and this will affect the fire resistance of the column. The beams of a building have in the past been considered in isolation as far as fire resistance was concerned whereas in fact they are part of a rectangular lattice. This means that the effect on the fire performance of reverse bending moments at the supports will have to be taken into account.

In the near future consideration will be given to escape routes in buildings, in particular the conditions that may exist on the staircases of multistoried buildings. At present an alternative staircase must be provided for all multistoried buildings. If it were possible to provide adequate safety with only one staircase, this would lead to a great economy in building. During the next year a particular examination will be made of the records of fires in multistoried buildings and measurements will be made of the toxic and thermal conditions on staircases in experimental buildings when adjacent apartments are on fire.

Fire Detection, Extinction, and Equipment

Just as it is necessary to model fires in buildings to learn something about fire conditions, it is also necessary to understand the use of models in fire extinction, to determine in the case of water, the relative importance of the various cooling mechanisms, replacement of oxygen by steam, etc. Side by side with this experimental work, an attempt will have to be made to study the operational use of water by Fire Brigades. This cannot be done entirely by sending observers from the Fire Research Station as the number of fires they could see would be too few. The most likely means of getting information will be through special reports from the Fire Brigades supplemented as far as possible by visits to some fires while they are actually in progress. It might be noted in passing that two members of the staff are on call during the day and regularly sleep overnight at the Middlesex County Fire Station in order to visit any fire of importance. Middlesex is a mixed industrial, commercial, and residential area adjacent to London covering about 230 square miles and having a population of two and a quarter million.

During the coming year an examination will be made of the use of inert gases in fighting fires in buildings, particularly basements. A jet engine is being modified to produce about 50,000 cu ft/min of inert gases with a view to using these both to clear the smoke and extinguish the fire but it is too early yet to even guess whether the idea will be successful or what operational problems will be encountered.

About one-half of the fire loss is caused by 0.3 per cent of all the fires which occur and the large majority of these became big fires because they were not dealt with in the very early stages. Close attention is therefore being given to fire alarms and sprinklers. Measurements are being made of the temperature and velocity of hot gases at the ceiling level of compartments with a view to ascertaining the best location for sprinklers and fire alarms. Of course the locating of sprinklers is also conditioned by the intensity of water spray which can be produced at various distances from the head and this will have to be evaluated in terms of the fire that can be controlled.

Special Hazards

The work under this heading is mainly directed towards studying the fire problems associated with industrial processes. Many industries are concerned with solvent removal and it is therefore necessary to transmit flammable vapours to recovery plant. Methods have to be found to do this with safety, which involve the study of devices for flame suppression and explosion reliefs. A long term project will involve the investigation of the reliability of apparatus for the continuous monitoring of flammable vapours. If this could be done precisely, it might be worth considering increasing the allowable levels of flammable vapours with a view to increasing plant efficiency. Similar hazards occur in the case of the dusts produced in cutting, milling, and in spray drying and these are also being investigated.

The growth of the chemical industry has led to the large-scale industrial use of chemical compounds which a few years ago would have been found only in small amounts in laboratories. The importance of these compounds is their chemical reactivity and yet it is this property that causes them to be hazardous. It will be necessary to study the reaction kinetics of such compounds with a view to devising safe methods for their storage.

The size of aircraft and consequently the fuel loads carried is increasing continuously and the question arises as to how long it will be possible to keep the fire teams and equipment commensurate with the size of aircraft. Consideration must also be given to the effect of increasing the size of aircraft on the chance of survival of the passengers and on the population in the vicinity of a crash. Perhaps larger aircraft will bring new opportunities of survival; the impact forces on the passengers should be smaller and there may be an opportunity of providing more built-in fire protection and rescue facilities. All these factors need consideration and the starting point must be a survey of the large aircraft crashes during the last few years.

CONCLUSION

It will be seen that fire research offers a large number of varied and challenging problems. In planning a programme a judicious course has to be steered between carrying out arbitrary tests at one end of the scale and the quest for fundamental research at the other end. At the present time the latter is probably the greater danger because fire problems have suffered from so much shallow thinking in the past that there is a natural tendency to make the equally big mistake of studying scientific abstractions. In restricting short term narrow problems one avoids scientific sterility; at the same time by endeavouring to solve a basic problem in three or four years, a sense of urgency is generated which helps to keep up the tempo of research. Only by making sure that each item of research will be able to fill some public need in the not too distant future can a laboratory function in a healthy and purposeful manner.

List of Reports Published up to August, 1959

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Fire Research at the National Bureau of Standards

by

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To successfully carry out its mission of developing and maintaining standards of measurement and of studying the fundamental properties of materials, the National Bureau of Standards engages in research activities touching on many aspects of physics, chemistry, mathematics, and engineering. Although only a very small portion of the staff and funds used by the Bureau are specifically directed towards fire research (which may be simply defined as the scientific study of unwanted fires), it is, however, true that a considerable portion of the work performed at the National Bureau of Standards is rather closely related to this subject. For example, a list of projects pertinent to the field of fire research which were active during the past fiscal year, would include the following:

1) Thermal Degradation of Polymers at Temperatures above 1000°C
2) Chemical Reactions of Inorganic Materials at High Temperatures
3) Properties of Concrete at Elevated Temperatures
4) Properties of Metals at High Temperatures
5) Heat Resisting Fluorine Polymers
6) Transport Properties of Air at Elevated Temperatures
7) Auto-ignition of Hydrocarbon Fuels
8) Mass Spectrometric Studies of Free Radicals
9) Forced Mixing in Boundary Layers
10) Measurement of Temperatures of Streams of Hot Gas

Many others equally pertinent could have been selected from the total of more than 1,000 projects active during the year.

Attention will be confined to work directly concerned with the problem of unwanted fires now being performed by a small group of about ten technical workers comprising the Fire Protection Section. This group has been concerned with a very wide range of problems associated with such fires.[1, 2] Some of these problems have been of a very practical or applied nature dealing with current fire protection methods while others have dealt with research studies which would qualify under the category Fundamental Fire Research. Both types of problems will be discussed here because of their strong interdependence.

It has frequently been said that the NBS has an interest in and concern for all types of unwanted fires. Actually the recent work performed by the Bureau is much more restricted than this. Other governmental agencies have specific fire problems associated with their primary missions. Organizations such as the Bureau of Mines, Forest Service, Department of Defense, Coast Guard, Atomic Energy Commission, National Aeronautics and Space Administration, Federal Aviation Agency, and numerous others have either done significant work in the field of fire research or have sponsored such work. In many instances the NBS cooperates with these agencies in the solution of specific problems or in the performance of research studies. Care is exercised to avoid duplication of the work of others such as the Forest Service with their forest fire problem or the Federal Aviation Agency with their problems related to aircraft fires. Much of the fire research work that has been performed at the NBS has been concerned with fires in buildings and in building materials. This appears appropriate when it is considered that approximately three-fourths of the annual monetary fire loss involves fires associated with buildings.

It has been customary at NBS to classify fire studies into five general categories:

1) Ignition
2) Detection and Signaling
3) Growth and Spread
4) Confinement
5) Extinguishment

These aspects of the problem will be discussed in the order listed.

Ignition studies have been in progress at the Bureau for a long time.[3, 4, 5, 6, 7] Setchkin's work [7] represents a summary of work extending over many years. The work reported by Mitchell [6] emphasized the need for consideration of pile size and thermal properties in considering ignition resulting from self-heating reactions. The adiabatic furnace apparatus [8] has been used recently in studies of the self-ignition behavior of a wide variety of materials. Genensky [9] prepared an analysis of the maximum temperature rise to be expected within spherical piles of materials subject to self heating. Results of recent work in this field are contained in reference [10] where methods are suggested for estimating critical pile sizes and ambient storage conditions for such materials.

The apparatus used for these experiments, although very sensitive, exhibits a drift rate of the order of 0.25°C/hr with an inert material as a specimen. This corresponds to a power loss of about 4 milliwatts for the 346 cc. specimen used. The reduction in the rate of heat loss to this level allows measurements to be made on oils and other materials active at temperatures near 50°C. However, the rate of self heating of typical cellulosic materials generally requires operation at temperatures above 100°C. Experience to date seems to indicate that the apparatus itself is the limit to observation of self-heating phenomena at or below normal ambient temperatures.

No detailed study has been made of the mechanism involved in these low temperature reactions. However, information currently available seems to confirm the belief of others that much of the heat developed at these low temperatures is a result of recombination of molecular fragments resulting from degradation of the complex molecular chains. It appears that the initial phases of these reactions may not require an external supply of oxygen. Study of these reactions is one of the worthy objectives of a comprehensive fire research program.

Fire Detection and Signaling studies are not currently being conducted at NBS. However, a paper [11] was prepared several years ago describing work performed for the Air Force on problems related to detection of fires in aircraft engine spaces. In connection with this study particular attention was given to a study of the flickering behavior of flames.[12] Early detection and warning of the presence of a fire can often in large measure reduce the magnitude of the loss. While many of the problems associated with such devices are of an applied nature, there are many fundamental problems for investigation in connection with such systems.

Growth and Spread of fires is an important subject. The time interval between the ignition and the full development of a fire, in many cases, represents the only time available for life-saving evacuation of the building or for effective property-saving control of the fire. It is therefore important that a really good understanding be achieved of the mechanism by which fires grow from small to large proportions.

In general, we know that the rate of fire growth is largely a question of the surface flammability of the material involved and the extent to which flames and heat are supplied to the unignited portions. For when fuel and oxygen supply are not limiting factors, rapid fire propagation requires a rate of supply of energy to the unignited portions of the material in excess of the rate of heat loss by radiation, conduction, and convection.

Such a statement of the problem is not sufficiently detailed to permit prediction of fire behavior in any but very general terms. It is important that an understanding be developed of the importance of the various heat and material transfer mechanisms in operation during fires. It is also important to know and be able to measure the properties of materials that are effective in influencing fire growth.

The problems involved have long been recognized at NBS. However, the original thinking was that full-scale experiments were required. Some were performed,[13, 14] but the time and cost involved in such studies has been excessive and only qualitative or very rough quantitative results have been achieved. Nevertheless, the recent rapid development of new materials and processes made it important to have available for general use a method of measuring the surface flammability of materials. Such a method [15, 16] has recently been developed by the Bureau. Although the flame spread classifications produced by use of this method are of rather arbitrary character, they are based on independent measurements of two important material properties. These are (a) the ease of ignition and (b) the heat release characteristics of the materials under test.

A test method such as this is often justified on the basis of expediency for qualitative tests of materials. It is, however, important to develop a technical understanding of the relationship, if any, between the classification resulting from such a test and the behavior of the material under full-scale fire conditions. It is planned to initiate study of this problem with the use of relatively simple models. If the factors affecting fire growth in such models can be understood, it should be possible to progress to more complex models involving variables more closely simulating those acting during full-size fires. A start has already been made in this work in the form of a study on the burning behavior of wooden cribs. However, the large number of variables involved makes the size of this problem very great, and there is a real need for additional studies of this type.

One aspect of the fire growth problem involves the study and development of fire retardant treatments. Although the NBS has not been active in research on effective treatments, work has been done on evaluation methods for assessing their merit.[17, 18]

Confinement of fires provides one means for increasing the time available for effective attack. The problem is one of devising means for erection of barriers around the fire in such a manner that its spread to other portions of the structure is delayed if not prevented. The problem which at first glance may appear simple is in fact very complex. It is not sufficient to have a construction that will have high heat capacity and thermal insulation characteristics. The material or assembly must be capable of remaining structurally stable and of enduring the high thermal stresses involved without developing fissures or cracks. Here again the custom has developed of studying the usefulness of different constructions by performing tests on full-scale building structural components.[19] It is likely that work of this character will be necessary as long as such studies are of importance. However, it seems necessary to try to develop means for characterizing the properties of materials in such a manner that probable fire behavior of structural assemblies composed of these materials can be made with some accuracy.

Some progress in this direction has been made in the form of application of digital and analog computers to the study of transient heat flow in such structures.[1, 20] However, a tremendous amount of additional work is necessary before really effective application of such techniques is possible to fire confinement predictions. Some of this work involves better understanding of the mechanism of heat transfer during fire conditions, better information on working behavior of structures under fire exposure, and a great increase in engineering information on the thermal properties of materials under conditions effective during fire. Here again small scale studies can be very effective in permitting detailed studies of transient thermal behavior of materials. Studies of some of these factors are currently being performed at NBS.

Extinguishment of unwanted fires is of course the immediate objective of the fire fighter. Numerous forms and types of fire-fighting equipment and agents have been promoted. The manner in which these agents are effective in controlling fires is only imperfectly understood. Here again, if the operating mechanism of a device is uncertain, appropriate methods for improving it or measuring its performance are difficult to develop.

The NBS has for several years been studying the mechanism of fire extinguishment with dry chemical powders.[21] A parallel empirical investigation was also carried on of the relative behavior of various types of extinguishing devices.[22] This study was planned to permit statistical analysis of the effect of both controlled and uncontrolled variables on the performance of various devices when used against a series of ten fire problems. The results of this study have influenced trends in design of modern fire extinguishers.

Another study just recently completed and to be reported shortly has involved measurement of the effectiveness of dry powder extinguishing agents. Special techniques for powder preparation, separation, and application to fires were devised. It has been shown that the physical-chemical properties of the powders is an important factor in influencing their effectiveness. Particle size, application techniques, and specific surface of the powder also appear important. An important finding of this work is the fact that when proper precautions are taken small laboratory fires may be used for prediction of relative effectiveness of powders when applied to full-size fires.

Further work is in progress on study of the basic mechanism involved during extinguishment. This work is still in an early stage of study but shows good promise of providing a new and clearer picture of the processes involved in both combustion and extinguishment reactions.

In concluding this review it must be emphasized that the whole field of fire research is so broad that there are almost limitless opportunities for performing highly significant and useful scientific studies in our continual guard and fight against unwanted fire. It is encouraging to note the success of the Committee on Fire Research in stimulating interest in fundamental studies in this field.

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ABSTRACTS

I. Ignition Phenomena

Wolfhard, H. G. and Bruszak, A. E. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Communication of Flame Through Cylindrical Channels," *Bureau of Mines Report of Investigations* 5457 (1958)

A jet of hot gas resulting from stoichiometric combustion of ethane, methane, and hydrogen in admixture with nitrogen was used to ignite a series of combustible mixtures of variable stoichiometry. The experimental apparatus consisted of a small explosion vessel connected to a larger, partly enclosing, vessel by a channel which either contained a flame trap or was small enough to prevent passage of a flame. A stoichiometric mixture was ignited in the inner vessel and the products of the explosion passed through the channel, issuing into the outer vessel as a small jet of hot gases which ignited a combustible mixture in the outer vessel. The temperature of the jet was varied by changing the oxygen index $[O_2/(O_2+N_2)]$ without changing the stoichiometry. A 35 mm. Fastax camera was used in schlieren arrangement to observe the outer vessel.

Ethane-oxygen-nitrogen mixtures were ignited in the inner vessel using a channel 1.19 mm. in diameter and 6.3 mm. in length. When the oxygen index of the inner mixture was plotted against the mixture strength (actual fuel-air ratio divided by stoichiometric fuel-air ratio) of the outer mixture, all the saturated hydrocarbons tested produced similar curves. All ignited at approximately the same oxygen index (0.23) of the inner mixture when mixture strength of the outer mixture was unity and shifted on the lean and rich side in accordance with their lean and rich limits of flame propagation. The curves for propylene and isobutylene were close to those for the saturated hydrocarbons; ethylene, carbon monoxide, and hydrogen ignited more easily. The use of larger jets from channels up to 5 mm. in diameter produced no significant change in results.

Similar results were obtained when hydrogen-oxygen-nitrogen mixtures were used in the inner vessel with methane-, ethane-, and carbon monoxide-air mixtures outside. Methane and ethane had a minimum oxygen index of 0.17 with the hydrogen inner mixture compared to 0.23 for the ethane inner mixture. Hydrogen at an oxygen index of 0.17 was 200°C cooler than ethane at 0.23, indicating that temperature alone did not determine the ignition of the outer mixture.

Further qualitative experiments were made by changing the velocity and ejection time of the jet. The effect of changing the oxygen indices of outer stoichiometric fuel mixtures is graphically illustrated. Methane, ethane, and carbon monoxide mixtures are more difficult to ignite if they contain less oxygen than air. Oxygen indices higher than air have no influence over a certain range, after which the ignitibility increases strongly.

The optical observations during the experiments are illustrated by six sets of schlieren pictures of the outer vessel showing ignition and nonignition of the outer mixture, ignition under critical and noncritical conditions, and the jet issuing into air only in the outer vessel.

Turbulent jet theory explains, at least partially, why the ignition process is critical under experimental conditions of such high energy and temperature. Ignition evidently occurs under critical conditions only when a turbulence ball of high temperature is thrown out of the jet and becomes stationary in space. This occurs at moderate heights in the jet and only at the beginning of the jet emission, when the turbulence balls are large enough to be effective and yet retain a high temperature.

Subject Headings: *Ignition, by hot gases; Gases, combustible, ignition by hot gas.*

C. R. Orr

Wolfhard, H. G. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "The Ignition of Combustible Mixtures by Hot Gases," *Jet Propulsion,* 28, 798–804 (1958)

In an earlier work,* the author tested the ignition of combustible mixtures by hot burned gases from flames. It was first proposed to extend this investigation by burning pilot flames in hydrocarbon-air mixtures. However, both very small and larger highly dilute, *i.e.,* cooler, pilot flames invariably led to ignition, and minimum conditions for ignition could not be investigated in an apparatus allowing only relatively small flow rates. It was necessary therefore to heat gases in a furnace, and then lead them into explosive mixtures.

Work on ignition by inert hot gases has fundamental interest because of the parallels with spark ignition energy and spontaneous ignition temperatures. There are relevant engineering applications to the design and operation of flame stabilizers.

A jet of gas which had been heated in a furnace passed into a large column of slowly moving cold fuel or fuel-air mixtures. In the case of the cold fuel, the hot gas was air, so that a diffusion flame resulted whenever ignition occurred. In the case of the cold fuel-air mixture, the hot gas was inert, such as nitrogen, carbon dioxide, argon, and others. In the latter instance, a luminous column appeared before ignition.

Temperatures of the hot gas jet were measured in the absence of fuel, so that this temperature became the independent variable of the experiments. It was found that the minimum jet temperatures obtained in this case (called the gas ignition temperature) was in all cases somewhat higher than the spontaneous ignition temperature, as reported by other workers, dealing with hot solid surfaces. There was no correlation between these two ignition temperatures, with regard to ease of igniting different fuels. In the case of hot gas ignition, different diffusion rates were the primary complicating factor.

The effect of different diffusion rates is pointed up by the fact that gas ignition temperature of hot air injected into cold hydrogen is different than that of hot hydrogen injected into cold air. But in cases where diffusion effects are similar, reaction rates are the controlling factor, for the gas ignition temperature obtained by injecting hot inert gas into a combustible mixture did not depend on the nature of the hot inert gas. Even varying the oxygen index of the combustible mixture had little effect because temperature has much more effect on reaction rate than oxygen index. These results are similar to the ones obtained with pilot flame ignition in the earlier experiments, where only the temperature and heat flow of the pilots determined ignition, and not the nature of the pilot mixture, as long as it was stoichiometric.

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* Wolfhard, H. G. and Burgess, D. S. "The Ignition of Combustible Gases by Flames," *Combustion and Flame* 2, 3–12 (1958) Abstract: FIRE RESEARCH ABSTRACTS AND REVIEWS Volume I, No. 2, page 48

Because of the necessity of maintaining uniform temperature profiles in the hot jet, the gas flow was not varied significantly. For this reason, the effect of jet velocity, as well as jet diameter, has not been studied.

Subject Headings: *Ignition, by hot gases; Gases, ignition, of combustible mixtures by.*

J. K. Richmond

Wolfhard, H. G. and Bruszak, A. E. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Suppression and Transmission of Explosions by Cylindrical Channels," *Bureau of Mines Report of Investigation 5495* (1959)

If two containers, connected by a narrow passage, are filled with combustible mixtures, and the mixture in one of the containers is ignited, there are three mechanisms by which the flame can spread to the mixture in the other container, *i.e.,* laminar flame propagation through the passage, turbulent flame propagation through the passage, and ignition of the second mixture by the hot products of combustion from the first mixture issuing through the passage. The last mechanism is the subject of the present paper.

The study grew out of the observation that certain "flames" (hot gases emitting visible radiation) do not cause ignition when ejected into a combustible mixture. Such "flames" issue from the ventilating passages in certain flameproofed equipment used in mines. The explanation for the lack of ignition is that the visible jets are not really flames but rather hot inert products of combustion from the burning taking place in the equipment. The observed radiation is not chemiluminescent; it is simply thermally excited. Whether ignition occurs in the ambient combustible mixture depends on the temperature of the jet as well as on the aerodynamics of the mixing between the jet and the ambient gas.

The authors have undertaken a practical study of the physical variables affecting combustion transmission by the above mechanism. Cylindrical passages were used to connect the two chambers filled with combustible mixtures. The fundamental experimental variables were the combustion temperature of the primary gas, the diameter and length of the cylindrical connecting passage, and the chemical composition and equivalence ratio of the secondary gas. The secondary gases tested were methane, ethane, and carbon monoxide. The passage dimensions varied from 0.5 to 50 mm. in length and from 0.6 to 3.0 mm. in diameter.

From the resulting graphs, one can determine for given primary and secondary mixtures just what combinations of passage dimensions will transmit combustion by the hot-gas mechanism. This mechanism will quite generally transmit combustion for passage diameters so small that true laminar or turbulent flame propagation would be quenched. For example, the quenching distance for laminar flame propagation of the primary gas is about 3 mm. and for turbulent flame propagation considerably larger, whereas by the hot-gas mechanism combustion has been transmitted through a hole as small as 0.6 mm.

