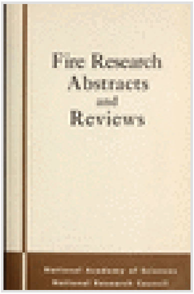

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Fire Research Abstracts and Reviews

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FIRE RESEARCH ABSTRACTS AND REVIEWS
Robert M. Fristrom, Editor

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FIRE RESEARCH ABSTRACTS AND REVIEWS will abstract papers published in scientific journals, progress reports of sponsored research, patents, and research reports from technical laboratories. At intervals, reviews on subjects of particular importance will be published. The coverage will be limited to articles of significance in fire research, centered on the quantitative understanding of fire and its spread.

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Volume 10 Number 1

Fire Research Abstracts and Reviews

Committee on Fire Research
Division of Engineering
National Research Council
National Academy of Sciences—National Academy of Engineering

NATIONAL ACADEMY OF SCIENCES—NATIONAL RESEARCH COUNCIL
Washington, D. C.
1968

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FOREWORD

The Fire Research and Safety Act has been passed by Congress and signed by the President. This is a compromise bill which calls for both a research and study program on the problems of unwanted fires. It will be administered by the U.S. Department of Commerce through the National Bureau of Standards. The principal modification of the original proposal has been a budget cut from $10,000,000 for a one-year period to $5,000,000 for a two-year program. Despite the fourfold reduction, this is a substantial step in the right direction and should allow a meaningful program to be initiated.

The Twelfth International Symposium on Combustion will be held at the University of Poitiers, Poitiers, France, July 14–20. Sessions on *Mass Fires, Flame Structure,* and *Chemical Kinetics of Flames* should be of special interest.

This issue of FRAR contains abstracts from papers delivered at the first meeting of the Eastern Section of the Combustion Institute, held at the Carnegie-Mellon University, Pittsburgh, Pennsylvania, November 27–28, 1967, co-sponsored by the Committee on Fire Research. The theme was "Discussion on Scientific Aspects of Fire Hazards (Emphasizing Solids and Liquids)." Thirty-four papers were presented and a very fruitful discussion ensued. A survey based on this meeting appears in this issue of FRAR as a review by Dr. Raymond Friedman of the Atlantic Research Corporation. It is entitled "A Survey of Knowledge about Idealized Fire Spread over Surfaces," and it provides a clear and concise survey to the status of the field.

Beginning with this issue new section headings will be used. They give a rough classification and it is hoped that the new division will be a more convenient categorization of fire research studies. The section number appropriate to the old system appears at the end of each abstract. The relations between the old and new classifications are shown in Table 1.

Fifteen categories have been selected. They are of two classes: research objectives and research techniques. The six research objectives are: A. Prevention of Fires and Fire Safety Measures; B. Ignition of Fires; C. Detection of Fires; D. Propagation of Fires; E. Suppression of Fires; F. Fire Damage and Salvage. This group can clearly be related to fire research and provides the crucial links between a reservoir of scientific knowledge and practical application. The nine research techniques are: G. Combustion Engineering; H. Chemical Aspects of Fires; I. Physical Aspects of Fires; J. Meteorological Aspects of Fires; K. Physiological and Psychological Problems from Fires; L. Operations Research, Mathematical Methods and Statistics; Model Studies and Scaling Laws; N. Instrumentation and Fire Equipment; O. Miscellaneous. These provide the tools for fire studies.

Any classification system must be somewhat arbitrary since very few studies can be simply categorized under a single heading. Most research papers have multiple objectives, stated, implied, or potential, and often involve more than one technique. Thus, many articles could be classified in several ways. The situation can be illustrated by a matrix (Fig. 1). The rows are assigned to objectives and the columns to techniques. Abstracts that are primarily concerned with an applied objective or primarily with technique fall in the initial row or column. Most ab-

TABLE 1. (a)
New and old section headings for Fire Research Abstracts and Reviews