An interesting minimum occurs in the study. If other variables are held constant and the passage length is systematically increased from that of an orifice to that of a long tube, the passage at first tends to become a poorer flame inhibitor, then goes through a minimum, and becomes an increasingly better flame inhibitor. Thus, short tubes and long tubes are better flame inhibitors than medium-length tubes. The authors attempt to explain this minimum as a competition between heat lost to the passage wall and heat diffused away in the jet mixing process.

It appears that the ignition of a combustible mixture by a hot inert jet is a problem deserving additional study on a fundamental level because of its basic importance in many combustion phenomena.

Subject Headings: *Flame, inhibition by channels; Inhibition, of flames, by channels; Ignition, by hot gases.*

A. B. Schaffer

Wolfhard, H. G. and Vanpée, M. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Ignition of Fuel-Air Mixtures by Hot Gases and Its Relationship to Firedamp Explosions," *Seventh Symposium (International) on Combusion,* London: Butterworths Scientific Publications, 446–453 (1959)

When an explosive is detonated in a shothole, the hot gases issuing from the hole after the shock wave may cause ignition of the firedamp atmosphere in a mine. The present investigation was undertaken to learn more about such ignitions—that is, ignition by a hot jet of gas. It is a continuation of some earlier work in which a 4 mm. jet of hot nitrogen or air was injected into a cold combustible mixture and the ignition temperature of the mixture was measured. In the earlier study, it was found that ignition temperatures were lower when hot air was injected into a pure, cold fuel than when a jet of hot nitrogen was injected into a cold explosive mixture. (In the first case, only the fuel must diffuse into the hot jet; in the second case, both fuel and air must diffuse.) However, temperatures obtained were not in agreement with ignition temperatures obtained by other means—in fact, no good correlation was found between the two.

The present paper reports an extension of this work to include conditions that may be expected to prevail in the ignition of firedamp by hot detonation gases. The experimental procedure consisted of passing the gas to be heated through a furnace containing a 2 foot length of 4 mm. ceramic furnace tube. The heated jet emerged into a vessel 10 cm. in diameter and 50 cm. long through which the mixture to be tested flowed at about 200 cc. per second. A platinum-platinum rhodium thermocouple was used to measure the temperature of the jet immediately upon leaving the furnace. The temperature of the jet could be varied up to 1200°C. Ignition temperatures of a variety of fuels and fuel mixtures are reported. Reported values were reproducible to within 20°C.

The study showed that the velocity of the jet has little effect on the measured ignition temperature. This was especially true when a hot jet of air was injected into a pure, cold fuel. When hot nitrogen was injected into a fuel-air mixture, the measured ignition temperature rose very slightly with increased velocity.

Gas mixtures were also studied in some detail since firedamp itself is a mixture of gases (methane, ethane, etc.). Ignition temperatures of such systems as methane-ethane, ethane-propylene, hydrogen-methane, carbon monoxide-propane, and hydrogen-carbon monoxide were determined using jets of hot air. For hydrocarbon fuels, there was almost a linear relationship between ignition temperature and fuel mixture. However, when hydrogen was used as one of the fuels, there was a marked deviation from linearity—a small amount of hydrogen caused an abrupt decrease in ignition temperature when mixed with a hydrocarbon fuel. This was true for ignition by hot jets of air as well as nitrogen. Furthermore, when traces of hydrogen were added to the hot jet, the most ignitable mixture of a hydrocarbon-air mixture occurred at the lean limit. Since most fuel-air mixtures encountered in mines are near the lean limit, the investigation points out the dangers of small traces of hydrogen in mine operations.

Ignition temperatures were also measured as a function of the oxygen index (defined as $O_2/(O_2+N_2)$ over a range from 0.10 to 1.00. Of all the fuels tested, methane was the only one which showed a significant decrease in ignition temperature (air jet in pure fuel) as the oxygen index increased. When ignition was attempted using a hot jet of nitrogen into fuel-air mixtures, explosions became too violent for oxygen indices greater than about 0.40. For oxygen indices below 0.21 (air), the ignition temperature rises quite steeply with decreasing oxygen concentration.

Subject Headings: *Fire damp, explosions; Ignition, by hot gases; Gases, ignition, of fire damp.*

I. R. King

Churchill, S. W., Kruggel, R. W., and Brier, J. C. (University of Michigan, Ann Arbor, Michigan) "Ignition of Solid Propellants by Forced Convection," *American Institute of Chemical Engineers Journal* **2**, 568–571 (1956)

Grains of solid propellant were placed in a flowing oxidizing atmosphere at temperatures from 578 to 1070°K. Pyrocellulose and double-base propellants were used. The grains were about ⅛ inch diameter and extended through the gas stream, so that ignition was forced to take place on the cylindrical surface rather than on the end of the grain. The time required to ignite the cylindrical grain surface after immersion in the stream was found to be a function of the free-stream gas temperature, the mole fraction of oxygen in the gas, the gas flow rate, and the propellant type. These data were correlated by characterizing the gas flow by Reynolds number and the temperature effect by an exponential function of the reciprocal of temperature, the form often used to describe the effect of temperature on reaction rate, for each propellant and oxygen concentration of the flowing stream. Disclosure of the source of the particular form of the equation describing the transient heat transfer would have been helpful in following the brief analytical portion of the paper.

Activation energies (8182 to 9935 cal/gm mole) were appreciably lower than those reported for steady state combustion (16,000 to 60,000 cal/gm mole), perhaps indicating that the controlling reactions were different or that surface temperature may be more important than gas temperature. The importance of both convection and reaction rates on the ignition process was well illustrated by the data.

The influence of oxygen content of the flowing stream on the ignition time strongly suggests the controlling nature of oxidation reactions on the ignition process. All the propellants tested were oxygen deficient.

For application to propulsion situations these data must be extrapolated to higher temperatures. The reported correlation may be used for this purpose. One wonders, however, whether at some higher temperature, where the oxygen in the propellant is adequate to sustain a reaction, the mechanism of the ignition process might change sufficiently to make the empirical equation invalid.

Subject Headings: *Propellants, ignition by forced convection; Ignition, of propellants; Convection, forced, ignition of propellants by.*

A. E. Noreen

Martin, S. B. and Lai, W. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Thermal Radiation Damage to Cellulosic Materials. Part III. Ignition of Alpha Cellulose by Pulses Simulating Nuclear Weapon Air Bursts," *Research and Development Technical Report USNRDL-TR-252, AFSWP-1082* (May 1958)

Experiments were designed to study the ignition behavior of blackened alpha-cellulose exposed to thermal pulses typical of nuclear weapons as part of an extended investigation into the incendiary consequences of nuclear weapons.

The details of experimentation such as the geometry and techniques of exposure, radiant power measurement, etc., were fully covered in the second part of this series.* However, two features were new. Thicker samples were used and the experiment was designed according to a statistical sequential method, described fully in the appendix.

The method of data treatment used started with the development of a simple relationship between the charring of wood by a nuclear radiation pulse and that caused by the more experimentally expedient square-wave input. The work at constant irradiance exposure was then extended to the ignition of blackened alpha-cellulose in sheet form, an idealized model of common kindling fuels. A generalized ignition behavior pattern was established by normalizing the exposure parameters with the appropriate physical properties of the cellulose as indicated by solution of the heat conduction equation for the opaque infinite slab. Tests on newspaper and cotton fabric demonstrated the validity of this approach.

Accordingly, the ignition behavior of pulse-irradiated cellulose was defined by plotting the modified energy modulus [the mean value of radiant exposure (Q), divided by the product of the density (ρ), specific heat capacity (c), and thickness (L) of the material] versus the irradiance modulus [the peak radiant power of the exposure (H_p), times the ratio of the thickness of the material to its thermal conductivity (K)]. The ignition pattern showed three regions of different threshold effects; sustained glowing ignition at low irradiances and long times, sustained flaming ignition at shorter exposure and correspondingly higher irradiances, and finally unsustained flaming ignition for very short times and quite high peak irradiances separated from the sustaining case by considerable amounts of energy over a region of transient flaming.

This pattern obtained with the simulated weapon pulse is quite similar to that for a square-wave exposure. No simple equivalence could be established between the two but somewhat equivalent effects were observed for weapon pulses having peak irradiances of approximately three times the irradiance level of the square-wave input. The simulated weapon pulse sustained flaming ignition at the higher irradiances with 40 per cent less energy but required a third more energy to cause sustained glowing.

Subject Headings: *Radiation, damage, to cellulose; Cellulose, thermal radiation damage of; Ignition, of cellulose, by thermal radiation.*

G. M. Steffan

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* Butler, C. P., Martin, S., and Lai, W. "Thermal Radiation Damage to Cellulosic Materials. Part II. Ignition of Alpha Cellulose by Square-Wave Exposure," *USNRDL-TR-135* (*AFSWP-906*) (November 1956)

Martin, S., Lincoln, K. A., and Ramstad, R. W. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Thermal Radiation Damage to Cellulosic Materials. Part IV. Influence of the Moisture Content and the Radiant Absorptivity of Cellulosic Materials on their Ignition Behavior," *Research and Development Technical Report USNRDL-TR-295, AFSWP-1117* (December 1958)

This, the fourth and final part of a series, is a report of the experimental investigation of the influence of the moisture content and the radiant absorptance on the ignition behavior of cellulosic kindling fuels. The choice of fuel was 1½ by 1¾ inch alpha-cellulose paper. A modified chemical glove box, having controlled conditions of temperature and humidity, provided the exposure environment. The last lens of the optical system for a carbon arc source served as a window in the exposure end of the box. Instrumentation was such that temperature and humidity could be continuously monitored throughout an experimental run. Air of the proper temperature and humidity was fed into the opposite end of the box at a rate sufficient to exchange the air and to effectively carry away the decomposition-combustion products.

Relative humidity levels of 10, 30, and 87 per cent were used, with specimen moisture content ranging between 2.3 to 2.6, 3.8 to 4.4, and 11.1 to 11.9 per cent of dry weight, respectively.

Specimens with optical absorptivities of 0.1, 0.7, 0.8, and 0.9 were obtained by varying the carbon-black content from 0, 0.25, 1.0, and 2.5 per cent of dry weight, respectively.

The correlation pattern of previous ignition data was plotted on log-log co-ordinates in the form of an energy modulus $= Q/\rho cL$ and an irradiance modulus $= HL/K$, in which Q is the radiant energy per unit area, ρ the density, c the specific heat capacity, L the thickness of the specimen, H the radiant energy per unit area per unit time, and K the thermal conductivity.

In the present work, the effects of moisture content and absorptivity were normalized by adding the heat capacity of the water to that of the dry cellulose and by multiplying both the radiant energy and irradiance values by the appropriate radiant absorptance, *i.e.*, a modified energy modulus $= aQ/\rho_0 c_0 L_0 (1 + mc_w/c_0)$ and a modified irradiance modulus $= aHL/K$, in which a is the radiant absorptance, and m the moisture content in per cent of dry weight; subscripts w and o refer to values on a wet and dry basis, respectively; the remainder of the notation is unchanged. It was found that the data normalized in the above manner fitted well to the correlation pattern of ignition data of previous investigations, particularly for materials having absorptivities of 50 per cent or more. For lighter colored materials having absorptivities less than 50 per cent, a better fitting was obtained if the modified irradiance modulus $= a^n HL/K$, in which n is equal or less than 1. Limited experimentation with white cellulose indicated that the exponent n approached a value of roughly ½ for white, highly diathermanous materials.

It is suggested that this ignition pattern is sufficiently general to be used to predict the ignition behavior of a broad class of kindling fuels.

Subject Headings: *Radiation, damage, to cellulose; Cellulose, thermal radiation damage of; Ignition, of cellulose, by thermal radiation.*

W. G. Labes

Nelson, L. S. and Lundberg, J. L. (Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey) "Heterogeneous Flash Initiation of Thermal Reactions," *The Journal of Physical Chemistry* 63, 433–436 (1959)

In this paper, as well as in two preceding publications,* the authors describe some qualitative results obtained in their experimental study on flash heating of transparent solids and liquids containing various radiation absorbing dispersoids. The apparatus consists of a spiral flash lamp (filled with xenon) with an output of the order of 10^{19} to 10^{20} quanta/flash cm^2 in the region from 2000 to 4000 Å. The flash time varies from 2 to 5 milliseconds.

In the case of some finely divided metals (diameter $<$ 100 microns) suspended on the walls of an evacuated Pyrex tube, rapid vaporization with deposition of mirrors is found following a single flash. Heterogeneous pyrolytic reactions are observed when gaseous, liquid or solid reactants such as hydrocarbons, mineral oil, and inorganic polymers, containing a metallic powder suspension or filament, are exposed to the radiation.

Qualitatively the results may be expressed by thermal reactions following the absorption of a radiation pulse at the surface of finely divided material. The quantitative analysis presented by the authors suffers from such approximation as (1) infinite thermal conductivity of particle; (2) a square-wave function in the radiation flux; and (3) absence of endothermic or exothermic reactions. Nevertheless, this experimental technique represents an interesting extension of the method of initiation of homogeneous chemical reactions by flash photolysis.

Subject Headings: *Radiation, high intensity, initiation of reaction by.*

H. Wise

Lundberg, J. L. and Nelson, L. S. (Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey) "Initiation of Thermal Reactions by the Flash Illumination of Absorbing Bodies," *Nature* 183, 1560–1562 (1959)

The authors used intense flashes of visible light to heat absorbers immersed in transparent matrices to temperatures of several thousand degrees and to initiate thermal reactions rapidly. The samples were flashed while placed along the axis of a spiral quartz discharge lamp. The degradation of polymeric matrices occurred around particulate impurities and was independent of the chemical nature of the polymers. Polymers free of impurities were not pyrolysed.

Simple heat balance equations yielded estimates of the surface temperatures of the absorbers. These were checked by vaporizing metallic particles *in vacuo*. The surface temperatures of spherical or cylindrical absorbers in condensed matrices depended strongly on radius and showed a maximum near 10μ. The surface temperatures of foils or platelets showed little dependence on thickness. Temperatures as high as 10,000°C seemed readily attainable.

The following effects of flash illumination were studied: evaporation of metallic particles and foils; pyrolysis of methane; initiation of explosions in explosive gas mixtures; degradation of mineral oil; evaporation and redeposition of zinc dust; degradation of polymeric matrices containing dark particles.

The method was suggested as a means of producing free radicals, and its

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* Lundberg, J. L. and Nelson, L. S. *Nature* 179, 367 (1957)

Lundberg, J. L., Nelson, L. S., and Hellman, M. Y. *Proc. Third Conference on Carbon*, Buffalo, N.Y. (1957) p. 411, Pergamon Press, N.Y. (1959)

chemical effects were compared with those of shock waves. It had little dependence on wave length but often had a threshold intensity.

Subject Headings: *Radiation, high intensity, initiation of reaction by.*

R. H. Atalla

Matson, A. F., Dufour, R. E., and Breen, J. F. (Underwriters' Laboratories, Inc., Chicago, Illinois) "Survey of Available Information on Ignition of Wood Exposed to Moderately Elevated Temperatures," *Underwriters' Laboratories, Inc., Bulletin of Research, No. 51, Part II* (May 1959)

Records of actual incidents, laboratory reports on experiments, and published technical literature indicated authentic instances of the ignition of wood surfaces exposed for long periods of time to low-pressure steam pipes and similar heat sources. The temperatures of these heat sources were in the order of 100 to 120°C (212 to 248°F).

Experimental investigation of the ignition of wood at moderately elevated temperatures appears to be difficult since the results may be influenced by such factors as the total duration of heating, intermittent heating and cooling, variations in the humidity of the ambient air, oxygen supply, and to some extent the size of the specimen.

Most available experimental data indicate that the ignition temperature of wood is of the order of 200°C (392°F) or higher, but these values are for prompt ignition of relatively small specimens heated for comparatively short durations. The experimental data are of limited application where wood is heated for long periods of time at moderately elevated temperatures. Mitchell, at the National Bureau of Standards, observed the ignition of wood fiberboard temperatures as low as 109°C (228°F) after heating for 96⅔ hours. These results were obtained with fiberboard stacked as an octagonal prism 12 by 22 inches.

Published reports of fires in the United States and Canada together with some observations from Sweden and Finland show instances of the ignition of wood surfaces exposed to moderately elevated temperatures for long periods in buildings or equipment. Various heat sources were involved in these incidents, the most common being low- or high-pressure steam pipes. In many cases actual temperature measurements or the conditions of the steam supply indicate that the temperature of the heat source was in the vicinity of 100 to 120°C (212 to 248°F). Isolated cases of the ignition of wood after prolonged heating in industrial installations at temperatures as low as 68°C (134°F) are recorded.

Decomposition of wood in the formation of carbon (charcoal) near steam pipes or other source of heat were reported in many instances where wood was ignited at relatively low temperatures, particularly where the fire was discovered and extinguished promptly. In view of the recognized adsorption of oxygen by charcoal and the resulting evolution of heat, it appears that "pyrophoric" carbon may have played a part in the ignition of the wood. Ignition appears to be more likely where the heating is intermittent or where there are wide variations in the humidity of the ambient air, both of these conditions being favorable for repeated adsorption of oxygen by the charcoal.

An extensive compilation of reports of fires of this sort was made by an insurance inspection bureau in 1910 (*Quarterly,* National Fire Protection Association, Volume IV, No. 3, January 1910, Pages 312–22). In 1919, the Committee on Gases of the National Fire Protection Association promulgated a limitation on the temperature to which wood may be exposed in installation, maintenance, and use of piping and fittings for city gas, as follows:

> "Gas-consuming appliances shall be arranged so that their continued operation will not raise the temperature of surrounding combustible materials, including woodwork, more than 90 degrees Fahrenheit from a normal temperature of 70 degrees Fahrenheit, that is, a maximum of 160 degrees Fahrenheit."

Work done in recent years (1952) at the British Fire Research Station to investigate the heating of panels by flue pipes showed that below 100°C (212°F) a combustible panel may be considered to offer a low fire hazard. As the temperatures increase beyond this limit, the rate of decomposition of cellulose materials was noted to increase progressively until a temperature of 250°C (480°F) is reached when the reaction becomes exothermic and combustible gases are rapidly evolved. According to the British report "if decomposition is to be avoided, wood should not be repeatedly heated above 100°C (212°F); and it is therefore essential to maintain any combustible panel at a sufficient distance from a flue pipe to avoid this."

This paper was prepared to supplement a report on the performance of Type B gas vents for gas-fired appliances. It brings together in one place most of the available information on this subject with a competent bibliography.

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

H. Bond

Schnizlein, J. G., Porte, H. A., Pizzolato, P. J., Woods, J. D., Bingle, J. D., Fischer, D. F., Mishler, L. W., Martin, P., Tonne, P. C., and Vogel, R. X. (Argonne National Laboratory, Lemont, Illinois) "Metal Oxidation and Ignition," *Argonne National Laboratory Chemical Engineering Division Summary Report 5924 ANL-RCV-SG-1421* (July, August, and September 1958)

This article reports on part of a continuing study of factors influencing the self-ignition and oxidation of the reactor materials, uranium and zirconium.

The uranium ignition studies investigated the dependence on several variables of the heating curve, *i.e.*, sample temperature *vs.* time. Variation of the oxygen flow rate produced a negligible effect. However, a decrease in heating rate did decrease the ignition temperature of pure uranium. This emphasizes the fact that ignition temperatures should be compared only within a standardized test procedure. Additive effects were superseded by the importance of the specific area of the alloy samples. While aluminum and copper decreased the ignition temperature of uranium cubes, they had no effect on foils.

Since uranium ignites in air in a unique thermocycling process, studies have been made of varying helium-oxygen and nitrogen-oxygen atmospheres. Ignition temperatures vary differently with oxygen concentrations in the two systems and results seem to be strongly dependent on the metallurgical history of the uranium.

An ignition test for zirconium foils has been developed in which they are rapidly brought to a high temperature by electrical heating. The ignition, current and voltage are recorded simultaneously by a Fastax camera. In general, the zirconium-titanium alloy required less energy for ignition than the pure zirconium and both reacted more quickly and violently in oxygen than in air. Attempts to ignite zirconium foils at lower temperatures than those required in helium-shielded tests by using vacuum or annealing to maintain an unoxidized surface failed.

The effect of twenty additives on the oxidation resistance of pure zirconium was determined at concentrations of one, two, and four atom per cent. Only copper, nickel, beryllium, and hafnium alloys proved effective. The largest group of alloys followed the cubic rate for the oxidation reaction. The rest showed deviations after initially following the cubic rate law, or, in a few cases, the parabolic rate law.

Subject Headings: *Ignition, of metals; Metals, ignition of; Uranium, ignition of; Zirconium, ignition of.*

G. M. Steffan

Line, L. E., Jr.,* Rhodes, A. A., and Gilmer, T. E., Jr. (Experiment Incorporated, Richmond, Virginia) "The Spark Ignition of Dust Clouds," *The Journal of Physical Chemistry* 63, 290–294 (1959)

This paper is concerned with the spark ignition characteristics of a nonturbulent cylindrical column of lycopodium "dust" suspended in mixtures of oxygen and nitrogen. The dust cloud is either wall-free, stabilized by an envelope of premixed oxydizer gas, or wall-confined, surrounded by an open-end glass tube. Most of the work reported is for a 1 inch diameter column (average flow of 30 cm/sec), although a few curves for a 2 inch configuration are also included.

The purpose of the investigation was to determine: (a) the condenser energy needed for ignition at a fixed oxygen- and dust-concentration; (b) the limiting oxygen concentration for ignition at a fixed condenser energy and dust concentration for both "wall-free" and "wall-confined" dust columns. The rate and manner in which the spark was introduced across a 6 mm. gap in the center of the column were altered by employing either an inductance or a variable resistance in the discharge circuit.

The results are given in graphical form as ignition frequency (*i.e.*, the number of times out of 10 trials ignition occurs) *vs.* either condenser energy or mole per cent O_2. The environmental effect of a confining wall for an unmoderated spark discharge produces a ninefold reduction in the minimum condenser energy (the energy which causes ignition 50 per cent of the time) and a 1.7-fold reduction in the oxygen concentration. The insertion of either the optimum resistance (10^5 ohms) or inductance (27μh) in the spark circuit makes this effect slight as does an increase in the size of the dust column from 1 to 2 inches.

The insertion of a low-resistance inductance into the spark circuit lengthens the discharge time without materially decreasing the energy delivered to the gap. On the other hand, the addition of a resistance decreases the energy delivered to the gap and may lengthen the discharge time provided $R^2=4L/C$. The variation of the minimum condenser energy, E, with variation in R from 0 to 10^7 ohms is explained accordingly in that E increases to a maximum at about $R^2=4L/C$ (14 ohms) and then decreases to a minimum at $R=10^5$ ohms where the advantage of the longer discharge time produces ignition in spite of the reduction in gap energy. Beyond this value of R the energy losses in the external circuit and the

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* Line, L. E., Clark, W. J., and Rahman, J. C. "An Apparatus for Studying the Burning of Dust Clouds" Abstract: FIRE RESEARCH ABSTRACTS AND REVIEWS, Volume I, No. 3, p. 116

reduction in gap energy outweigh the advantages of a slow spark discharge and hence the condenser energy again increases.

High speed motion pictures show that within 2 milliseconds the short duration spark (without ignition) pushes the dust particles back, forming an essentially void zone of about 4 cc., while the long duration spark disturbs the dust column very little. The authors suggest that ignition with fast sparks is more difficult because a considerable part of gap energy is absorbed in expansion work and the more ignition energy is required by virtue of the enlarged surface area. The violent expansion with the fast spark in the 1 inch diameter wall-confined column produces turbulence which should increase the burning velocity, thereby making ignition easier than in the wall-free case. The fact that it matters little whether a wall surrounds the 2 inch diameter column when using a short duration discharge is further justification of the above argument.

Subject Headings: ***Dusts, spark ignition of; Ignition, of dusts by sparks; Sparks, ignition of dusts by.***

P. A. Ross

II. Thermal Decomposition

Tesner, P. A. (All Union Institute of Natural Gas, Moscow, USSR) "Formation of Dispersed Carbon by Thermal Decomposition of Hydrocarbons," *Seventh Symposium (International) on Combustion,* London: Butterworths Scientific Publications, 546–553 (1959)

Carbon formation by thermal decomposition of hydrocarbons was studied experimentally and theoretically. The main conclusion was that thermal decomposition of hydrocarbons leading to carbon formation is a process typical of formation of a solid dispersed phase from a gas. The contradictory nature of previous papers on studies of thermal decomposition of gases was attributed to their emphasis on chemical kinetics rather than on the processes of formation of a dispersed phase. Tesner believes that the purely physical process of heating the hydrocarbon is more important than the chemical mechanism. From this standpoint, thermal decomposition is regarded as proceeding simultaneously in two separate stages: (1) homogeneous transformation in the bulk gas to form primary nuclei and (2) heterogeneous thermal decomposition on a solid surface to form a growing layer of carbon.

These two stages were studied in separate experiments.

1) Carbon surface growth experiments:

Three techniques were used for studying the kinetics of growth of a carbon surface in contact with an atmosphere of heated hydrocarbon: (a) the growth pattern was followed progressively with an electron microscope; (b) the amount of carbon forming on a surface was weighed; (c) the carbon-hydrogen ratio of the new carbon surface was compared with the ratio of the original hydrocarbon. It was concluded that carbon atoms did not migrate along the surface but remained at the active carbon sites where the reaction occurred. Growth was not due to decomposition of radicals or polymers at the surface but mainly to decomposition of hydrocarbon molecules. Rate of growth was proportional to hydrocarbon concentration, increased with temperature, and was greatly retarded by hydrogen formed during the reaction. The velocity of formation depended on the physical and chemical nature of the growing surface; for example, carbon growth on a carbon surface was faster than carbon growth on a noncarbon surface.

2) Dispersed carbon formation experiments:

In these experiments, carbon blacks were collected from gaseous hydrocarbons flowing through externally heated reaction tubes at various flow rates. The carbons were quantitatively weighed and measured for degree of dispersion. The extent of solid carbon formation relative to the spontaneous formation of new carbon nuclei was determined. Experiments indicated that the rate of formation and dispersion of the carbon nuclei and the rate of particle growth was strongly dependent on temperature and rate of heating within the system. A higher rate of heating of hydrocarbon (shorter contact time by increased flow rate or smaller tube diameter) led to a higher rate of decomposition and to a higher degree of dispersion of carbon black but not to an increased total yield of carbon black. Formation of primary nuclei required a much higher temperature than necessary for particle growth or for decomposition of the hydrocarbons on the walls to form a layer of solid carbon (approximately 150 to 200°C higher). This temperature increase was considered equivalent to the amount of "superheat" or "supersaturation" required for the formation of carbon black nuclei. An observation of settling carbon particulates within the heated reaction tube showed that carbon particles could not coagulate in a zone of intensive formation and growth. Tesner believes that each growing particle was protected by a stream of hydrogen directed outward from the particle. Thus, dispersed carbon particulates did not settle in the hottest zone where solid carbon formed in layers, but only near the end of the reaction tubes where hydrocarbon concentration was low and flow of hydrogen from carbon particles and solid carbon layers was insignificant. If hydrogen was added to the reaction chamber, the initial stage of development of carbon was retarded, shifting the zone of carbon black formation towards a higher temperature zone within the reaction chamber, thereby increasing the rate of particle formation and the dispersity of the carbon black.

The author states that carbon formation in combustion processes also are essentially of thermal nature, the only difference being that the hydrocarbon is diluted with combustion products diffusing from the combustion front. This reviewer notes the obvious complicating factor of oxidation reactions in combustion processes. Carbon nucleation and carbon growth mechanisms may be modified or nullified by the presence of water, carbon dioxide, carbon monoxide, and other oxygenated intermediates in the combustion gases. Chemical mechanisms and equilibrium considerations may no longer be minimized in favor of purely physical processes. Probably, both chemical kinetics and physical dispersed-phase experiments are mutually interdependent and necessary for the study of carbon formation in combustion processes.

This reviewer believes that the heat transfer history of the gases within the reaction tube may affect carbon black yields in nucleation and growth, requiring further consideration in the contact time experiments.

Subject Headings: *Hydrocarbons, thermal decomposition of; Thermal decomposition, of hydrocarbons; Carbon formation, in thermal decomposition of hydrocarbons.*

J. M. Singer

Milberg, M. E. (Scientific Laboratory, Ford Motor Company, Dearborn, Michigan) "Carbon Formation in an Acetylene-Air Diffusion Flame," *Journal of Physical Chemistry* 63, 578–582 (1959)

The soot issuing from an acetylene-air diffusion flame was collected on a glass wool filter and weighed. By collecting soot for various lengths of time, the sooting rate could be determined. The burner was a concentric tube-type burner, with acetylene fed into the center tube, and air into the annulus. The chamber in which the flame occurred could be evacuated, and total pressures were varied from 40 to 400 mm. Hg. The pressure range depended on the fuel/air ratio. The soot deposits were extracted, using acetone, carbon tetrachloride and benzene as solvents. The extracts were subjected to chromatographic separations, and infrared and ultraviolet spectra were taken. About 13 per cent of the deposit proved to be volatile in a stream of nitrogen at 500–550°C. Soot samples were heated in a mass spectrometer inlet system and the volatile portion examined mass-spectrometrically. Electron microscopy of the soot showed particle sizes in the range 200 to 500 Å, independent of burner conditions.

The sooting rates were found to be substantially linear over a large part of the pressure range of deposit collection. The curve for the 12:1 fuel-air ratio curved steeply downward at about 145 mm. Hg. The extrapolated linear portion of the 12:1 fuel/air ratio curve fitted exactly the curve for the 9:1 fuel/air ratio. The curve for the 15:1 fuel/air ratio was initially steeper than the 12:1 fuel/air ratio curve, but then approached this curve in the higher pressure region (about 350–400 mm. Hg.).

The approach of all the curves to a single linear curve was taken to imply that the soot formation rate is independent of fuel/air ratio, and is linear with pressure. Deviations from linearity were interpreted in terms of the variation of the soot consumption rate with pressure and/or fuel/air ratio.

The infrared absorption spectra were similar to those previously obtained on soot extracts. Functional groups such as hydroxyl, carbonyl, ester, aromatic rings, carbon-carbon double bonds, and methylene chains were present. Only a broad continuous absorption was observed in the ultraviolet absorption spectra, in contrast to the results of two recent investigations,* in which specific polynuclear aromatics were identified by a combination of chromatography and ultraviolet spectroscopy of soot extracts. The mass-spectrometric analysis of the volatile portion indicated principally polycyclic aromatic hydrocarbons in the relative proportions 5 ring$<$4 ring$>$3 ring$>$2 ring. Minor amounts of aliphatic and alicyclic hydrocarbons were also detected in the mass-spectrum analysis.

The mechanism suggested to account for these data is that carbon is formed by polymerization of acetylene to form large aromatic molecules. These are then "laid down" as carbon. If the author is correct in interpreting the sooting rate as being independent of fuel/air ratio, then, oxygen is not involved in a rate controlling step in the carbon formation process. The data presented in this paper will assist in evaluating the important mechanisms in carbon formation in flames.

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* Arthur, J. R., *et al.* "Formation of Polycyclic Hydrocarbons in Diffusion Flames," *Combustion and Flame 2,* 267–272 (1958)

Badakshan, A., Garner, F. H., and Long, R. "A Note on Polycyclic Hydrocarbons in Association with the Carbonaceous Residues from Diffusion Flames," *Combustion and Flame 2,* 437–438 (1958)

If, in fact, it is correct to infer oxygen does not participate in the rate-controlling steps, a vexing question will have been disposed of.

Subject Headings: *Diffusion flames, carbon formation in; Carbon formation, in diffusion flames.*

P. R. Ryason

Singer, J. M. and Grumer, J. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Carbon Formation in Very Rich Hydrocarbon-Air Flames I. Studies of Chemical Content, Temperature, Ionization and Particulate Matter," *Seventh Symposium (International) on Combustion,* London: Butterworths Scientific Publications, 559–569 (1959)

The following types of measurements on the mechanism of carbon formation in rich hydrocarbon-air flames were made:

1) mass spectrometer analysis of stable species at several stations within the flames
2) coated thermocouple temperature profiles
3) apparent electrical conductivity profiles
4) electron microscope observations of particulate matter collected on screens placed in the yellow (luminous) zone

Of the observations reported, the most significant appear to be the following:

a) With the exception of propane, the C—C—C and longer chain hydrocarbon content of the flame gases is small, being less than 0.06 per cent. These traces are consumed in the initial regions of the yellow zone. No compounds of molecular weight exceeding 92 (toluene) are observed.
b) Conical diffusion flames and flat premixed flames contain essentially the same species but in different compositions. The CO_2/CO ratio in diffusion flames exceeds that of the premixed flame by a factor of approximately five.
c) Observed concentrations of CO and H_2 in rich propane-air and ethylene-air flames are lower than those corresponding to local thermochemical equilibrium.
d) The effective electrical conductivity in flat flames passes through a maximum a short distance downstream of the start of the yellow zone, at a position where the temperature is decreasing and most of the over-all reaction has already been completed.
e) Particulate matter collected on screens in rich ethylene-air flames differs in appearance from that collected in propane-air flames, the former being granular-spherical, the latter being comprised of apparently hollow filaments reminiscent of those obtained by other investigators from heated carbon monoxide in contact with metal catalysts.

These observations tend to support the postulate that thermal decomposition products of the fuel form nuclei which then grow through a surface mechanism involving the reaction of carbon monoxide to form solid carbon. This carbonaceous material is apparently responsible for the ions observed in these flames.

Subject Headings: *Carbon formation, in rich flames; Flame, carbon formation in rich premixed.*

D. W. Rosner

Patat, F. and Derst, P. (Institut für Chemische Technologie der T. H. München, Germany) "The Thermal Degradation of Polymeric Phosphorus Nitrile Chlorides," *Angewante Chemie* 71, 105–110 (1959)

Polymeric phosphorus nitrile chlorides are degraded to low molecular weight products by heating. The polymers were sealed into 20 ml. ampules and heated in a specially designed calorimeter regulated to ±2°C. The temperature of reaction varied from 250 to 700°C. Quartz dust of various particle sizes was added for surface. When the layer of polymer is <0.08 mm. thick, then influence of diffusion and poor heat conductivity is not important to over-all rate or course of reaction.*

Increasing the reaction pressure or temperature respectively raises and lowers the yield of high molecular weight polymers. The reaction is therefore exothermic. The primary degradation products found here were units of 3–7 ($PNCl_2$) units. Only approximate statements can be made regarding the kinetics, principally since the uncertain diffusion data of the reaction intermediates from the polymer would determine the over-all rate of the reaction. An attempt was made to determine the mechanism of the reaction and to determine it kinetically. From the mechanism of the depolymerization reaction and from the products of decomposition, a statement could be made of the structure of $(PNCl_2)_n$ utilizing the kinetic data of polymerization.

The course of the depolymerization can be distinguished kinetically in the following ways:

1) continuous break of the chains
2) gradual splitting off from end of chain of polymer
3) depolymerization in a chain reaction
    a) chain can statistically break with subsequent splitting off from both radical-like ends, or
    b) the chain breaks at end with subsequent splitting off of monomers

The depolymerization follows first order kinetics. Mechanisms (1) and (2) are thus eliminated. Since high polymer $(PNCl_2)_n$ occur as rings, breaks at end of chain are not possible, which leaves (3) (a) as the only mechanism. The initial reaction consists of splitting large rings, in which case two active chain ends originate. The decomposition reaction occurs when low molecular weight polymers are split off from active chain ends. The reaction is terminated through a ring formation of low molecular weight homologs of original rings. The length of the chains must be equal to the average degree of polymerization, since after partial depolymerization no soluble portions are found.

No influence of oxygen as a chain breaker was observed. The only influence oxygen had was noted through the cross-linking of the polymer products and no influence on rate of reaction is observed. This does not exclude a radical reaction in decomposition. The peculiar nature of the $(PNCl_2)_n$ can explain these observations. The open chain of $(PNCl_2)_n$ has no pure radical character with free electrons. Therefore, the influence of oxygen can only be negligible. Oxygen apparently attacks $(PNCl_2)_n$ only through secondary reactions.

The end product of depolymerization consists of rings consisting of from 10 to 50 trimer units which are statistically interlocked; thus the limited solubility. A high molecular weight has been noted but according to this observation it is

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* Grassie, N. and Melville, H. W., *Proc. Roy. Soc.* A199, 1, 14, 24, 39 (1949)

strictly illusory. Temperature has the effect of making larger rings as the polymerization temperature rises. From the activation energy of 26 ± 2 kcal/mole for depolymerization, a value of 31.3 kcal/mole has been arrived at for the P-N bond energy.

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

P. Breisacher

III. Heat and Material Transfer

Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "On the Thermal Conduction Equation for Self-Heating Materials with Surface Cooling," *Transactions of the Faraday Society* 54, 60–65 (1958)

Thermal explosions have been explained theoretically on the basis of self-heating. When the rate of heat generation is continually in excess of the heat loss to the environment, ignition and/or explosion ensues. The limiting cases of a uniform temperature field in the material with arbitrary surface cooling, *i.e.,* material thermal conductivity infinite, and the extreme case of infinite surface conductance, have been examined previously. While the case of gaseous explosions may be considered to be covered by the above, it is doubtful that they are applicable to the case of a self-heating solid because of the higher thermal conductivity of the solid.

The case of a material heating by a zero order reaction obeying the Arrhenius law is assumed. The heating considered is symmetric. Consideration of the particular boundary conditions along with the steady state temperature field equation with internal heat generation yields solutions for the slab, sphere, and cylinder. The analytic results are presented in graphical form and give the relation of the heating parameter, surface temperature parameter, and center temperature parameter for values of the surface transfer parameter (Nusselt number) between those of the extreme cases previously considered, *i.e.,* zero and infinity.

From the analysis it can be concluded that the critical values of the heating parameter, based on the case of surface transfer equal to infinity, are too high. The present analysis shows the range of validity of the elementary analysis of a uniform temperature field in the self-heating material to be rather narrow.

Subject Headings: *Thermal conduction, equation for self-heating.*

H. N. McManus, Jr.

Scesa, S. (California Forest and Range Experiment Station, Berkeley, California) "Transfer of Heat by Forced Convection from a Line Combustion Source," *Interim Technical Report AFSWP-865* (February 1957)

This report considers the forced convective heat transfer from a ground level line heat source under conditions of atmospheric turbulence. It is assumed that the line heat source is representative of a line fire with a heat release per unit length Q/L.

The aerothermodynamic equations for conservation of mass, momentum, and energy are written. Compressibility is neglected except for the buoyancy term. These equations are simplified by assuming $\frac{U_\infty X_0}{\nu_\infty} \gg 1$ where U_∞ is the wind velocity and X_0 a characteristic distance along the ground. This step corresponds to the Prandtl boundary layer hypothesis and means the thermal layer is close to the ground. It follows that the solutions are valid only for relatively high wind velocities. The author also shows that buoyancy effects may be neglected completely if $Q/L \ll \rho_\infty c_p T_\infty U^3_\infty$.

Under the above assumptions the thermal boundary layer problem may be solved if a diffusion mechanism is specified. The author chooses a form of the eddy viscosity proposed by Deacon,*

$$K_m = 0.4\nu_\infty \left(\frac{u_\tau Z_0}{\nu_\infty}\right) \left(\frac{Z}{Z_0}\right)^\beta$$

where K_m is the eddy viscosity for the transfer of momentum; u_τ, friction velocity ($\sqrt{\tau_w/\rho_\infty}$); Z, vertical height; Z_0, roughness height; and β, the atmospheric stability parameter.

Assuming the eddy viscosities of momentum and heat to be equal, the equations are solved numerically. The results are discussed in terms of the heat transfer from a combustion zone to the unburned material downwind. The solution shows the heat transfer to be higher if subadiabatic conditions are present in the atmosphere. If superadiabatic conditions are present, the temperature layer is thicker and the heat transfer lower. Also, as the surface roughness is increased the importance of the atmospheric stability on the heat transfer is decreased.

Subject Headings: *Heat transfer, by forced convection; Convection, forced heat transfer by.*

D. L. Turcotte

IV. Diffusion Flames

Wise, H. and Agoston, G. A. (Stanford Research Institute, Menlo Park, California) "Burning of a Liquid Droplet," *Advances in Chemistry Series* **20**, 116–135 (1958)

This article constitutes a fairly complete review of the theoretical and experimental investigations of the combustion of a single liquid fuel droplet, completed prior to 1958. The discussion is restricted largely to the practically more important case of bipropellant burning (a fuel droplet with gaseous oxidizer at infinity), with relatively little attention being given to monopropellant droplets. The presentation is well organized, and the paper collects important data on droplet burning which were previously scattered throughout a number of different journals and reports.

In addition to defining the spherically-symmetric flame surface approximation, the authors discuss in detail the implications of an illuminating numerical analysis of the distributed reaction zone by H. Wise and his co-workers. In this analysis, the thickness of the flame zone was found to increase with a decreasing specific reaction rate constant. At low reaction rates the flame zone was found to broaden to such an extent that the temperature gradient at the droplet surface became too small to support the heat transfer required for vaporization; the nonexistence of

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* Deacon, E. L. "Vertical Diffusion in the Lowest Layers of the Atmosphere, *Quarterly Journal Royal Meteorological Society* 75, 89–103 (1949)

the steady-state solution was interpreted as defining the flammability limits for the non-premixed system.

The semi-empirical procedures for determining the effects of forced and natural convection upon droplet burning rates are presented. The authors describe experiments which show the change in the droplet burning rate caused by varying the gas velocity. These experiments tend to support the validity of the semi-empirical methods.

The authors discuss the quartz filament (suspended droplet), porous sphere, and projected droplet methods for measuring burning rates. Experimental results concerning the nature and duration of the preignition period are collected, and a comprehensive table of evaporation rate constants (the constants of proportionality between the square of the droplet diameter and time) is given for the combustion period. The preignition time increases with increasing droplet diameter and decreasing ambient oxygen concentration, while the evaporation rate constants, which are relatively insensitive to pressure, increase with increasing diffusivities, ambient temperature, ambient oxidizer concentration, and heat of reaction. These experimental results concerning the evaporation rate constants are shown to be substantially in agreement with the theories. Measurements of the position of the flame surface are discussed, and their disagreement with theories based upon spherically-symmetric models is noted. The complications associated with cracking, polymerization, and fractional distillation make the effect of liquid composition upon the burning rate and mechanism one of the most difficult to determine a priori.

For a porous sphere, as the gas velocity is increased, an "extinction velocity" is reached at which the flame blows off of the forward part of the sphere and burning continues only in the wake. Theoretical and experimental results on the value of this extinction velocity and its dependence upon ambient temperature, ambient oxidizer concentration, and turbulence intensity are discussed. Measurements of the drag of burning wetted spheres are described, and the decrease in drag coefficient associated with wake burning is noted. This last effect may be of considerable importance in the spreading of fires.

In the practical application of these theoretical and experimental results on droplet combustion, the main difficulties are associated with the period of unsteady burning of single droplets, the changes in the physical properties of droplets (e.g., polymerization and selective vaporization of the more volatile liquid constituents), and the relation of the behavior of individual droplets to that of a spray. The unsteady period, which has not been described well theoretically, may compose nearly half of the total vaporization time. The formation of smoke and soot is often related to the accumulation of less volatile residues within the droplet; some work on the associated complex physical and chemical processes occurring inside and in the neighborhood of the droplet is cited. Some of the studies of the relation between the measurements on single droplets and the burning characteristics of sprays are mentioned. As the effects neglected in the treatments of sprays, the authors list the relative gas velocity, droplet interactions, flame extinction, heterogeneous combustion instability, and aerodynamic turbulence. Since the publication of this review, the first two of these effects have partially been included in spray analyses. But the authors' conclusion that the relatively large advances in the understanding of the combustion of single droplets does not enable us to predict the behavior of sprays in most practical combustors, will probably remain valid for a number of years.

Subject Headings: ***Droplets, combustion of; Liquids, burning of droplets.***

F. A. Williams

Gordon, A. S., Smith, S. R. and McNesby, J. R. (U.S. Naval Ordnance Test Station, China Lake, California) "Study of the Chemistry of Diffusion Flames," *Seventh Symposium (International) on Combustion,* London: Butterworths Scientific Publications, 317–324 (1959)

The authors' studies concerning the quantitative chemical mechanism of hydrocarbon diffusion flames, together with other studies, indicate that the rate determining reaction of the fuel molecules is their pyrolysis. These pyrolysis reactions can be quantitatively evaluated with analytical techniques which are presently available.

A conical flame, approximately one inch in diameter at the burner port, was probed by a small quartz tube. The burner was mounted on a micro manipulator so that various regions of the flame could be probed. Gas samples were analysed by using mass-spectrometric techniques and by gas chromatography. Peaks on the chromatography unit that could not be identified easily were trapped; the fraction was then identified by the mass spectrometer.

In all cases the normal pyrolysis breakdown of the fuel molecule was observed. The methane diffusion flame and the methanol diffusion flame were two of the technically important flames investigated. Major constituents inside the methane diffusion flame cone were obtained as a function of the fractional distance of the probe from the flame axis relative to the total distance from the axis to the edge of the luminous zone. Temperatures also were measured.

These data revealed six important conclusions. (1) Methane disappears very rapidly and it is at zero concentration level at the edge of the flame. (2) Water and carbon dioxide concentrations are at a maximum close to the edge of the flame. (3) Nitrogen is at a high concentration at all points in the flame. (4) There is always some oxygen in the samples. (5) The total oxygen, in both the combined and uncombined form, inside the flame cone compared to the nitrogen content at the same flame point is higher than the O_2/N_2 ratio in air. (6) Equilibrium constants for the water gas reaction were calculated from the concentration of CO, CO_2, H_2, and H_2O in the samples. Temperatures corresponding to the calculated equilibrium constants inside the flame cone were compared with the observed temperatures and they were always found to be several hundred degrees too high. Therefore, it was concluded that water gas equilibrium is not set up inside the flame mantle.

No oxygenated hydrocarbons were found. Special attempts were made to find formaldehyde in the flame without success. Large amounts of formaldehyde were easily detected when paraformaldehyde pellets were volatilized into the methane flame from the burner port.

Analyses of the methanol diffusion flames showed: (1) Formaldehyde is an important intermediary and it is relatively stable even up to 1150°C. (2) No ethane was detected although small amounts of ethylene and acetylene were noted. (3) Carbon monoxide and hydrogen are present in larger concentrations than in the methane diffusion flame.

In many of the flames studied the acetylene concentration increased with the tendency of the flame to form soot, in agreement with the mechanism suggested by G. Porter. The most glaring exception is the benzene diffusion flame. Unsaturated compounds must be present for carbon formation. The most likely way that carbon particles can be formed is via free radical polymerization, forming a polymer which does not depolymerize but rather dehydrogenates at higher temperatures. Ethylene, found in the flame, will add on radicals but at the observed flame temperatures the radicals should be unstable, and break down to ethylene and a small free radical. Acetylene offers a better path. By adding other acteylene molecules, a benzene free radical would be easily formed and would be resonance stabilized. Continued build-up of large condensed rings followed by carbonization through the loss of hydrogen in the hotter regions of the flame, accounts for the ability of benzene to carbonize readily.

In their free radical studies, the authors studied the Arrhenius factors for the abstraction of various types of hydrogen, mostly by methyl radicals. The abstraction of hydrogen atoms by the allyl radical was determined. In addition to the investigation of the pyrolysis of large free radicals, they also studied some additional reactions of free radicals to unsaturated compounds.

Subject Headings: ***Diffusion flames, chemistry of; Flame, chemistry of diffusion.***

L. E. Bollinger

Potter, A. E. Jr. and Butler, J. N. (National Aeronautics and Space Administration, Cleveland, Ohio) "A Novel Combustion Measurement Based on the Extinguishment of Diffusion Flames," *American Rocket Society Journal* **29,** 54–56 (1959)

A device is proposed for the measurement of relative reactivities of gas mixtures which are self-igniting or of very high reactivity. The measurements are made by studying the flame formed at the point of impingement of jets of the fuel and oxidizer. At sufficiently high flow rates, the flame at the stagnation point between the jets is extinguished. When this flame breakdown occurs, the average mass flow rate per unit area of the oxidizer and fuel near the stagnation stream lines is taken as a measure of the reactivity of the fuel-oxidizer system, and is called the flame strength. Justification for this identification of reactivity and flame strength is obtained theoretically from work of Zeldovitch * and Spalding † on diffusion flames. Experimental justification was obtained by the authors, who found that the flame strength was almost directly proportional to the rate of consumption of fuel in a laminar stoichiometric flame. The experiments were carried out using propane, cyclopropane, acetylene, and ethylene with air as the oxidizer. Although argon-"air" agreed with the other data, helium-"air" results did not.

The authors suggest that the device can be used to determine the relative reactivities of systems by comparison of their flame strengths; they also feel that the same type of information concerning kinetics of the combustion reaction which is derived from quenching distance and flame speed data may be obtained with the device. However, in view of the fact that the process of flame breakdown is

* Zeldovich, Y. B. *J. Tech. Phys.* Moscow, Vol. 19, No. 1199 (1949) Translated as *NACA Tech. Memo 1296* (1951)

† Spalding, D. B. *Fuel,* Vol. 33, No. 253 (1954) See also "Some Fundamentals of Combustion," *Academic Press,* New York, p. 215 (1955)

not understood, the extrapolation of results obtained with systems of hydrocarbon-air mixtures to systems of very high reactivity using different oxidizers still appears to be dubious. More experimental work is needed before the results obtained can be considered to be qualitatively correct for these more reactive systems.

Subject Headings: *Diffusion flames, extinguishment of; Extinguishment, of diffusion flames.*

E. E. Zukoski

V. Combustion Principles

Cheaney, D. E. (National Coal Board, Coal Research Establishment, Cheltenham, England), **Davies, D. A., Davis, A., Hoare, D. E., Protheroe, J., and Walsh, A. D.** (Queen's College, University of St. Andrews, Dundee, Scotland) "Effects of Surfaces on Combustion of Methane and Mode of Action of Antiknocks Containing Metals," *Seventh Symposium (International) on Combustion,* London: Butterworths Scientific Publications, 183–187 (1959)

The authors of this article present postulates and supporting evidence of their own or other researchers regarding the division of combustion-vessel surfaces into three categories, because these categories yield different kinetic laws governing the slow oxidation of methane. The surfaces in these categories are as follows:

Surface Category	*Compounds in Respective Category*
I	silicic acid, boric acid, phosphoric acid, germanium dioxide, and titanium dioxide
II	metallic oxides (and probably hydroxides) and salts in general
III	noble metals

This empirical division arises from the inhibiting effect of category II and III surfaces on the formation of the oxidation intermediates (HO_2 radicals and H_2O_2) as compared to the category I surfaces. Oxidation reactions in contact with category I (acidic) surfaces either preserve the HO_2 radicals or generate H_2O_2 and O_2 by surface reaction $HO_2 \rightarrow (HO_2)_{ads.} \xrightarrow{H+} \frac{1}{2}H_2O_2 + \frac{1}{2}O_2$ and do not destroy the generated H_2O_2. Category II surfaces donate electrons to the HO_2 radicals which results in a slower rate and a different order of reaction $HO_2 \rightarrow (HO_2)_{ads.} \xrightarrow{\epsilon} \frac{1}{2}H_2O + \frac{3}{4}O_2$ and is diffusion controlled. In addition, any H_2O_2 formed ($HO_2 + CH_4 \rightarrow H_2O_2 + CH_3$) is destroyed by a nondiffusion controlled surface process by surface-donated electrons $H_2O_2 \rightarrow (H_2O_2)_{ads.} \xrightarrow{\epsilon} H_2O + \frac{1}{2}O_2$. Category III surfaces follow the category II route except that the H_2O_2 is absorbed on the surfaces readily and its destruction rate is controlled by diffusion. Experimental evidence is cited to support these proposed routes of reaction. In addition, it is pointed out that if the surfaces of categories II and III were arranged in their order of effectiveness as catalysts for the heterogeneous destruction of H_2O_2, this order would be exactly the same as the order of effectiveness of those surfaces as inhibitors of the slow combustion of methane.

Following this groundwork, the authors develop a theory as to the mode of action of tetraethyl lead on the low-temperature ignition of paraffins in engines. Experimental evidence obtained from non-engine and engine test apparatus is cited to verify reasonably the theory. This theory is that when tetraethyl lead is oxidized in an engine, a lead oxide fog of solid particles is formed which provides the very short diffusion path required to inhibit the formation of the low-temperature chain carriers in the short period of the engine cycle. The authors state, further, that the theory is not surprising, since other antiknock metallic derivatives, as diethyl tellurium, pentacarbonyl iron, and tetracarbonyl nickel, are known or are strongly expected to produce similar fogs during oxidation. In addition, it is significant that the alkyls of bismuth, lead, and thallium are antiknocks and the alkyls of mercury are not, since the mercury derivatives are the only compounds which do not form solid particles of fog during oxidation. It is concluded, that if the above antiknocks perform their inhibiting action in the form of the metallic oxides, the effect on the kinetics of reaction should be those of the category II surfaces.

Subject Headings: ***Antiknock compounds, modes of action of; Methane, effect of surface on combustion of; Surface, effect on combustion of methane.***

R. A. Gorski

Falconer, J. W. and Knox, J. H. (University of Edinburgh, Edinburgh, Scotland) "The High-Temperature Oxidation of Propane," *Proceedings of The Royal Society* A250, 493–513 (1959)

The oxidation of propane at temperatures between 400 and 475°C was studied by means of a conventional static reaction system. Mixtures of gases were allowed to react in a Pyrex vessel in a furnace; gas pressures were followed during the course of the reaction, and the products of reaction after various time intervals were analyzed by gas chromatography and by volumetric methods.

Propane was found to be oxidized by a two-stage degenerately branching chain reaction, in the temperature range studied. In the first stage, propylene is formed by the action of HO_2 chain carriers on propane:

$$C_3H_8 + HO_2 \rightarrow C_3H_7 + H_2O_2 \qquad (1)$$

$$C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \qquad (2)$$

Some of the propyl radicals decompose to form formaldehyde, whose subsequent oxidation brings about chain branching:

$$C_3H_7 \rightarrow C_2H_4 + CH_3 \qquad (3)$$

$$CH_3 + O_2 + M \rightarrow CH_2O + OH + M \qquad (4)$$

$$CH_2O + O_2 \rightarrow 2 \text{ free radicals} \qquad (12)$$

As the oxidation proceeds, propylene accumulates and is removed to form alkyl and allyl peroxy radicals and higher aldehydes:

$$C_3H_6 + HO_2 \rightarrow C_3H_7OO \rightarrow C_2H_5CHO + OH \qquad (8a)$$

$$C_3H_6 + HO_2 \rightarrow C_3H_5 + H_2O_2 \qquad (8b)$$

These new free radicals and higher aldehydes, being more reactive than formaldehyde, take over the branching function, and cause the reaction to accelerate; this is the second stage of the oxidation.

Chain termination is brought about by destruction of OH and OH_2 chain carriers at the walls, a diffusion-controlled process.

Added carbon dioxide had a strong accelerating effect upon the oxidation at 460°C, increasing both the acceleration constant and the maximum reaction rate. This was explained as an inert-gas effect. Added chain-initiating substances (formaldehyde, acetaldehyde, propionaldehyde) indicated that the maximum reaction rate was limited both by consumption of reactants and by removal of branching intermediates. Added propylene, a known inhibitor for simple chain reactions, caused the propane oxidation to be accelerated; this was explained by the abstraction of OH and OH_2 chain carriers:

$$OH + C_3H_6 \rightarrow H_2O + C_3H_5 \qquad (18)$$

Although in a simple chain reaction this process would act to inhibit the reaction, in this degenerate chain-branching hydrocarbon oxidation, the less reactive allyl or alkylperoxy radicals would not be removed at the walls as readily as the OH and HO_2 radicals, resulting in longer chains and an accelerated reaction.

It is predicted that propane oxidation at temperatures above 475°C might show a third stage of reaction, based upon H_2O_2 branching.

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

B. Greifer

Zeldovich, Y. B. and Barenblatt, G. I. (Petroleum Institute, Academy of Sciences, USSR) "Theory of Flame Propagation," *Combustion and Flame* **3**, 61–74 (1959)

The paper deals with the conditions of steady-state propagation of flat flames. In more complex cases under this heading, where the Zeldovich-Frank-Kamenetsky approach cannot be applied, the authors consider the best method of solution to be that of numerical integration of the appropriate unsteady-state heat conduction and diffusion equations containing heat and species generation terms. This automatically secures entry into the steady-state propagation if such exists.* The method is also suitable for evaluating the condition for ignition.

The numerical integration method is used to investigate the effect on the velocity of propagation in a particular simple case where the mixture composition is described by the concentration of the main component of:

a) Varying the ratio of thermal diffusivity, K, to diffusion coefficient D. In agreement with earlier approximate theories, the velocity of propagation is proportional to $K/D^{1/2}$ for $0.5 \leqq K/D \leqq 2$.

b) The effect of heat loss. This leads to the conclusion that the steady state is only possible when the heat loss parameter is less than a critical value. The velocity of flame propagation and the flame temperature in the critical state are again in reasonable agreement with the predictions of Zeldovich from an approximate theory.†

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* Spalding, D. B. *Phil. Trans.* A249 (1956) 1

† Zeldovich, Y. B. *Zh. eksp. teor. Fiz.* 11 (No. 1) (1941)

The authors next deal with a slightly more complex system involving an intermediate product where the latter is produced and destroyed only by reactions which are first order with respect to itself. Again a steady state only exists when the rate of removal is less than a critical value.

The paper concludes with an analysis of the conditions of steady-state flame propagation for the simple problem with $K/D=1$ and properties dependent on one concentration only. The authors deduce that in the absence of thermal losses there is always a steady-state condition of propagation in this case. They feel that the conclusions of Rosen,* that instability is possible without heat loss, are based on an incorrect appraisal of the stability condition.

Subject Headings: ***Flame, theory of propagation of.***

G. Dixon-Lewis

Zeldovich, Y. B., Kogarko, S. M., and Simonov, N. N. "An Experimental Investigation of Spherical Detonation of Gases," *Soviet Physics, Technical Physics,* Vol. 1, No. 8 (August 1956) Translation of the Journal of Technical Physics of the Academy of Sciences of the USSR (Russian Original Vol. 26, No. 8 (1956) Published by the American Institute of Physics, Inc.)

This paper represents one of the clearest and most comprehensive coverages of the subject of spherical detonation appearing in the literature to date. There has been some controversy as to whether spherical detonation can occur at all. Among those who have claimed spherical detonations, reproducibility has been poor, and it has been difficult to correlate the occurrence of detonation with parameters such as the strength of the initiating source.

In addition to the fundamental interest in the subject, the authors point out that the possibility of spherical detonation is of great practical importance in industrial situations where large volumes such as containers or large sections of pipe filled with explosive mixture may be fed by a much smaller pipe. A plane detonation wave proceeding down the small pipe may initiate a spherical detonation wave upon entering the larger section. With this type of geometry, many previous workers have observed that the plane detonation wave collapsed upon leaving the small section and that only ordinary burning continued in the larger volume. They then concluded that a spherical detonation under these circumstances was impossible.

Zeldovich and co-workers did produce many instances of spherical detonations in a large vessel, supplied by a tube leading to the center of the vessel, with mixtures of several quite different fuels with oxygen. They found that spherical detonation waves were always produced in the larger volume, provided only that the diameter of the smaller tube exceeded a critical value, in which case the plane detonation wave proceeding from the smaller tube was sufficiently energetic. They were able to correlate this minimum detonating energy for a spherical wave with the energy required to initiate the plane detonation wave, the latter by a spark, igniter, or by spontaneous generation. In all cases the velocity of propagation of the spherical detonation wave was the same as that of the plane detonation wave which produced it. The occurrence of spherical detonation is independent of the diameter of the larger vessel, and of the ratio of diameters of the larger vessel and the small tube, and depends only on the diameter of the small tube.

Although the exact details of the initiation of the spherical detonation are not known, it appears that it may be correlated with the strength as well as the

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* Rosen, *J. Chem. Phys.* 22, 733, 743, 750 (1954)

diameter and thickness of the plane shock wave preceding the plane detonation wave. The thicker the shock wave, the more gas can be compressed per unit of time, a condition more favorable for initiating a spherical detonation. There is a measurable time lag, in the order of a few microseconds, between the visible collapse of the plane detonation and the appearance of the spherical detonation wave. This time lag as well as the minimum critical tube diameter are both increased by decreasing the "reactivity" of the mixture, *i.e.*, by going to slower burning fuels or by the addition of inerts.

Subject Headings: *Detonation, spherical, of gases; Gases, spherical detonation of.*

J. K. Richmond

Essenhigh, R. H. and Woodhead, D. W. (University of Sheffield, Sheffield, England) "Speed of Flame in Slowly Moving Clouds of Cork Dust," *Combustion and Flame* **2**, 365-382 (1958)

This paper reports observations and quantitative measurements of flame propagation for cork-dust clouds in air using photographic techniques. The cork dust was metered into the top of a vertical Pyrex tube (17 feet long and either 2 or 3 inches in diameter) where it fell freely through the air contained in the tube. The terminal velocity of the dust particles was of the order of 50 cm/sec. Butterfly valves and magnesium powder igniters at the top and bottom of the tube could be operated to give various combinations of upward and downward flame propagation and flame confinement. The progress of the flame was recorded as a function of time with a revolving-drum camera which covered a central 9-foot length of the flame tube. The vertically moving flame and the horizontally revolving drum generated a distance time trace, the slope of which was the flame velocity.

Analysis of the cork dust indicated an empirical formula of approximately $C_5H_7O_2$. The stoichiometric concentration of the material was 0.15 gm/1. Two levels of fineness were investigated. Both samples would pass through 30-mesh sieves, but one of the samples contained a considerable proportion of fines smaller than 120-mesh.

Flame speeds were found to accelerate for burning from a closed-end to open-end tube for both upward and downward propagation reaching values of greater than 2000 cm/sec and about 200 cm/sec respectively in contrast to flames burning open-end to closed-end in both upward and downward propagation which had relatively constant velocities of about 45 to 100 cm/sec and about 12 cm/sec respectively. The twentyfold difference in flame speed for the two types of confinement was thought to be caused by thermal expansion of the hot combustion gases, although a greater degree of turbulence may have increased the rate of flame propagation directly. Flame propagation was about 5 to 10 times faster in the upward direction than in the downward direction for both types of flame confinement. This suggested that, if propagation is mainly a thermal phenomenon, then it is significantly aided in upward propagation by convection.

More detailed quantitative experiments were carried out for upward, open-end to closed-end propagation (steady upward propagation flames). The lower concentration limit for flame propagation was 0.05 gm/1 for both the fine and coarse dust samples; an upper limit of 1.8 gm/1 was established for the fine sample only. Within these concentration limits, two distinct types of flame structure were observed which were independent of the fineness of the dust and tube diameters used. At dust concentrations between 0.05 and 0.1 gm/1 the flame zone was characteristically thin (10 cm.) relative to the thick flames (50 to 100 cm.) present at higher concentrations. Only the volatile components of the dust were thought to burn in the thin flames whereas the thick flames were composed of incandescent burning particles as well. Photographic evidence indicated that dust particles entering either type of flame were brought nearly to rest and then accelerated uniformly to the rear of the flame by the expanding combustion gases.

The flame speed increased uniformly with dust concentration and reached an optimum value at 1.1 gm/1 for the dust with fines and 0.6 gm/1 for the coarser dust. The optimum flame speeds were roughly double the value (35 cm/sec) at the low concentration limit and increased somewhat with fineness and tube diameter.

Subject Headings: *Flame speed, in cork dust; Dusts, flame speed of cork; Cork dust, flame speed of.*

C. P. Talley

VI. Radiation

Sleicher, C. A. and Churchill, S. W. (University of Michigan, Ann Arbor, Michigan) "Radiant Heating of Dispersed Particles," *Industrial and Engineering Chemistry* 48, 1819–1824 (1956)

The results of a theoretical investigation of the over-all process which occurs when a dispersion of solid or liquid particles in air is subjected to a radiant flux are presented. Consideration is given to the energy absorbed by the particles, their consequent rise in temperature and the transfer of energy from the particles to the air. Also, if the particles have an appreciable vapor pressure, the mass transferred to the gas phase becomes significant.

The protection of adjacent buildings against radiation from a fire with a spray of water droplets and the protection of cities against thermal radiation from a nuclear fireball with a smoke screen are but two of the possible applications of this analysis.

Rate mechanisms are postulated for each of the individual processes of radiation, conduction, and evaporation, and the problem is formulated in terms of differential energy and material balances for a single particle and the associated air.

It is first shown that the temperature distribution within a particle is sufficiently uniform so that its effect can be neglected at all times for either internal or surface absorption. For example, in a uniform radiant flux corresponding to radiation from surfaces at 2000° F., the maximum temperature difference within a spherical particle of coal 50 microns in diameter was calculated to be 0.78°F.

Initially, the effect of adjacent particles is negligible and the behavior of a dispersion is typified by considering a single particle in an infinite medium. The temperature history of the single particle is presented graphically in dimensionless coordinates. It is here indicated that equilibrium values of temperature are approached in five microseconds for one micron diameter fog oil, 16 milliseconds for the 50 micron coal and 50 milliseconds for 100 micron dodecane. The equations as developed here do not depend on the assumption of a constant heat transfer coefficient, but if such is assumed, considerable simplification results with an accompanying error of the order of 3 per cent.

A three term approximate equation is next developed for a dense dispersion of nonvolatile particles. Because the exponential term in this equation falls extremely rapidly, it is shown that in times of the order of 20 microseconds (for the fog oil) to 100 milliseconds (for the dodecane) the temperature of the particle rises to a pseudo-equilibrium value in which the energy received by radiation equals the heat lost by conduction. The temperature subsequently rises much more slowly as the conducted heat warms the finite amount of air associated with each particle. For these relatively long times, the linear term of the equation is controlling and the rate of rise becomes independent of the properties of the particle.

In the radiant flux corresponding to radiations from surfaces at 2000°F, this pseudo-equilibrium temperature rise is 310°F for the 50 micron coal particle, 34°F for the 100 micron dodecane, and less than 0.004°F for the one micron fog oil. Evaporation is neglected in the foregoing calculations. It is thus shown that it is not possible to heat a coal particle or oil droplet of the sizes considered to the ignition temperature without first heating the surrounding air. Indeed, the dispersion of absorbing particles is a very efficient air heater.

Consideration is next given to the effect of evaporation on a single volatile droplet in an infinite medium. The droplet is shown to approach a pseudo steady-state temperature which changes as evaporation decreases its radius. The calculation is next applied to a dispersion of droplets. From this analysis it is concluded that volatile droplets as well as nonvolatile particles below the sizes considered cannot be heated radiantly to the ignition temperature without first heating the associated air, the temperature rise increasing with radius and absorptivity and decreasing with volatility. For sufficiently volatile materials, the temperature may even remain below the ambient temperature.

Subject Headings: ***Particles, radiant heating of.***

A. Strasser

Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "The Absorption of Radiant Heat by Fire-Fighting Foam," *Journal of Applied Chemistry* 9, 265–268 (1959)

This paper is an attempt to correlate previous experimental work on the time of destruction of fire-fighting foam by radiation. The experimental results are presented in the form of a plot of relative heat resistance h (the ratio of the time measured for the destruction of the foam to the time calculated to evaporate the water content of the foam under similar conditions) against the product of expansion E (the ratio, by volume, of foam to liquid) and critical shearing strength q. By plotting in this fashion the results correlate quite reasonably, although no attempt is made to fit the best curve through the points to give a clear indication of the scatter involved.

The author also presents a theoretical study of the problem, which is based on a radiation balance within a layer of foam and on a study of transmission through an individual bubble wall. This leads to a curve for h against E·q which is superimposed upon the plot of experimental results. The deviation of theoretical from practical results, particularly at the lower values of E·q, is such that the theory is of little value for the accurate prediction of the practical performance of a foam. As suggested by the author, the discrepancy is probably due to the fact that the theory takes no account of drainage from the foam.

Subject Headings: *Foam, absorption of radiation by; Radiation, absorption by foam.*

R. G. Siddall

Sherman, R. A. (Battelle Memorial Institute, Columbus, Ohio) "Heat Transfer by Radiation from Flames," (A Summary of the Work of the International Flame Research Foundation) *Transactions of the ASME* 79, 1727-1741 (1957)

The author has provided, for the first time in the United States, a comprehensive account of the objectives, method of operation, and the results of the work of the International Flame Research Foundation. The Foundation's program of research on radiation from flames in industrial furnaces which has been conducted at the Royal Netherlands Blast Furnace and Steel Works appears almost unique as an example of international cooperation.

In November, 1955, the International Joint Committee for Flame Radiation, prior to that time a rather informal and loosely knit organization, was formalized by its registration in Holland as the International Flame Research Foundation. Its objectives are the attainment of knowledge and experience on the combustion of gaseous, liquid, and solid fuel, in particular as the combustion aims at the heating of materials, and the placing of that knowledge and experience at the disposal of others for further development and industrial application. The Foundation is nonprofit and is required by its charter to apply its income and property solely toward the promotion of its stated objectives.

The original experimental furnace and testing facilities installed by the Royal Netherlands Steel Works were used from the start of the work through 1953 for a series of seven sets of formal tests and much supplementary investigation. Since then, a new furnace for gas and oil studies, housed in a permanent special building 65 x 79 ft., has been available. The building also provides rooms for gas analysis, instruments, fuel pumps, and supplies. In an attached, partly enclosed structure is a plant for the preparation of pulverized coal, and at one side is an air preheater.

To obtain data on the radiating characteristics of the flames, which is the principal objective of the research, a series of ports in the form of vertical slots is provided in one wall of each furnace. By an ingenious arrangement, the radiometers can be moved up or down for a vertical traverse of the flame and the ports can be closed to avoid inflow of air.

Three types of radiometers have been built and used. One consists of a thermopile mounted on the end of a water-cooled tube which contains a series of diaphragms to limit the field of view of the thermopile. The second type uses a fixed-focus rhodium-plated mirror to reflect the radiation onto a thermopile. A third type is based on this same principle but is designed to measure radiation from two sources simultaneously. Electrically heated tube or sphere furnaces are used at frequent intervals for purposes of calibration of the radiometers.

Two general classes of tests have been made: (a) "performance" or "industrial" tests, and (b) "combustion mechanism" or "scientific" tests. The purpose of the performance tests is to determine the effects of certain variables, such as type of fuel, type of burner, type of atomizing agent, degree of mixing of air, excess of air, or rate of heat input upon the radiating characteristics of the flame.

It is to be expected that the results of such tests can be immediately applicable in industrial furnaces. Seven series of performance tests, each series consisting of many separate tests, had been completed through 1955.

The purpose of the combustion-mechanism tests is to examine a few flames in considerable detail. For example, the rate of mixing and the appearance and disappearance of carbon in the flame are studied both longitudinally and laterally and, by maintaining the radiation of small elements of the flame, an attempt is made to relate the carbon content and the radiating characteristics of the flame. Only two series of these tests have been made.

The factorial method of planning the experiments has been used in all series of tests. Thus, in a series of tests of five variables, 32 separate tests were so selected as to give all combinations of high and low values of each variable from which not only the effect of the high and low levels could be obtained but also the interaction of the several variables.

The data have been analyzed statistically and the confidence level of each derived data point has been calculated.

Because of the large number of data obtained from this research over the years, no attempt has been made in the author's paper to present other than certain high lights. The interested reader can consult the author's paper as well as the published British and French papers listed in the bibliography for details. In presenting the high lights of the results, the author has covered in a very clear manner the effects of the characteristics of the fuels used, the types of burners, the rate of firing, the type of atomizing agent, the method of mixing of combustion air, the amount of excess air, and the temperature of the combustion air. The need for further information on the relation between the radiating power of flames and the heat transferred to the work has been emphasized.

Several excellent discussions of this paper are available in the *Transactions of the American Society of Mechanical Engineers,* November 1957.

Subject Headings: *Flame, heat transfer by radiation; Radiation, heat transfer of flames; Heat transfer, by radiation of flames.*

E. C. Woodward, Jr.

VII. Suppression of Combustion

Levy, J. B. and Friedman, R. (Atlantic Research Corporation, Alexandria, Virginia) "Survey of Fundamental Knowledge of Mechanisms of Action of Flame-Extinguishing Agents: First Supplementary Report," *Wright Air Development Center, Aeronautical Laboratory Contract AF 33(616)–5569. WADC Technical Report 56–568* (September 1958)

This report is the second in a series of papers which survey current research in the field of flame extinguishment. It is presented in two parts; the first section is an extensive review of work directed toward the understanding of chemical agent action in extinguishing flames, and the final section is concerned with current efforts in relevant background areas. All work to May 1958 is included.

Volatile halogen compounds have been used by several researchers in studying the effects upon burning velocity and the lower pressure limit of flame propagation. The two approaches have yielded thus far inconclusive results. In the lower limit studies, methyl bromide was shown to be less effective in inhibiting the flame than methyl iodide even with the former additive present in much greater quantity. In the burning velocity studies, the two additives in *equal* amounts showed the bromide somewhat more effective than the iodide. The authors attempt an explanation for this phenomenon after noting other burning velocity results showing equal effectiveness for the two additives.

Work on the behavior of salts as extinguishing agents has not been too abundant. References on the subject are tabulated and one set of experiments with the system methane-air-aluminum chloride is described in some detail.

Water vapor is discussed as a chemical agent for extinguishing flames. Though it is commonly considered chemically inert, the authors cite dissociative products of water at flame temperature reacting with other molecules and fragments of molecules in the flame. Two papers are briefly described where water vapor was used in studies on the lean flammability limit and ignition at relatively high temperatures (to 287°C).

The final section of this report gives an excellent survey of "current research in relevant background areas." Here a brief resume of current thinking on steady-state flame propagation is presented, and an extensive discussion on the controversial theory of flammability limits is given. New experimental flame-research techniques are discussed including flame sampling techniques, emission, and absorption spectroscopy, ionization kinetics, and temperature gradients measurement by a refractometry method.

Other topics covered are: cool flame phenomena, flames involving unusual fuels or oxidants, and combustion reaction mechanisms. Little progress has been made on this last subject, but the problem is being attacked from many angles in many laboratories.

In summary, this paper is a very good account of current research on flame extinguishment by chemical agents. In addition, it is a good review of all combustion work relevant to the primary topic. An extensive bibliography of 80 items makes the paper useful for almost everyone concerned with fundamental combustion problems.

Subject Headings: *Flame, extinguishment, mode of agents; Extinguishment, of flames, mode of agents.*

R. O'Neal, Jr.

Rosser, W. A., Wise, H., and Miller, J. (Stanford Research Institute, Menlo Park, California) "Mechanism of Combustion Inhibition by Compounds Containing Halogen," *Seventh Symposium (International) on Combustion,* London: Butterworths Scientific Publications, 175–182 (1959)

This group has reported earlier on the inhibition by halogen-containing compounds of the burning in air of liquid ethanol droplets.* In the present paper the inhibition of methane-air and ammonia-air flames by volatile halogen-containing compounds was investigated. Flame speeds were measured using the bunsen burner method. It was found that the addition of a few hundredths of a per cent of halogenated compound effected a linear decrease in the burning velocity of both of the above flame systems. The slope of the curve of burning velocity *vs.* per cent

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* Wood, B. J., Wise, H., and Rosser, W. A. "Burning of a Liquid Droplet. IV. Combustion Inhibition in a Fuel-Oxidizer System," *Journal of Chemical Physics* 27, 807–808 (1957)

added inhibitor was taken as a measure of the inhibitor effectiveness. The inhibitors examined were methyl bromide, dibromodifluoromethane, trifluoromethyl bromide, bromine, methylene bromide, tribromomethane, chlorobromomethane, methyl iodide, and isopropyl iodide.

In addition to flame speed measurements, flame temperatures were measured for methane-air flames with and without added methyl bromide and added hydrogen bromide. Spectroscopic measurements of the effect of inhibitors on the OH, C_2 and CH emission were also carried out.

The general conclusions reached were: (a) compounds containing iodine and bromine were about equally effective, both being much more effective than chlorine-containing compounds; (b) for bromine-containing compounds the flame-inhibiting effectiveness was proportional to the number of bromine atoms per molecule; (c) inhibition by these agents was not accompanied by any reduction in flame temperatures; (d) the spectroscopic observations were quite inconclusive for C_2 and CH but the OH concentration decreased with added inhibitor.

These results are similar to those reported by Simmons and Wolfhard * and support the general picture that it is the halogen atom or some halogen compound that is the effective inhibiting agent rather than the particular starting substance. The authors have taken this concept further and propose very plausibly that it is the hydrogen halide that interrupts chain reactions and lowers the flame speed. They point out that at the temperatures involved in these flames it would be expected that halogenated hydrocarbon inhibitors, such as methyl bromide, for example, would be converted, either by thermal decomposition or by the attack of various species present, to hydrogen bromide. The reaction between an active species and the hydrogen halide would occur as follows, using OH as an example:

$$OH + HBr \rightarrow HOH + Br \qquad (a)$$

$$Br + RH \rightarrow HBr + R \qquad (b)$$

where RH is any hydrogen-containing species. The net result is to replace OH by a less active species Br or R. For the case of an alkyl chloride inhibitor, the H-Cl bond is so strong that step (a) is too slow. The H-Br and H-I bond strengths are smaller and hence those species are more effective. The spectroscopic observation that the concentration of excited OH in the flame was lowered by the addition of inhibitors is in harmony with this picture.

Subject Headings: ***Inhibition, of flames by halogen-containing compounds; Halogenated compounds, inhibition of flames by.***

J. B. Levy

van Tiggelen, A. (University of Louvain, Louvain, Belgium) "The Kinetics of Flame Inhibition," *Final Technical Report I, Office, Chief of Research and Development, U.S. Department of Army, European Office Contract DA-91-EUC-295* (March 1959)

This paper represents an extension of the general theory of laminar flame propagation, reviewed in *Fire Research Abstracts and Reviews* Volume I, No. 3, page 109, to a general interpretation of the inhibition of flame reactions by the introduction of a third substance.

In the general theory, combustions and flames are regarded as branched chain

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* Abstract: FIRE RESEARCH ABSTRACTS AND REVIEWS, Volume I, No. 1, p. 19 (1958)

reactions. If δ is the probability of chain branching and β is the probability of chain termination, then explosion or flame propagation will occur when $\delta-\beta\geqq 0$. The number of chain carriers will increase and the result will be a very large increase of reaction velocity. There will be a limitation due to losses of energy by radiation, conductivity, etc., but the flame will propagate with a finite velocity. Using this concept an expression for the propagation velocity V_0 is derived from simple kinetic theory in terms of β and δ.

$$V_0=4\frac{T_0}{\pi}\sqrt{\frac{2R(\delta-\beta)}{3MT}}$$

Methods of calculating values of the mean temperature T, mean molecular weight M, are given, and also δ in terms of the activation energy and lifetime of the reacting species.

The presence of a small quantity of inhibitor will mainly effect the parameters δ and β. The chain termination probability β will be increased leading to a narrowing of the flammability limits. The chain branching probability δ will be altered, most likely decreased, resulting in a decrease of propagation velocity. If the concentration of inhibitor is not small then the flame temperature and the mean molecular weight of the chain carrier may be altered. The chain termination probability β increases in the presence of an inhibitor because of the appearance of a carrier consuming reaction. If β is considered as a sum $\beta=\beta_n+\beta_t$ where β_n is the value of β in the absence of inhibitor while β_t corresponds to the significant increase of β due to some reaction between the inhibiting substance I and the chain propagating radicals R, significant inhibition occurs when $\beta_t \gg \beta_n$.

In a reaction scheme

$$I+R\rightarrow I'+F$$
$$I'+R\rightarrow G+I$$

the inhibitor is not consumed by the inhibiting reaction and its concentration remains practically unchanged through the flame. This is a necessary condition for an inhibitor which is able to suppress completely the onset of an explosion. If E_t is the activation energy of the inhibiting reaction, the value β_t is given by

$$\beta_t=\frac{(I)}{p}e^{-E_t/RT}$$

thus for suppression of ignition $\beta_t>\delta$. An expression for δ is given in similar form.

It may well be that the initial inhibiting substance is only active either by its dissociation products or by some product which is formed in its reaction with one or both constituents of the flammable mixture. Thus the species I does not necessarily represent the primary added substance.

The inhibition by solid particles can be explained if it is assumed that any collision of a chain carrier with a surface leads to chain termination. A calculation to determine the minimum weight of solid required to give inhibition is stated.

In general when a third substance is added to a binary flammable mixture, the reactions of this new component must be considered and will interfere with the reactions of the fuel (and/or the oxidant) molecules with the chain carriers: the propagation of the chain will be perturbed by the presence of some new radicals (or atoms) in the flame front and new propagation steps will have to be considered. In the general case of a substance J interfering in the reaction of A (oxidant) and B (fuel) the possible reaction scheme can be illustrated thus:

alongside is the simple reaction scheme of H_2/O_2 mixture in the presence of Cl_2 which is the first of the experimental systems studied. Z represents a new radical (or atom) whose formation alternates with that of X and Y.

Chain propagation

$$B+Y \rightarrow X+C \qquad\qquad H_2+HO_2 \rightarrow H_2O_2+H$$

$$A+X \rightarrow Y+D \qquad\qquad H+O_2 \rightarrow HO_2$$

Reaction due to J

$$J+X \rightarrow Z+K \qquad\qquad H+Cl_2 \rightarrow HCl+Cl$$

$$Z+B \rightarrow X+L \qquad\qquad Cl+H_2 \rightarrow HCl+H$$

Branching reaction

$$X+A \rightarrow E+2Y \qquad\qquad H+O_2 \rightarrow HO+O$$

$$\left\{\begin{array}{l} O+H_2 \rightarrow OH+H \\ OH+H_2 \rightarrow H_2O+H \end{array}\right\} 2H$$

Branching probabilities are calculated in terms of the lifetime of the radicals and their activation energies with inhibitor present and absent. With inhibitor present the lifetime of radical X will be shortened by reaction with inhibitor J.

The interference of elementary reactions in the presence of an inhibitor may be considered as a particular case of the more general behavior of ternary flammable mixtures. Since H_2/Cl_2 mixtures are themselves flammable it is reasonable to ask why Cl_2 acts as a real inhibitor in the H_2/O_2 flames as the experimental evidence shows it to do. Explanation of this in terms of reaction kinetics is sought by considering two kinds of ternary mixtures; either mixtures of two different fuels (B and B′) and one single oxidant (A) or a mixture of two different oxidants (A and A′) and one single fuel (B). The interference due to reaction kinetics can be explained by considering only mixtures which are stoichiometrically equivalent: in this case any ternary mixture may be considered as being formed by combining two binary flammable mixtures of the same strength. If two stoichiometric mixtures are considered of M (A+B) and M′ (A+B′), for each mixture there will be a burning velocity V_0, V'_0 and a flame temperature T_f, T'_f. If a ternary mixture of X per cent of M and (1−X) per cent of M′ is prepared, the final flame temperature is assumed to be given by linear interpolation, but any linear interpolation of the burning velocity V_0 is most improbable because of the exponential dependence of burning velocity on temperature. Examples are given of all the possible variations of V_0 with X and it is shown how this variation from linear interpolation can give rise to inhibiting effects.

The preliminary experiments have been made on hydrogen-oxygen flames inhibited by chlorine. The inhibiting properties of halogen compounds on hydrogen and hydrocarbon/oxygen flames have been attributed to the presence of halogen atoms in their molecule; thus it is assumed that the real active species are some very simple halogen containing molecules which are formed in the thermal decomposition of the initial parent inhibitor molecule in the flame front. A systematic study of the inhibiting effects on the H_2/O_2 reaction of the halogens is to be undertaken, followed by that of the halogen halides. A further advantage of a study of $H_2/X_2/O_2$ mixtures (X=halogen) is that all possible species in the flame front, H_2, O_2, X_2, H, O, X, OH, HX, HO_2 are known and halogen-oxygen compounds can be disregarded because of their instability.

The flame velocities were determined by the total area method, applied to the schlieren image, the surface of the flame cone was calculated on a tenfold enlargement of the photographic image, each result being the average of three measurements. A stainless steel water jacketed burner was used, 0.4 cm. diameter and 1 meter long, its mouth having a conical shape to obtain a better laminar gas flow.

The flame speeds of a range of H_2/H_2+O_2 compositions with an amount of chlorine additive from 0 to 4 per cent are quoted. The flame speed is shown to be markedly decreased with 1 per cent chlorine addition, increasing again with further addition. The inhibiting reaction seems to be greatest in a mixture which is a little leaner than the stoichiometric.

Flame temperatures for the mixtures have been calculated assuming additive properties of the temperature and are combined with the measured flame speed to give an activation energy. The results show that the activation energy does not vary linearly from pure H_2/O_2 to pure H_2/Cl_2 but reaches a maximum at about 40 per cent of the stoichiometric H_2/Cl_2 mixture. It appears that the inhibition of Cl_2 on H_2/O_2 is stronger than that of O_2 on H_2/Cl_2.

Further investigations into the band spectra emitted from flames with inhibitors present are planned. Preliminary results also show a marked decrease in ion concentration in halogen containing flammable mixtures.

Subject Headings: ***Flame, inhibition, kinetics of; Inhibition, of flames, kinetics of.***

G. L. Isles

Laffitte, P. and Bouchet, R. (University of Paris, Paris, France) "Suppression of Explosion Waves in Gaseous Mixtures by Means of Fine Powders," *Seventh Symposium (International) on Combustion,* London: Butterworths Scientific Publications, 504–508 (1959)

The authors report a series of experiments on the extinction of flames propagating at high velocities under conditions where the velocities of the deflagration and detonation fronts are measured just before the quenching occurs. The flame velocities were measured by the chronophotographic recording method of Mallard and Le Chatelier.

In one series of experiments, the extinguishing material was placed on a small brass plate within a horizontal glass combustion tube. The distribution of the quenching material into the quenching area depended upon the shock disturbances preceding the deflagration waves and flames in the predetonation period. Quenching with potassium oxalate (25-micron particle size) was observed only for accelerating flame fronts in methane-oxygen and propane-oxygen mixtures where the velocity was not greater than 450 m/sec at the time of quenching.

Because at very high flame velocities, the quenching material was probably not distributed in the gas mixture before the flame front passed, a second series of experiments was undertaken in a vertical combustion tube equipped with a device to drop known quantities of dust into the top end as an explosion wave was ignited simultaneously at the bottom end. The propagation of the explosion was recorded chronophotographically on the rotating drum of a film recorder so that the velocity of the wave as well as the extinction of the wave could be determined as it traveled through the quenching cloud. In this manner, it was possible to quench detonation waves in all cases studied whatever the combustion wave velocity.

The effect of surface area of particles of silica and potassium chloride on detonation quenching was studied in a methane-oxygen-nitrogen mixture supporting a 1850 m/sec detonation wave. It appears that in these cases the minimum quantity of material producing quenching is inversely proportional to the surface area of the particles.

The effectiveness of different materials of equal particle size (10–20 microns) was studied in the same methane-oxygen-nitrogen mixture. In order of decreasing effectiveness in quenching detonations (in terms of surface area of quenching material), the materials studied were: silica, potassium bicarbonate, potassium bitartrate, potassium oxalate, potassium chloride, and sodium bitartrate.

The quenching of explosion waves in different mixtures of oxygen with hydrogen, methane, propane, isobutane, acetylene, and diethyl ether was studied using potassium bitartrate (10–20 microns) as the quenching material. The minimum quantities of potassium bitartrate required to quench the detonations vary with composition of the oxygen-fuel composition showing maxima at approximately stoichiometric compositions. These maxima do not coincide with the observed maxima in flame speed which occurred in fuel rich mixtures.

Subject Headings: ***Powders, suppression of explosion waves by; Extinguishment, of explosive waves by powders; Explosions, suppression by powders.***

L. R. Griffith

Dolan, J. E. (Imperial Chemical Industries, Stevenston, Scotland) "The Suppression of Methane/Air Ignitions by Fine Powders," *Sixth Symposium (International) on Combustion,* New York: Reinhold Publishing Corporation, 787–794 (1957)

Resuming work by Dolan and Dempster,* Dolan describes a refined experimental set-up for measuring the influence on flame speed of the addition of uniformly dispersed suspensions of alkali halide and other salt powders as function of gas composition and particle surface area per unit volume. The latter quantity had been found decisive in the earlier work, justifying its preference over weight concentration and particle size as parameters. The surface area was determined by the air permeability method.† The flame velocity was observed in a vertical glass cylinder of 7 cm. diameter and measured by the time interval for passage of the flame between two phototubes at 20 and 35 cm. distance from the point of initiation (or, in not specified cases by rotating film photography). The same tubes served, before ignition, for the measurement of dust concentration by the photoextinction method. Powders are injected by the flow of the gas mixture through a small volume receptacle (dust generator) into the evacuated test tube. The particle size of the applied powders was chosen within a narrow range (no data given) after treatment in a high speed hammer mill (and in certain not specified cases by subsequent air elutriation). Four initiation methods were employed: (a) a charcoal-potassium chlorate fusehead; (b) a gasless fusehead containing a 50/50 cerium/magnesium alloy and red lead; (c) a capacitance spark discharge of 16μf at 1.5 kv.; (d) the same as (c) fired at the closed end of a

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* Dolan, J. E. and Dempster, P. B. *Journal of Applied Chemistry* 5, 510 (1955)

† Rigden, P. J. *Journal Society of Chemical Industry* 62, 1 (1943)

horizontal, 2.5 cm. diameter, 16 cm. long side tube filled with dust-free gas, the ignition source being the flame advancing into the dust laden mixture. Ignition was initiated either at the closed bottom (I) or at the open end (II).

I. "Constant" Speed Flames.

For a 10 per cent methane-air mixture flame speeds of 70, 75, and 220 cm/sec were observed with ignition by (c), (a), and (b). However the flame velocity through dust laden gases was found independent of the source. The dust concentrations required for flame suppression are considerably less (about ½) than for accelerated flames, but depend on the mode of ignition, being smaller for (a) than for (c) (about ⅓ to ½). The sequence of efficiencies of different salts is the same as for II.

II. "Accelerated" Flames.

For a nearly stoichiometric mixture, flame speeds of 44, 73, 80, and 85 m/sec result from (a), (d), (c), and (b). Correspondingly smaller velocities are measured with other methane concentrations in the same sequence of magnitude. On injection of dust the flame speed reduces; with increasing concentration it passes through a quenching range before the flame fades out entirely at a well-defined suppression point which is not affected by the mode of ignition.

As it was found that quenching of accelerated flames, regardless of the salt applied, occurs at about the same flame speed and temperature, a thermal (cooling) mechanism seems to suggest itself. If that is true the computed temperatures associated with different suppressing agents ought to be the same. This assumption is ruled out by comparison of the behavior of iron oxide and the alkali halides. As a significant result, the constancy of dust surface area with variation in particle size (data for NaCl and $NaHCO_3$) is confirmed. The most efficient agent is $AlCl_3$, followed by KF, KI, cryolite, KCl, $NaHCO_3$, NaCl, NH_4HCO_3 while NH_4Cl is inefficient. Of these compounds $AlCl_3$ has the lowest boiling point (183°C). Contrary to observations by Lafitte and co-workers, Dolan finds the potassium salts superior to sodium salts ($KHCO_3$ was not tested).

Dolan's work originated from interest in the improvement of sheathing materials for permissible explosives. He justly advises the replacement of conventional substances by more efficient agents.

Subject Headings: *Suppression, of ignition by powders; Powders, suppression of ignition by; Ignition, suppression of, by powders.*

H. M. Cassel

McCamy, C. S., Shoub, H., and Lee, T. G. (National Bureau of Standards, Washington, D.C.) "Fire Extinguishment by Means of Dry Powder," *Sixth Symposium (International) on Combustion,* New York: Reinhold Publishing Corporation, 795–801 (1957)

A common type of commercial fire extinguisher is charged with a dry powder known as "dry chemical" (*i.e.,* finely ground sodium bicarbonate with small amounts of additives to improve flow properties) which is expelled by the discharge of compressed gas. Numerous experiments have demonstrated the effectiveness of such extinguishers in fighting flammable liquid fires (*i.e.,* one series of tests on commercially available 4 to 5 pound dry chemical extinguishers proved them equal to 10 pound carbon dioxide extinguishers on flammable liquid fires of ten different conformations).

It is sometimes proposed that the sodium bicarbonate decomposes when heated and liberates enough carbon dioxide to extinguish the fire. If it were completely decomposed, the sodium bicarbonate would only liberate about 26 per cent of its weight as carbon dioxide. Sampling after actual extinguishment has shown that less than 4 per cent by weight of the powder is liberated as carbon dioxide.

Thus, the carbon dioxide theory does not account for a large part of the dry chemical's extinguishing action. The objective of this work was to determine the mechanism of dry chemical extinguishment.

A brief consideration of the general nature of flammable liquid fires has prompted the authors to suggest some mechanisms of extinguishment. Among the physical methods suggested are: (1) Throttling—the influx of fuel is stopped; (2) Cooling—heat is removed until combustion ceases; (3) Blowing-out—the velocity of the gaseous fuel or air exceeds the velocity of the combustion wave and the combustion wave recedes, finally disappearing as a result of other mechanisms; (4) Smothering—the influx of air or oxygen is stopped; (5) Diluting—inert gas is mixed with the atmosphere; (6) Shielding—material is interposed between the flame and the fuel to prevent the transfer of energy by radiation. Chemical mechanisms of extinguishment include: (1) Chain-breaking—material is introduced into the flame so that potentially reactive particles encountering this material will not propagate the reaction chain; (2) Preferential oxdiation—a material with a strong tendency to unite with oxygen is introduced into the flame so that the available oxygen combines with the extinguishing agent rather than with the fuel.

The results of the authors' preliminary experiments (*i.e.*, a comparison of the effectiveness of a variety of powders in extinguishing gasoline fires) indicated that the mechanisms of throttling, cooling, blowing-out, smothering, and diluting are of minor importance if operative at all. Since the preferential oxidation theory was inapplicable to the best dry powders tested, the list of mechanisms under consideration was reduced to two principal mechanims, shielding and chain-breaking.

In order to determine the possibilities of the shielding hypothesis, measurements were made to determine how much of the incident radiant energy would be transmitted without deviation through a cloud of powder and how much would be deflected through various angles. The uncertainties involved in interpreting laboratory data in terms of fire-fighting conditions made it desirable to simulate actual conditions. A group of measurements was made of the effect of dry chemical on the radiant energy from a flame during actual extinguishment. The objective was to determine how much of the energy radiated toward the fuel was transmitted by the dry chemical cloud. Since quantitative considerations of the mechanism of extinguishment hinge upon knowledge of the concentration of material required for extinguishment, optical methods were employed to measure several related physical quantities from which the concentration was calculated.

The experimental evidence indicates that the mechanism of dry powder extinguishment is not principally that of excluding oxygen, diluting the atmosphere, cutting off the fuel supply, or blowing out the fire. In the light of prevailing theories of combustion and flame propagation, it appears that dry-powder extinguishment may be largely attributable to the interruption of chain-reactions in the combustion process. The rapidity of the action, the apparent dependence of effectiveness on fineness, and the small concentration required, as determined in these experiments, seem to support this view. However, it appears that a full account of the mechanism of dry-powder extinguishment of flammable-liquid fires must also include the factor of radiation shielding.

Subject Headings: *Powders, fire extinguishment by; Fires, extinguishment by powders; Extinguishment, of fires by powders.*

E. C. Woodward, Jr.

Scheichl, L. "Types, Mode of Action and Limits of Applicability of Dry Fire-Extinguishing Powder," *VFDB Zeitschrift* 6, 111–117 (1957) U.S. Naval Research Laboratory Translation No. 654

Sodium bicarbonate has long been known as a chemical for dry fire-extinguishing powder. By the end of World War II, equipment for projecting it pneumatically in air, with carbon dioxide or nitrogen as carrier gases, was developed and the method established its place competitively for liquid and gas fires of relatively minor dimensions, and for fires in textile mills. Subsequent improvements have multiplied the effectiveness of powder extinguishers by factors of four or five and have made them suitable for larger fires in oil wells, refineries, and aviation accidents. Mobile units up to 250 kg. capacity and vehicles to dispense as much as 1500 kg. of powder were developed. Recently sodium bicarbonate powders have been partly replaced by ABC extinguishing powders that are effective against Class A fires in combustible organic solids like wood as well as for the liquid and gas fires, Classes B and C.

Sodium bicarbonate for extinguishing powder should contain at least 50 per cent of unground, well-formed monoclinic prismatic crystals of 0.05 mm. average particle size with the ratio of smallest to largest particle diameter not greater than 1:10. The balance may consist of coarser crystals that have been ground in a rod mill or hammer mill, but not in a friction mill, to a grain size equal to that of the smallest natural crystals. Such powders have best "quasi-liquid" transport in pneumatic equipment and give best "fullness" and effectiveness in the dust cloud. Transport characteristics may be improved by fine-grained additives such as calcium carbonate, silicates, magnesium carbonate, or phosphates. Water repellency is imparted by 0.5 to 2 per cent of fatty substances, waxes, sulfonates, magnesium stearate, and the like, in such manner as to coat the powder grains.

ABC powders contain additional fireproofing salts to suppress afterglow in solid fuels. A typical formula discloses sodium bicarbonate, sand, ammonium sulfate, alkaline earth carbonate, and sulfur. The sulfur together with the alkaline earth sulfate presumably formed on heating makes a crust over the burning solid to prevent reignition. A commercial ABC powder that prevents reignition by foaming contains urea-formaldehyde resin and phosphoric or boric acids and their compounds.

The extinguishing action of powders depends on their anticatalytic and suffocating effects. In the anticatalytic or antioxidant effect, the dust particles furnish "walls" at which the chain reactions of combustion are terminated. Gaseous decomposition products also may inhibit flaming. Glow inhibitors in ABC powders exert an antipyrogenic effect at the surface of burning solid. In the suffocating effect combustion is suppressed by exclusion of air by the powder, its carrier gas, and decomposition products and the burning solid is isolated by formation of crusts or foams. Cooling by absorption of heat in decomposition of the powder is negligible. There exists a "turbulence layer" effect whereby the dust cloud facilitates dissipation of heat from burning fuel, and a "damming effect" whereby blister layers of crust or foam retard absorption of the heat from the flame zone by the solid fuel.

Dry powder extinguishers are not yet entirely satisfactory for extinguishing burning light metals, electrical installations, or carbon disulfide fires.

Subject Headings: ***Powders, mode of action of extinguishment of; Extinguishment, mode of action of powders in.***

F. L. Browne

Palmer, K. N. (Joint Fire Research Organization, Boreham Wood, England) "The Quenching of Flames by Wire Gauzes," *Seventh Symposium (International) on Combustion,* London: Butterworths Scientific Publications, 497–503 (1959)

The purpose of this paper is to provide fundamental information which might lead to a relation between the performance of wire gauze flame arresters and the properties of the flames, the nature of the explosive gas mixtures, and the dimensions of the systems in which the arresters were installed. The fuels used were propane, ethylene, and town gas, mixed with air and, for faster flames, enriched with oxygen. Brass, steel, and phosphor bronze gauzes of various meshes were employed, both singly and in packs. The gauzes were sandwiched tightly between two sections of Perspex tube, both of 6.4 cm. diameter, and 58.5 and 111.5 cm. long, respectively. Either length could be used as the run-up length, the other end of the tube being closed. Ignition was by a gas flame at the open end of the tube. Both upward and downward propagation were studied. Flame velocities about 1.5 cm. in front of the gauze surface and, if the flame passed through the gauze, about 1.5 cm. behind the latter, were measured by recording the flame movement on a rotating drum camera. The gauzes were washed with carbon tetrachloride before use. When multiple layers of coarse gauzes were used the meshes were aligned and the edges soldered together. Multiple layers of thin gauzes were not used due to the difficulty of obtaining alignment.

The authors found that there was a critical velocity of approach of a flame below which the flame was quenched and above which the flame passed through the arrester. If the flame did not pass through the gauze, the damage to the latter was small, consisting only of slight discoloration of the very fine gauzes. Gauzes coarser than 18-mesh were not much damaged by flames passing through them, but gauzes finer than 60-mesh were usually destroyed, with emission of light from the molten metal. Gauzes of intermediate mesh were often split.

With single layers of gauze the critical velocity of approach of the flame was approximately inversely proportional to the width of the mesh of the gauze, over a wide range of mesh sizes. The relation between the critical velocity and mesh width was similar for the propane, ethylene, and town gas flames and was very little affected by change in the direction of propagation and length of the run-up of the flame to the gauze. Brass and steel gauzes gave similar results, mesh widths of, for example, approximately 0.02 cm. and 0.2 cm. giving rise to critical velocities of 2000 and 100–150 cm. sec.$^{-1}$, respectively.

If coarse gauzes (10 mesh) were built into multiple layers, the critical flame velocity for quenching of upward propagating propane flames increased slightly at first but then became constant, so that after three layers there was no further increase in effectiveness. The critical velocity had then increased from about 170 cm. sec.$^{-1}$ for a single gauze to just over 300 cm. sec.$^{-1}$ Again for propane flames propagating upwards, combinations of coarse gauzes and a fine gauze were less effective than the fine gauze alone.

The results for propane flames were found to be in general agreement with a simple theory based on the assumption that the quenching results from the abstraction of heat from the flames by the wire gauze.

Subject Headings: ***Extinguishment, by wire gauzes.***

G. Dixon-Lewis

Hough, R. L. (Wright Air Development Center, Wright-Patterson Air Force Base, Ohio) "Tests of Fire Extinguishing Agents for Magnesium Fires," *Wright Air Development Center Technical Note 59–71* (March 1959)

In the discussion of the investigation background, the author cites the desirability of a liquid rather than a powder extinguishing agent for magnesium fires, since a liquid may more easily penetrate cracks and crevasses than a powder. The investigation was then undertaken with six liquid agents: tricresyl phosphate, triethylene glycol to which 1.65 lbs. orthoboric acid were added per gallon, mixture of 50 per cent di-isodecyl phthalate and 50 per cent bromochloromethane, mixture of 50 per cent di-2-ethylhexyl phthalate and 50 per cent bromochloromethane, trimethoxyboroxine, and a 50–50 per cent mixture of trimethoxyboroxine and bromochloromethane.

A standard test fire was made using AZ91 and AZ92 magnesium alloy castings. The castings, weighing about 2¼ lbs. each, were hollow with open ends and square cross sections, 4 in. by 4 in. by 6 in. and ⅜ in. wall thickness. For the test fire, four castings were placed in a pan of 2 sq. ft. surface area with a rim 2 in. high. Two castings were placed in the pan with the 6 in. dimension vertical, with the corners touching. The two remaining castings were placed such that each rested on one of the bottom castings with their sides at 45° to those of the bottom casting. Two gallons of fuel, 80 octane gasoline, JP-4, or 100–145 octane gasoline, were poured into the pan and ignited to start the test. Reorientation of the castings was made during the burning of the hydrocarbons if deemed desirable to facilitate the ignition of the magnesium. Pan fires with only JP-4, and aircraft tire fires were also used in the evaluation of the liquid extinguishing agents.

The first series of magnesium fire tests were conducted using a fixed pattern spray distributer to apply the liquid agents, but this series was inconclusive since much of the liquids was dispersed outside the test fire area. With tricresyl phosphate it was reported that obnoxious by-products were formed and no further testing with this liquid was undertaken. Unfortunately, no discussion of the nature of the by-products was presented. The mixtures of di-isodecyl phthalate with bromochloromethane and di-2-ethylhexyl phthalate were analogous in their effect, and since the latter mixture is less costly and has lower viscosity at lower temperatures, it alone was retained for further evaluation.

In the second series, a manually manipulated applicator was used to direct the liquid agents onto the test fires. In these tests, it was decided to delete the triethylene glycol and orthoboric acid mixtures from the study because crystallization in long-term storage was observed.

In the final series of tests, the agents were discharged manually onto the test fires from maintained pressure type extinguishers with one to two gallon liquid charges. The JP-4 and the tire fires were included in this series.

From the tests conducted, it was concluded that the mixture of di-2-ethylhexyl phthalate and bromochloromethane applied as a coarse spray in short bursts was the most promising in the extinguishment of magnesium fires. The other fuel fires may also be extinguished by this mixture.

Disadvantages of trimethoxyboroxine were discussed, *i.e.,* corrosive effect, low temperature instability, high viscosity at low temperature, and higher cost than the above phthalate mixture.

A discussion is given to explain the observed delay in ignition of the bottom magnesium castings in the test configuration until after the combustion of all the hydrocarbon fuel.

Subject Headings: *Extinguishment, of magnesium fires; Magnesium, extingushment of fires of; Fires, magnesium, extinguishment of.*

J. E. Malcolm

Jablonski, E. J. and Gipe, R. L. (U.S. Naval Research Laboratory, Washington, D.C.) "A New Method for Determining the Degree of Compatability of Dry Chemical Powders with Mechanical Foams," *U.S. Naval Research Laboratory Report 5329* (June 1959)

Lack of adequate indoor test facilities, the unpredictability of wind and weather conditions, and difficulty in duplication of experimental data were factors which suggested that a laboratory foam-compatability test for dry powders be devised to replace current outdoor tests.

The test adopted utilizes uncomplicated bench apparatus and involves the preparation of the sample by beating the foam with a kitchen mixer and then dusting on the dry powder. Drainage volumes are recorded at intervals as the sample is heated on a hot plate.

Average drainage rates of the liquid from the foam sample were determined for six dry chemical powders and one control (no powder) for each of four foam-concentrates. The relative behavior of the powders based on the drainage rate data was the same as that experienced in outdoor foam-breakdown tests.

The criterion used for selection of acceptable dry chemical powders is that the drainage rate of a foam sample with powder added be no greater than twice the drainage rate of the foam sample without the powder.

Using the above standard, the laboratory test gave the same results as the outdoor gasoline tests, with regard to the acceptability or nonacceptability of the powder, for foam concentrates that have high ability to buffer the alkaline powders. For protein-base foam concentrates that are sensitive to pH changes, the addition of a basic powder leads to the denaturation of the proteins, the collapse of the bubble walls, and increased liquid drainage. The sensitivity to pH changes helps to explain the differences in the ability of the foam concentrate to resist breakdown by the powder. For certain foams, it was found that the heat-resistance property is improved by the addition of the dry chemical powder.

It was recommended that the presently specified outdoor fire test be replaced with the above laboratory test.

Subject Headings: *Foam, compatibility of, with powders; Powders, compatibility of, with foam.*

A. L. Goldstein

VIII. Model Studies and Scaling Laws

Sekine, T. (Building Research Institute, Ministry of Construction, Japan) "Room Temperature in Fire of a Fire-Resistive Room," *Building Research Institute Report No. 29,* 13–24 (1959)

For the condition in which a fire-resistive room is filled completely with flame, a method is offered for estimating the room temperature under fire conditions by application of a heat balance according to the equation:

$$Q_h = Q_w + Q_b + Q_1$$

where Q_h is the rate of heat release to the room by the fire, Q_w the rate of heat transfer from the flame to the enclosure, Q_b the rate of heat loss by radiation through a window, and Q_1 the rate of heat loss by the flow of hot gas through the window.

For experimental purposes, the fuel was wood and the heat input to the room $Q_h = V \cdot H$ (Kcal/hr), where V is the weight rate of combustion of wood and H the calorific value of wood given by the equation: $H = 3558\ m + 1098\ (1 - m)$, in which m is the fraction of complete combustion and 3558 Kcal/kg is used as the lower calorific value of wood.

According to Kawagoe,* the combustion rate $V = a'u'_m H'\ B/L$, in which $u'_m = 2/3\ \{2gH'\ (\rho_0 - \rho_1)/\rho_0\}^{\frac{1}{2}}$, where a′ is the area contraction coefficient for fresh air flow into the window, u'_m the mean inflow velocity, H′ the partial height of window for air inflow, B the window width, L the theoretical quantity of air required for complete combustion of unit weight of fuel, g the acceleration of gravity, ρ_1 the density of hot gas in the room, and ρ_0 the density of outdoor air.

Using a coefficient of cubical expansion $b = 1/273.2$, in the equation $\rho_0 = \rho_1(1 + b\ t_g)$, where t_g is the flame temperature, and considering that H′ is proportional to the total height of the window W, and that the window area $A_b = WB$, it is shown that the weight rate of combustion of the fuel is given by $V = k\ W^{\frac{1}{2}}\ A_b$, where k is a proportionality constant.

It is also shown that:

$$Q_w = A_c\, \epsilon_c (E_g - E_c) + A_c\, \alpha_c (t_g - t_c)$$
$$Q_b = A_b (E_g - E_b)$$
$$Q_1 = G_0\ V\ C_p (t_g - t_0)$$

where A_c is the area of the interior wall surface, ϵ_c the emissivity of the wall surface, α_c the coefficient of heat transfer to the enclosure by convection, G_0 the volume of combustion gases per unit weight of fuel burned, C_p the mean specific heat of the combustion gases at constant pressure; t_g, t_c and t_0 represent the temperature of the flame, the interior wall surface and of the out-of-doors, respectively: E_g, E_c and E_b represent radiant heat quantities from the flame, the interior wall surface and the window "surface," respectively, as defined by the equation $E = 4.88\ (T/100)^4$ with the proper subscripts applied.

Considering that the heat quantity Q_w received on the interior wall surface by radiation and convection from the flame is equal to the heat quantity conducted into the wall, it is shown that $Q_w = A_c\ \lambda_c (t_c - t_1)/\Delta x$, where λ_c is the thermal

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* Kunio Kawagoe "Characteristics of Fire Inside a Room of Fire-Proof Construction," *Bulletin of Fire Prevention Society of Japan,* Vol. 2, No. 1, 1–3 (1952)

conductivity of the wall, Δx is a finite elemental thickness of the wall in which the temperature is t_1.

By substitution in the heat balance equation, and rearranging and dividing through by A_c, the following expression is derived:

$$\{H - G_0 C_p (t_g - t_0)\}(kW^{1/2} A_b/A_c) = \epsilon_c (E_g - E_c) + \alpha_c (t_g - t_c) + A_b/A_c (E_g - E_b)$$

As a first approximation ϵ_c, λ_c, α_c, and C_p are assumed constant; H and G_0 depend upon the fraction of complete combustion and the excess air ratio and are available from previous experimental fires. The room temperature t_g in the fire may be calculated from these equations if the window height W and the ratio A_b/A_c are given.

Experimental room temperature data presented compare favorably with the calculated room temperature for various values of W and A_b/A_c.

Subject Headings: ***Temperature, distribution, in burning rooms.***

W. G. Labes

Kawagoe, K. (The Building Research Institute, Tokyo, Japan) "Fire Behaviour in Rooms," *Report of the Building Research Institute No. 27* (September 1958)

In designing a structure which can withstand fire adequately, it is important for the structural engineer to know the temperature-time curve of the enclosed space during a typical fire. Such a temperature-time curve consists of four parts: (1) a period of flame spreading during which the general room temperature is low; (2) a period during which the temperature rises to a high level; (3) a period of active burning during which the temperature remains at the high level until most of the fuel is burned away; (4) a period of cooling. The third stage is of particular interest because the duration of this stage often approximates the period during which the structural members are exposed to a high temperature level. In this paper the term "fire duration" applies to the time consumed by stages (2) and (3).

At present in the United States, fire duration is commonly regarded to be proportional to the weight of combustibles (wood) per unit floor area ("fire load"); similarly, in England it is taken to be proportional to the calorific value per unit floor area. The author claims that the fire duration in typical rooms is dependent on both the window area and the weight of fuel.

In his analysis of a room fire the author takes into account the natural outward flow of hot combustion gases and the inward flow of relatively cold air through a window. Continuity considerations lead to the following equation:

$$\frac{H''}{H'} = \left(\frac{\rho_1}{\rho_0}\right)^{1/3} \left(\frac{G}{L}\right)^{2/3} \tag{1}$$

where H″ is the height of the upper portion of the window occupied by the outwardly flowing hot gases, H′ is the height of the lower portion of the window through which the incoming air flows, ρ_1 is the density of the hot gas, ρ_0 is the density of the incoming air, L is the volume (STP) of air actually supplied for burning a unit weight of combustible and G is the corresponding volume (STP) of hot gases (CO_2, CO, H_2O, O_2 and N_2).

The mean velocity of the air inflow v'_m is found to be

$$v'_m = \frac{2}{3}\sqrt{2gH'\frac{\rho_0 - \rho_1}{\rho_0}} \tag{2}$$

and the combustion rate w is given by

$$w = \frac{v'_m \, a \, H'B}{L} \tag{3}$$

where a is the vena contracta coefficient and B is the width of the window (or the sum of the widths of similar windows, if more than one is present). The weight of fuel divided by the combustion rate w yields the fire duration.

For the purpose of calculating the density ρ_1, the author presents a tabulation of the composition of the hot gases as a function both of the combustion completeness factor x (the fraction of carbon converted to CO_2, balance $(1-x)$ being converted to CO) and of the excess air factor n (the ratio of the amount of air supplied to the amount required for complete combustion). The weight composition of the wood is assumed to be carbon 43.5 per cent, hydrogen 5.2 per cent, oxygen 38.3 per cent, water 13.0 per cent. The stoichiometric relations for calculating L and G are easily derived.

The author demonstrates by calculations for a series of assumed situations that the rate of fuel combustion w is very sensitive to both n (range: 0.8 to 1.2) and a, but is practically uninfluenced by changes in x (range: 0.4 to 1.0) and room temperature (range: 600–900°C). He then presents many observations recorded during a number of experimental fires. An analysis of these observations leads to the following additional conclusions:

1) The temperature of the gases in the room may be considered to be uniform.
2) During active combustion n is about 0.8 to 1.2 and x is 0.5 to 0.8.
3) A good estimate of the fire duration can be made with the use of the above equations if n is assumed to be 1.0 and a is taken to be 0.7.
4) The current methods for estimating fire duration in Britain and the United States are evidently inadequate for contemporary buildings where window areas tend to be large. Fire duration in rooms should be evaluated on the basis of the weight of combustibles and the window dimensions.

The experimental fires studied by the author involved the following structures: small room models (40 cm x 40 cm x 20 cm), a one-third size model room (1 m x 1 m x 1 m), a one-half size two-storied structure, and nine full-size rooms constructed out of different common building materials. Among the measurements made in many of the reported experimental fires are (1) the weight of combustibles *vs.* time, (2) temperature *vs.* time at numerous locations, (3) composition of the leaving gas, (4) vertical velocity traverses across windows, and (5) thermal radiation *vs.* time at the window location. In addition, numerous observations were made of the effects of fire on the various building materials employed.

Subject Headings: ***Fires, behavior in rooms.***

G. A. Agoston

Yokoi, S. (Building Research Institute, Ministry of Construction, Japan) "A Study on Dimensions of Smoke Vent in Fire-Resistive Construction," *Building Research Institute Report No. 29,* 1–10 (1959)

Assuming fire in a room of a building of fire-resistive construction, a method is presented to determine the size of roof vent needed to remove combustion gases at a rate which should readily permit the approach of fire-fighting forces. Considering fresh air flow into the room through one or more wall openings, it is intended that the flow rate through the vent be sufficient to maintain the smoke level not lower than the upper part of the highest wall opening (window frame), but in no case lower than 3 meters.

By means of a material balance, and assuming values * of 300°C for the room temperature, a coefficient of cubical expansion of 1/273.2, 40 per cent complete combustion, and an excess air ratio of 1, the following equation is derived for the general case involving one smoke vent, and more than one wall opening, each with different areas and heights and with the upper portion of the frames *less than 3 meters:*

$$\frac{S''}{S_0}=1.2\left[\Sigma_i \frac{S_i'}{S_0}\sqrt{\frac{H_i}{h}}\left\{\sqrt{\left(1+\frac{h_i-h}{H_i}\right)^3}-\sqrt{\left(\frac{h_i-h}{H_i}\right)^3}\right\}\right]$$

where S'' is the smoke vent area, S_0 the room floor area, S' the respective wall opening area, H the height of the respective wall openings and h the height from the top of the smoke vent to the minimum intended smoke level 3 meters above the floor. The integrated effect of the various wall openings is included by considering each opening separately as the i-th opening (where $i=1, 2, 3, \ldots$). If there is only one wall opening, then $i=1$ and the summation sign is removed.

The above equation may be applied to situations in which at least one of a number of wall openings has its upper frame at or above the minimum level (3 meters). If this highest opening is assigned $i=1$, and h is replaced by h_1, one proceeds according to the revised equation. Following this plan for this case, if there is only one wall opening and $h_i=h_1$, then the term $\frac{h_i-h_1}{H_i}=0$, and only the portion of the equation to the left of the braces remains.

It should be pointed out that, while the author applied an average inflow air velocity equal to ⅔ the maximum velocity through the wall openings, no velocity coefficient or area coefficient was applied to the flow of hot gases through the roof vent. These values would, of course, depend upon the design of the roof opening, and could be combined into a discharge coefficient.

No experimental data were given to show that these equations apply to actual conditions. Since the author assumes a fire in a room of a building, the fire would have to be large enough and the room small enough to be substantially filled by the fire .

Subject Headings: ***Fire resistance, effect of smoke vent on; Smoke vent, effect of, on fire resistance.***

W. G. Labes

* Kunio Kawagoe "Fire Behavior in Fire-Resistive Construction," *Bulletin of Fire Prevention Society of Japan,* Vol. 2, No. 1, 16–18 (1952)

Fons, W. L., Pong, W. Y., Levy, A., and Bruce, H. D. (Pacific Southwest Forest and Range Experiment Station, Berkeley, California) "Project Fire Model," *Office of Civil and Defense Mobilization Contract No. DCM–SR–59–10 and U.S. Forest Service Contract No. 12–11–005–20170, Second Progress Report, Period February 1, 1959 to April 30, 1959* (May 1, 1959)

This report covers continuing work on fire models by research personnel at the Pacific Southwest Forest and Range Experiment Station, Berkeley, California.

Project Fire Model is designed to provide data on solid fuel combustion under controlled laboratory conditions and to develop scaling laws for fires in forest fuels. The installation of instruments and equipment and the development of experimental techniques have required a large percentage of the time and effort to date but burning of 19 preliminary fires has yielded data on the following factors: (1) reproducibility of test fires, (2) rate of spread of test fires in wood cribs, (3) convection column shape, and temperature at various locations above the fire, (4) velocity of combustion gases above the test fire, (5) total radiation from the fire, and (6) energy of radiation from the fires in relation to the heat energy in the fuel.

The physical apparatus designed to produce fires with uniform characteristics is briefly described and instrumentation for measuring these fires includes use of thermocouple installations, calorimeters, directional radiometers, pressure measuring devices, heat flow transducers, shadowgraphs for observing flame and convection column, fuel moisture content determination, and application of time-lapse motion picture cameras for recording fire behavior.

Diagrams showing radiation distribution, effect of specific gravity on rate of fire spread, and weight rate of burning and temperature distribution are included. The future program for study of model fires is outlined.

Subject Headings: *Combustion, of solid fuels; Fuels, combustion of solid.*

J. H. Dieterich

IX. Atomization of Liquids

Radusch, R. (Research Division for Technique of Extinguishing Fires, Karlsruhe Polytechnical Institute, Germany) "On the Vaporization of Water Drops," *Chemie-Ingenieur-Technik* 28, 275–277 (1956)

The author considers a number of geometric and empirical relationships associated with droplet evaporation and heat transfer, and derives therefrom some interesting conclusions regarding droplet vaporization, most of which were confirmed experimentally.

By following the example of O. Herterich,[1] who noted the primary importance of free surface area, Radusch proceeds to decimate a liter of water by algebraic manipulation and concludes that the total surface area resulting from the atomization of a given volume of water varies inversely with the diameter of the resultant uniform spray.

Edeling's [2] equation expressing the variation of the Nusselt number with the square root of the Peclet number

$$\mathrm{Nu}=0.75\ (\mathrm{Pe})^{\frac{1}{2}}$$

was investigated experimentally and found to be qualitatively correct but quantitatively too small. The concept of terminal velocity was introduced, thus facilitating the determination of the finite droplet diameter (0.35 mm.) which will permit the greatest heat absorption.

Subsequent experimental consideration of Ranz and Marshall's,[3] Frössling's,[4] and Findeisen's [5] equations

$$Nu=2+0.6\ (Pr)^{\frac{1}{3}}\ (Re)^{\frac{1}{2}}$$

for the Reynolds number effects, led to the conclusion that the Ranz and Marshall equation should be modified by increasing the magnitude of the constant term (to 2.83). This change was supported by further algebraic manipulation justified by introduction of the concept of the vapor film, which tends to increase heat transfer and hence evaporation rates. Theoretical results were confirmed experimentally.

The effect of the droplet's terminal velocity on the heat transfer coefficient is analyzed by substituting the diameter dependence of the terminal velocity into the modified Ranz and Marshall equation. The first term is independent of velocity and varies inversely as droplet diameter, whereas the second term varies as the square root of droplet diameter in the Stokes' Law range but inversely as the fourth root of the diameter for larger drops. Total heat transfer coefficient decreases with drop size.

References

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4. Frössling, N. *Gerlands Contribution to Geophysics* 52, 170 (1938)
5. Findeisen, W. *Meteorologische Zeitschrift* p. 453 (1939)

Subject Headings: *Droplets, vaporization of water; Vaporization, of water droplets; Water, vaporization of drops of.*

C. C. Miesse

Hinrichs, B. R. (Karlsruhe Polytechnical Institute, Germany) "Vergleichende Untersuchungen an Sprühstrahlrohren," *VFBD Zeitschrift, Forschung und Technik im Brandschutz* 7, 1–9 (1958)

The problem of comparative investigations of sprays from full-scale spray nozzles is treated. The object is to describe and evaluate experimental tests by which the pattern of water distribution can be measured reliably and quickly.

No effort was made to determine the droplet size or distribution in the spray or to study its effectiveness in combating a fire, nor were any relations obtained between nozzle design, water pressure, nozzle angle, and the resulting water distribution pattern. However, the author describes a testing procedure which permits comparisons among various nozzles. The technique consists in collecting the spray fall-out in a large number of vessels mounted on the floor of the spray test chamber. By weighing the collected water at the termination of the test a contour diagram of the fall-out rate can be obtained from which an instructive picture of the water deposition pattern can be obtained.

It was observed that wind effects had a large disturbing influence on the spray pattern. Even in closed rooms, however, the spray produced an induced airflow which generally prevented experiments beyond two minute duration.

It was concluded that this technique was markedly superior to photographic measurement of the spray outline which does not permit quantitative evaluation of the water distribution within the spray cone. Collection of water by a vertical, subdivided collection device is not only laborious and complicated but suffers, in addition, from air stagnation difficulties in front of the collector which gives rise to inadequate measurement of water distribution.

A variety of spray distribution patterns are presented for various nozzles as a function of either water pressure or nozzle angle. A definition of the "throwing power" of a nozzle is given as the distance at which 50 per cent of the collected water has been deposited, using water collection contours in excess of 0.2 cm/sec only.

Subject Headings: *Spray nozzles, investigation of; Nozzles, investigation of.*

W. G. Berl

Hinrichs, B. R. (Karlsruhe Polytechnical Institute, Germany) "Untersuchungen an Sprühstrahlrohren," *VFBD Zeitschrift, Forschung und Technik im Brandschutz* 8, 32–36 (1959)

Sprays of water were investigated at constant water pressure, varying the angle with the horizontal of the nozzle from 0 to 20 degrees. The average "throwing power" of the jet was defined as the distance where 50 per cent of the water is collected.

Variation in nozzle angle not only increases the "throwing power" of the jet but also enlarges the area covered by the water. A factor of effectiveness is defined as the ratio of the "throwing power" at the optimum nozzle angle to the "throwing power" of a horizontally mounted nozzle. This factor was approximately 1.3 for most cases except for nozzles giving very fine water sprays where the ratios were nearer to one.

Additional evaluations were made of the sidewise spreading power of various jets. For this purpose the nozzle was mounted vertically downward, 3 meters above the collecting vessels. Contour maps of lines of equal collecting rate were obtained from the experimental data.

Since the ratio of jet length to width is also accompanied by a marked variation in the droplet size spectrum and water distribution it is not possible to deduce from the length and width data alone what the effectiveness of a spray will be in an actual fire situation.

Subject Headings: *Spray nozzles, investigation of; Nozzles, investigation of spray.*

W. G. Berl

X. Meteorological Interactions

Estoque, M. A. (Air Force Cambridge Research Center, Bedford, Massachusetts) "Venting of Hot Gases Through Temperature Inversions," *Geophysics Research Directorate Research Notes No. 3, AFCRC-TN-58-623* (December 1958)

The problem under discussion is that of determining the temperature and velocity distribution in the atmosphere resulting from a large heat source on the ground. The problem is of particular importance in studying the distribution of contaminated gas in a nuclear explosion, but it has, of course, a wider sphere of interest.

The results of several papers, both theoretical and experimental, are presented. The basis of most of the theoretical work is formed by the fundamental equations of fluid mechanics, which for the problem in question may be written in the form

$$\frac{\partial}{\partial z}(rw\rho)+\frac{\partial}{\partial r}(ru\rho)=0$$

$$\frac{\partial}{\partial z}(rw^2\rho)+\frac{\partial}{\partial r}(ruw\rho)=r\frac{\theta-\theta_e}{\theta_e}\rho g$$

$$\frac{\partial}{\partial z}(rw\,\theta\rho)+\frac{\partial}{\partial r}(ru\,\theta\rho)=0$$

where

$r=$ radius
$z=$ elevation
$u=$ radial velocity component
$w=$ vertical velocity component
$\rho=$ density
$\theta=$ potential temperature
$\theta_e=$ environmental potential temperature
$g=$ gravitational constant

These equations are based on the laws of conservation of mass, momentum, and energy, respectively. They have been simplified mainly by omitting terms related to viscous forces. The equations are essentially those applying to an incompressible fluid. They are, however, extended to be applicable to the present case by introducing the so-called potential temperature. This temperature is defined as the one attained by a sample of air at any elevation when isentropically compressed to a standard pressure (usually taken as sea level pressure).

For the large scale motions in question, the flow is turbulent and additional assumptions and simplifications have to be introduced in order to make a solution of the equations feasible. As part of the assumptions the velocity and temperature profiles are taken to be of the form

$$w=f(z)e^{-\frac{r^2}{R^2}}$$

$$\theta'=\vartheta(z)e^{-\frac{r^2}{R^2}}$$

where R is the width of the hot gas plume at any elevation, and f and ϑ are functions of z only.

The most critical assumption, however, is related to the manner in which turbulence is taken into account. In the analysis considered, this is done by assuming that the induced radial inflow velocity at the edge of the hot gas plume is proportional to the maximum vertical velocity component at the same level, *i.e.,*

$$u_R=K^2w$$

where K is a constant. With these assumptions and for a constant atmospheric temperature gradient the distribution of hot gas may be found. For relatively small heat sources and large positive temperature gradients the hot gas plume will reach a maximum height. This height is given approximately by the equation

$$H = \frac{1}{K}\left(\frac{g}{\theta_e}\frac{\partial\theta_e}{\partial z}\right)^{-3/8}\left(\frac{gQ}{\theta_e \rho C_p}\right)^{1/4} \qquad (1)$$

where Q is the strength of the heat source. This expression approximates the results of at least two separate studies [*] which are based on different sets of assumptions. The coefficient K is determined experimentally. It is strongly dependent on atmospheric conditions. Its lowest value, corresponding to calm air is about 0.296.

A positive potential temperature gradient in the atmosphere, as assumed in the above expression, corresponds to a temperature inversion. If the height calculated by equation (1) is smaller than the height of the inversion layer, then the hot gas plume will reach the calculated height. If, on the other hand, the inversion layer is smaller than the calculated height, the hot glass plume will be "vented" through the inversion layer and will escape. If hazards from a radioactive gas are being studied, it should be realized that the determination of the plume height in an atmospheric inversion is only a first step in the problem. The redistribution of the gas after the dissolution of the inversion layer will also have to be considered.

In addition to the theoretical studies, two sets of experiments [†] are also reviewed.

Subject Headings: ***Gases, venting of, through temperature inversion; Inversions, venting of gases through.***

R. H. Sabersky

Spurr, G. (Central Electricity Research Laboratories, England) "The Penetration of Atmospheric Inversions by Hot Plumes," *Journal of Meteorology* **16,** 30–37 (1959)

In order to determine whether or not the hot gases emitted by power station chimneys can penetrate atmospheric temperature inversions, the data pertaining to two periods of thick smog in Britain were examined in detail using mathematical formulations by Sutton [‡] and Priestley.[§] It was shown that both formulations gave similar results, indicating that with calm or very light winds a plume from a chimney serving 100 megawatts of plant or more will penetrate the worst inversion on record, while plumes from a chimney serving one megawatt of plant will penetrate all but the "most severe" inversions.

Priestley's formula, being simpler to apply, can be used to calculate the heat

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[*] Morton, B. R., Taylor, G., and Turner, J. S. "Turbulent Gravitational Convection from Maintained and Instantaneous Sources," *Proceedings of the Royal Society* A234, 1–23 (1956)

Priestley, C. H. B. "A Working Theory of the Bent-Over Plume of Hot Gas." *Quarterly Journal Royal Meteorological Society* 82, 165–176 (1956)

[†] Morton, B. R., Taylor, G., and Turner, J. S. "Turbulent Gravitational Convection from Maintained and Instantaneous Sources," *Proceedings of the Royal Society* A234, 1–23 (1956)

Vehrencamp, J. E., Ambrosio, A., and Romie, F. E. "Convection from Heated Sources in an Inversion Layer," *Final Report Air Pollution Studies, Department of Engineering, University of California, Los Angeles, California* (1955)

[‡] Sutton, O. G. *Journal of Meteorology* 7, 307–312 (1950)

[§] Priestley, C. H. B. and Ball, F. K. *Quarterly Journal Royal Meteorological Society* 81, 144–158 (1955) rate necessary in a plume to insure penetration of any specified inversion. The admitted difficulty of the method is the relative paucity of information on the temperature distribution in the lower part of the atmosphere. In addition to the collection of more such data, the author suggests the use of balloons to trace visually the path of plumes during inversion conditions which occur in relatively dry air without the formation of fog. The frequency of such occurrences is not stated, but one study is cited in which balloon ascents to 1500 feet were made at Cardington, England three times daily for four years during which inversions were encountered in 76 ascents.

Subject Headings: *Inversions, penetration of, by hot plumes.*

A. Strasser

Barrows, J. S., Dieterich, J. H., O'Dell, C. A., and Kaehn, C. H. (U.S. Forest Service)—**Fuquay, D. M., Schaefer, V. J., and MacCready, P. B., Jr.** (The Munitalp Foundation, Inc.)—**Colson, D.** (U.S. Weather Bureau)—**Wells, H. J.** (Advisory Committee on Weather Control) "Project Skyfire," *Final Report of the Advisory Committee on Weather Control,* Vol. II, 105–125 (1957)

Project Skyfire is a cooperative effort by ten organizations to study the occurrence, behavior, and control of lightning-caused forest fires in the western United States. Work has been concentrated on study of past lightning fires, analysis of thunderstorms and associated phenomena in the northern Rocky Mountains, and experimental cloud seeding to inhibit lightning and/or increase precipitation.

Thunderstorms in the northern Rocky Mountains are mostly either the frontal or the air-mass type. Both types are potentially good targets for seeding with properly located, ground-based, silver iodide generators. To date, one storm track has been defined and used for experimental seeding. No cloud-breeding areas have been definitely located.

Preliminary cloud seeding was done from both the ground and aircraft in 1956 primarily to test techniques of operation and measurement of results. Some modification of clouds was observed; the most definite effects resulted from seeding with dry ice from a light plane. In response to demonstrated need, a high-output, silver-iodide acetone generator was developed and calibrated.

In 1957 on 29 days having favorable weather, clouds were seeded by a network of generators spaced at half-mile intervals in rough, mountain country. Glaciation resulted in large and small seeded cumulus clouds that were colder than −4°C. Small cumulus were converted to ice; the structure and growth rate of towering cumulus were altered. Virga sometimes resulted, and in two instances cloud-to-ground lightning occurred in the silver iodide plume area.

Subject Headings: *Fires, control of, by cloud seeding.*

G. R. Fahnestock

Berad, M. L. and Haugen, D. A. (Air Force Cambridge Research Center, Bedford, Massachusetts) "A Preliminary Evaluation of Sutton's Hypothesis for Diffusion from a Continuous Point Source," *Journal of Meteorology,* **16,** 12–20 (1959)

Because of the general similarity between the diffusive transfer of momentum, heat, and material, a solution for any one of these is of general interest. In this paper measurements on the diffusion of a contaminent injected into the atmosphere are compared with a theory proposed by O. G. Sutton.* The comparison indicates that the theory is inadequate because different values of the turbulent diffusivity parameter are found for the lateral and vertical directions. Also, neither value can be correlated with the turbulent diffusivity parameter for momentum.

The experiments were carried out by continuously injecting sulfur dioxide at a point either 0.5 or 1.5 meters above the ground. Measurements of the mean concentration were made on radial arcs from 50 to 800 meters downwind of the source and at various heights. The purpose of the paper is to compare these measurements with a theoretical expression proposed by Sutton * for the concentration of a gas downwind from a continuous source,

$$\frac{\overline{X}\overline{V}}{Q}=\frac{x^{n-2}}{\pi C_y C_z}e^{-\frac{y^2x^{n-2}}{C_y^2}}\left\{e^{-\frac{(z-h)^2x^{n-2}}{C_z^2}}+e^{-\frac{(z+h)^2x^{n-2}}{C_z^2}}\right\}$$

In this expression $\overline{X}$ is the mean concentration; $\overline{V}$ the mean wind velocity; Q the rate of gas emission; x the mean wind direction; y the direction of the crosswind; z the vertical direction; C_y and C_z lateral and vertical diffusion coefficients; h the height of the source above ground; and n a parameter "related to the diffusive power of the turbulence."

The comparison is limited to measurements in which the concentration distribution is Gaussian. The standard deviations of the distributions are related to the parameter n in the above expression by assuming the diffusion coefficients to be constant. Different values of n are found for the lateral and vertical distributions. Sutton † has also proposed that n may be evaluated from the mean wind profile,

$$\frac{\overline{V}_2}{\overline{V}_1}=\left(\frac{Z_2}{Z_1}\right)^{\frac{n}{2-n}}$$

where $\overline{V}_2$ and $\overline{V}_1$ are mean velocities at the heights Z_2, and Z_1, respectively. In general, this n does not agree with the value obtained for either the vertical or lateral concentration distributions.

Subject Headings: *Diffusion, continuous point source.*

D. L. Turcotte

Railston, W. (Royal Military College, Shrivenham, Wilts, England) "The Temperature Decay Law of a Naturally Convected Air Stream," *Proceedings of the Physical Society* 67B, 42–51 (1956)

This article is an account of a laboratory experiment to determine (1) the average excess of temperature in a laminar convective column at varying distances above the heat source, and (2) the radius of such a column at varying heights above the heat source. The observed results are in good agreement with the theoretical results of O. G. Sutton.‡

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* Sutton, O. G. "Theoretical Distribution of Airborne Pollution from Factory Chimneys," *Quarterly Journal Meteorological Society* 73, 426–436 (1947)

† Sutton, O. G. "The Problem of Diffusion in the Lower Atmosphere," *Quarterly Journal Meteorological Society* 73, 257–276 (1947)

‡ Sutton, O. G. *Quarterly Journal Royal Meteorological Society,* 74, 13 (1948) *Journal of Meteorology* 7, 307 (1950)

The experiment was carried on in a wooden box one meter square and two meters tall. Cool air entered through a hole in the bottom of the box and heated air passed out through a hole in the top. The heat source was a 3.5 cm. square of wire gauze with a maximum output of 20 watts. This produced a maximum measured rise in temperature of 21°C within the column at ambient temperatures between 10.4 and 16.0°C. A greater increase in temperature was not desired since the assumption was that there would be negligible change in density.

Temperatures were measured with thermistors aged to produce a stable calibration. The heat sensitive beads were 1 mm. in diameter and had a thermal capacity of 1.4 joules per degree C. Two thermistors were used, one to measure column temperature and the other the temperature of the ambient air at the same height.

To insure that column temperature was measured at the center of a uniform, stable jet of heated air, it was necessary to make the column visible. This was done by means of a schlieren system of illumination, which produces a shadow image of the column. Besides permitting exact location of the thermistors within the column, the schlieren system also permitted observation of the temperature gradient by interpretation of the image shading.

Temperature measurements were made at 5 cm. intervals at heights from 5 to 70 cm. above the gauze. Across the column, temperature was measured at 1 cm. intervals at heights of 20, 40, and 60 cm. above the gauze. Lateral measurements extended outward to where the temperature difference between column and ambient air was one-tenth its value at the column center. Transverse temperature distribution was found similar to the normal law of error. That part of the excess column temperature due to radiation and conduction was corrected by simultaneously measuring excess temperature at an equal distance directly below the heat source. Any excess below the heat source would be due to radiation and conduction. Separate sets of measurements were made using heat outputs of 4.87, 9.92, and 20.37 watts.

In order to compare observed results with Sutton's theoretical treatment, it was necessary to convert the distance from the 3.5 cm. square heat source to distance from a theoretical point heat source from which the air stream could be assumed to rise conically.

This experiment showed that the radius of the warm column could be expressed by $r=0.40z_0^{0.85}$, where z_0 is distance above the theoretical point heat source. The mean excess temperature of the heated column at any height was found to be $\overline{\Delta\theta}=91.3Q^{0.675}z_0-1.52$, where Q is the heat output in watts.

Equipment setup, analysis of the data, and comparison of results with the theoretical treatment of this problem by Schmidt * and Sutton are covered in detail.

Subject Headings: *Temperature, decay of air streams.*

O. P. Cramer

Woodward, B. (Imperial College, London, England) "The Motion In and Around Isolated Thermals," *Quarterly Journal of the Royal Meteorological Society* 85, 144–151 (1959)

The convection of isolated masses of buoyant fluid was studied by means of water models. Salt solution, made visible by a white precipitate, was allowed to

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* Schmidt, W. Z. *angew. Math. Mech.* 21, 265, 351 (1941)

sink through a column of water. Small polythene beads were used as tracers and their motion recorded by a movie camera.

The general motion of the buoyant fluid or "thermal" was found to be like that of a vortex ring. From measurements made at different stages in the history of a thermal, the motion was found to be *similar* at all stages. The author says that, "This implies that in and around the thermal the velocity at any point expressed as a fraction of the velocity of the cap of the thermal is a function only of the coordinates of the point expressed as a fraction of the height of the cap." The vertical velocity of the center of the thermal was found to be rising at slightly more than twice the rate of the thermal cap. Along the edge of the thermal, fluid was descending at slightly more than half the speed at which the cap was rising.

The thermal was also found to affect the surrounding fluid. As it rises, the fluid above was "pushed" up before it became engulfed; a downward motion along the edge of the thermal was evident, and some of the fluid to the rear flowed in and up. Approximately 60 per cent of the mixing occurred at the front of the thermal and 40 per cent at the rear. As the thermal rose it traversed a cone having a half angle of about 15°.

The author also studied the effects of the thermal on heavy particles (particles having a terminal velocity). She found that heavy particles having a terminal velocity of less than 0.4 times the velocity of rise of the cap could not escape the thermal. These particles would be carried toward the axis of the thermal by the inflow at the rear and then up the center. The greatest terminal velocity which any particle could have and still be retained in the thermal was found to have a terminal velocity of 1.6 times the velocity of rise of the cap. These particles, however, must be poised on the axis of the thermal. Because of the inflow at the rear of the thermal, particles which just fall out will fall down the axis. As the thermal decelerates, all particles having non-zero terminal velocity will eventually fall out.

The author states that the ultimate form of all convective elements in the atmosphere is the isolated thermal. This form will eventually take place regardless of the method of release or the shape of a convective element in the lower levels. The author further points out that no attempt is made to show similarity between the model thermal and convection in the lower several hundred meters of the atmosphere. It is only after the column has detached itself from the ground (at a height between 200 and 2000 meters) that an isolated thermal is formed.

Subject Headings: *Thermals, motion in.*

W. Y. Pong

Priestley, C. H. B. (Commonwealth Scientific Industrial Research Organization, Victoria, Australia) "A Working Theory of the Bent-Over Plume of Hot Gas," *Quarterly Journal of the Royal Meteorological Society* 82, 165–176 (1956)

An analytical solution has been obtained for the behavior of a continuous plume of buoyant gas or smoke moving through a constant velocity, turbulent, resistant environment. Thermal striations in the environment are neglected. The problem as presented is divided into three parts: (1) when mixing is generated by turbulence (eddies) induced by the plume's own motion, (2) when the buoyancy and rate of rise of the plume has decreased to such an extent that the environmental turbulence is the major contributor to mixing, and (3) when all buoyancy and vertical plume gas velocity having been lost, mixing is accomplished by pure environmental diffusion. Only the solutions for the first two stages are discussed since the analytical solution for the final stage is known.

The analytical solutions for the first two stages for a stagnant environment were previously derived by Priestley and Ball in the Quart. J. R. Met. Soc. *81,* 144 (1955) and Priestley in the Austr. J. Phys. *6, 279* (1953), respectively. The principal innovation in this paper is the conversion of these solutions for a stagnant environment to that for a dynamic environment. This conversion is accomplished in the solution for the first stage by retaining the previously derived equations for stagnant surroundings and re-defining two of the parameters; namely, the plume radius R and the spreading coefficient c. Since an initially circular plume cross section assumes upon ascension an elliptical cross section, the plume radius and spreading coefficient are defined as the geometric mean of the corresponding values along the principal axes of this ellipse. In the solution for the second stage the only additional assumptions made to the existing equations for a stagnant environment are that the mixing rate (for heat and momentum) is directly proportional to the environmental velocity and the previously designated plume radius is now the effective plume radius.

The complete solution for the problem is obtained by fitting together these solutions for the two stages at the point of equal lapse-rate-of-rise (the first derivative of plume gas velocity with respect to height). This complete solution gives rise to more stable plume configurations than was previously possible with either of the two first stage solutions individually.

Comparison of the results of this theory with experimental data obtained from smoke plumes of several industrial chimneys by Bosanquet * shows exceptionally good agreement. Both wind tunnel studies and "superheat" generated by water vapor condensation from plumes are discussed.

Subject Headings: ***Gases, bent-over plume of hot.***

H. E. Perlee

Johnson, O. (Meteorological Service of Canada) "An Examination of the Vertical Wind Profile in the Lowest Layers of the Atmosphere," *Journal of Meteorology* **16**, 144–148 (1959)

For conditions of neutral equilibrium, two "laws" have been presented in the literature to describe wind profiles. The logarithmic law states that the vertical profile of the wind speed in the lower atmosphere is most accurately represented by a logarithmic function of the height above the ground. The power law states that the wind speed is proportional to a power of the height above the ground. This paper presents a comparison of the accuracy of the logarithmic and power laws under conditions of various temperature gradients.

Wind profile measurements were made over a height range from 0.5 to 16 meters above the surface over prairie grass and over a snow surface at the Suffield Experimental Station, Ralston, Alberta, Canada. Wind profile measurements for a height range from 2 to 16 meters over short grass at the Great Plains Turbulence Project at O'Neill, Nebraska were studied as a comparison.

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* Bosanquet, C. H., Carey, W. F., and Halton, E. M. *Proceedings of Institute Mechanical Engineers Nos.* 1–4, 355 (1950)

The wind profiles obtained over prairie grass for a zero temperature gradient and a 2.0°C inversion condition were more closely represented by the power law than by the logarithmic law. The wind profiles obtained over a snow surface for lapse and inversion conditions were well represented by the power law.

The analysis of the wind profiles obtained at O'Neill, Nebraska showed that for adiabatic and lapse conditions the data were equally well represented by both laws. The power law best described the inversion conditions.

A comparison of the power law index for the various surfaces studied showed that the index increased with surface roughness and with increased atmospheric stability.

Gustiness studies showed that the contribution of mechanical turbulence is greater in the low elevations for inversion conditions than for lapse conditions.

Subject Headings: *Wind, profiles in lower atmosphere.*

A. W. McMasters

Obukhov, A. M. and Yaglom, A. M. (Institute for Physics of the Atmosphere, USSR) "On the Microstructure of Atmospheric Turbulence—A Review of Recent Work in the USSR," *Quarterly Journal of the Royal Meteorological Society* 85, 81–90 (1959)

The instantaneous spacial distribution of wind velocity, temperature, humidity, and other meteorological elements is characterized by random, and often large, fluctuations. Likewise, values of any of these elements at any given point are characterized by similar fluctuations in time. Although the term "turbulence" is usually associated with air movement, it can be used to describe fluctuations in any of the various meteorological fields because the same mathematical theory and general treatment in this paper apply to all. This paper is essentially a review of research in the USSR on small-scale turbulence which is characterized by periods of a few hundredths of a second to a few seconds and space scales of a few centimeters to several meters.

Basic to the mathematical treatment is the structure function D(r):

$$D(r) = \overline{[u(M) - u(M')]^2}$$

in which u(M) is the random function at point M and u(M′) the same function at point M′ situated a distance r from M. The bar indicates mean value. In the case of vector fields, such as the wind velocity field, two structure functions are required.

The experimental determination of the fluctuations in the wind field were made with special hot wire anemometers with platinum wire sensing elements 20μ in diameter. The timelag of these elements was very small (about 0.01 sec.). Fluctuations in the temperature field were measured with the same sensing elements used as resistance thermometers. Agreement between theoretical and experimental work was good.

Subject Headings: *Turbulence, atmospheric, microstructure of.*

G. M. Byram

XII. Instrumentation

Barsh, M. K., Andersen, W. H., Bills, K. W., Moe, G., and Schultz, R. D. (Chemical Division, Aerojet-General Corporation, Azusa, California) "Improved Instrument for the Measurement of Linear Pyrolysis Rates of Solids," *The Review of Scientific Instruments* 29, 392–395 (1958)

In the study of the pyrolysis of solid materials the use of pyrolysis rate measurements for the calculation of activation energies and frequency factors in the Arrhenius rate equation requires accurate knowledge of three parameters: (1) the weight lost from the solid sample in a known time interval; (2) the area of the surface from which the material was removed; and (3) the temperature of that surface. Because of the difficulty in measuring changes in weight, a change in linear dimension, which is usually easier to measure accurately, is sometimes preferred, as for example in the burning rate measurements of liquid fuel drops where the change in diameter is recorded photographically. The linear pyrolysis instrument devised by Barsh and his colleagues was primarily designed to take advantage of the ease of linear measurements as opposed to weight measurements by pyrolysing a solid rod of the material under investigation, by pressing one end of the rod firmly against an electrically heated plate, and recording continuously the rate at which the rod decreased in length. By using a rod, the area of the pyrolysed surface was known accurately and maintained constant.

The instrument therefore consists of (1) a horizontal Nichrome heating element and (2) a carefully balanced sample holder running in vertical guides, so that the sample rod can be brought vertically up to the pyrolysis plate from below or vertically down to it from above, its position being indicated continuously by a recording potentiometer. The sample was arranged to center on a thermocouple embedded in the hot plate and ground flush with the surface, the assumption being that the plate temperature was also that of the sample face. That this should be so requires good thermal contact which, the authors claim, was achieved by correct adjustment of the loading force pressing the sample on the hot plate. In this context, the correct loading force was any force inside the range over which the decomposition rate was found experimentally to be independent of the loading force. The whole unit was enclosed in a bell jar so that pyrolysis could be studied either in vacuo or in an inert atmosphere. The temperature range of the instrument was 300 to 600°C.

A range of materials, both organic and inorganic, is reported as having been tested, the details of which are to be described in a later publication; also mentioned were experiments using thin mica spacers, indicating that there was no catalytic effect of the Nichrome heating element on the substances tested. Two further points that in the reviewers opinion should be given some consideration are: (1) the possibility that contact pyrolysis of this sort differs in mechanism from free surface pyrolysis (without being catalytic); and (2) that the rate of pyrolysis may be influenced by the magnitude of the temperature gradient down the rod, *i.e.*, by the rate of heating as a given cross section approaches the pyrolysis surface. As a final point, the instrument is not thought to be quite as suitable as the authors would seem to suggest for investigating the combustion mechanism of solids, except in the case of those materials that vaporize or sublime at such a rate and temperature that the reaction surface is at a finite distance from the solid surface. Within the limits of these objections however the instrument seems to possess the two key requirements for any technique, *i.e.* accuracy and simplicity.

Subject Headings: *Solids, pyrolysis rate of; Pyrolysis rate, of solids.*

R. H. Essenhigh

Martin, S. B. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Application of Gas Chromatography to Problems in Rapid Degradative Reactions of Solids," *Research and Development Technical Report USNDRL–TR–197 NS 081–001* (October 1957)

Rapid degradative reactions of solids and liquids with low vapor pressures have been studied by carrying out the reactions directly in a stream of gas acting as a carrier in a gas chromatographic apparatus.

An organic solid was suspended in a helium stream and exposed to intense radiant energy. High temperatures resulted in the solid within fractions of a second, and the resulting vapors were collected in various traps for analysis.

Solids were suspended in the stream in the form of a thin circular wafer whose diameter was no greater than the area of uniform radiation emanating from the source. Liquids were suspended by impregnating asbestos or quartz fiber paper with the substance. The vapors were rapidly passed into the column to prevent attenuation of the incoming radiation as vapors collect over nonvaporized solid or liquid.

Hot wire detector cells were used and ⅜ inch columns used to facilitate the high flow rate necessary. Two-meter columns of dinonyl phthalate, dimethyl sulfolane, tetraethylene glycol, and tetraethylene glycol dimethylether were used. Calibrations were obtained by syringe injection of various mixtures. Packing was usually 40–50 mesh C-22 firebrick.

After exposure the condensed components were transferred to small volume sample tubes which were kept at liquid nitrogen temperatures. Samples as small as 10 mg. have been analyzed.

Analysis was conducted in another modified apparatus on the solid residue remaining after ignition. A dried weighed fraction of pyrolyzed cellulose was weighed into a closed-end quartz ignition tube and sealed in with glass wool. After sealing to the chromatographic system and evacuation, the chamber was filled with oxygen. The part of the tube filled with glass wool was heated to 900°C and the lower end kept cool. When the quartz was hot the bottom end was rapidly heated with a torch. Pressure measurements were made to determine the total pressure of carbon dioxide, oxygen, carbon monoxide, and water. The sample gases, while hot, were injected into the chromatograph directly for analysis. Absence of carbon monoxide is considered to indicate complete combustion. Thus ratios of carbon, hydrogen, and oxygen contained in the solid can be determined.

No data appeared in this paper on actual analysis; they will appear in a subsequent report.

Subject Headings: *Solids, gas chromatography in thermal decomposition of; Thermal degradation, of solids.*

P. Breisacher

COMMENTS AND DISCUSSIONS

Smith, K. N. (Johns-Manville Corporation, Manville, N.J.) Comments on the Discussion by P. H. Thomas, *Fire Research Abstracts and Reviews,* Volume 1, No. 3, 143 (1959)

The comments by P. H. Thomas on the paper by Gross and Robertson * stated that "the large value (of induction time) for the cotton linters suggests the presence of reaction inhibitors or an autocatalytic reaction." In a paper to be published,† evidence will be presented which shows that the rate of self-heating of wood fiber is related to the amount of material present that can be extracted with organic solvents. The extractable content of cotton linters is low, around 0.1 per cent ‡ whereas, wood fiber contains from 1.8 to 7.0 per cent extractable material. This could very well explain the fact that the induction time for cotton linters is 60 times longer than for wood fiberboard. It also suggests that the wood fiber contains an accelerator rather than the cotton linters an inhibitor.

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* Gross, D. and Robertson, A. F. "Self-Ignition Temperatures of Materials from Kinetic Reaction Data," *Journal of Research of the National Bureau of Standards,* 61, 413–417 (1958)

† Smith, K. N., presented at the 1959 meeting of TAPPI

‡ Gross, D., private communication

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