Old headings		New headings	
I	Ignition Phenomena	A	Prevention of Fires and Fire Safety Measures
II	Thermal Decomposition	B	Ignition of Fires
III	Heat and Material Transfer	C	Detection of Fires
IV	Diffusion Flames	D	Propagation of Fires
V	Combustion Principles	E	Suppression of Fires
VI	Radiation	F	Fire Damage and Salvage
VII	Suppression of Combustion	G	Combustion Engineering
VIII	Model Studies and Scaling Laws	H	Chemical Aspects of Fires
IX	Atomization of Liquids	I	Physical Aspects of Fires
X	Meterological Interactions	J	Meteorological Aspects of Fires
XI	Operational Research Principles Applied to Fire Research	K	Physiological and Psychological Problems from Fires
XII	Instrumentation	L	Operations Research, Mathematical Methods and Statistics
XIII	Fire Fighting Techniques, Equipment	M	Model Studies and Scaling Laws
XIV	Miscellaneous	N	Instrumentation and Fire Equipment
XV	Physiological Aspects of Fire	O	Miscellaneous

TABLE 1. (b)
Relationships between old and new section headings for Fire Research Abstracts and Reviews

Old	New	New	Old
I	B	A	XIII
II	C, F, G, H	B	I, XIII
III	D, I	C	II, V, VI, XII, XIII
IV	D, G, H, I	D	III, IV, V, VI, XIII
V	C, D, G, H, I	E	VII, XIII
VI	C, D, I	F	II, XIII
VII	E, H	G	II, IV, V
VIII	M	H	II, IV, V, VII
IX	G, I	I	III, IV, V, VI, IX
X	J	J	X
XI	L	K	XV
XII	C, N	L	XI
XIII	A, B, C, D, E, F, N	M	VIII
XIV	O	N	XII, XIII
XV	K	O	XIV

FIRE RESEARCH CLASSIFICATION

OBJECTIVES ➡ ⬇ TECHNIQUES	PREVENTION OF FIRES AND SAFETY MEASURES	IGNITION OF FIRES	DETECTION OF FIRES	PROPAGATION OF FIRES	SUPPRESSION OF FIRES	FIRE DAMAGE AND SALVAGE
COMBUSTION ENGINEERING						
CHEMICAL ASPECTS OF FIRES						
PHYSICAL ASPECTS OF FIRE						
METEROLOGICAL ASPECTS OF FIRES						
PHYSIOLOGICAL AND PSYCHOLOGICAL ASPECTS OF FIRES						
OPERATIONS RESEARCH, MATHEMATICAL METHODS AND STATISTICS						
MODEL STUDIES AND SCALING LAWS						
INSTRUMENTATION AND FIRE EQUIPMENT						
MISCELLANEOUS						

FIG. 1. Fire Research Classification.

stracts, however, occupy one or more intermediate boxes. Even this matrix formulation is an oversimplification since scientific disciplines or research objectives can only rarely fit into such neat boxes.

It is hoped that, in spite of these limitations, the new division in FRAR will prove to be a convenient one.

R. M. FRISTROM, *Editor*

CONTENTS

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C. Detection of Fires

D. Propagation of Fires

E. Suppression of Fires

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H. Chemical Aspects of Fires

I. Physical Aspects of Fires

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K. Physiological and Psychological Problems from Fires

L. Operations Research, Mathematical Methods, and Statistics

M. Model Studies and Scaling Laws

N. Instrumentation and Fire Equipment

O. Miscellaneous

MEETINGS

Abstracts of Papers

REVIEWS

A Survey of Knowledge about Idealized Fire Spread over Surfaces

R. FRIEDMAN
Atlantic Research Corporation, Alexandria, Virginia

I. *Introduction*

It is perhaps obvious that the advance of a flame across the surface of a combustible solid or liquid is an extremely complex process. Combustion science today is not able to specify mathematically the laws governing this process and indeed there is uncertainty as to which variables exert dominant effects. Clearly, conductive, convective, and radiative heat transfer may be involved, as well as aerodynamics, surface chemistry, gas phase chemistry, and interdiffusion of reactants and products. The intent of this review is to examine results of some idealized *experiments* conducted in several laboratories for flame spread under a variety of conditions, in order to obtain perspective on the relative importance of the variable parameters on the phenomena, and then to make some comments on the state of the *theory*.

II. *Experiment*

The data to be discussed were obtained in recent studies at Atlantic Research Corporation,[1,2] Naval Research Laboratory,[3] Stevens Institute of Technology,[4] Linde Division of Union Carbide,[5] and the U.S. Forest Service.[6] Table 1 shows data selected from the above-referenced reports, as do the other tables which will follow below, selected to illustrate various trends. The very strong effect of the physical nature of the combustible material is illustrated. It is intuitively obvious that a material with open texture or with exposed edges should propagate a flame faster than a completely smooth material. The table shows that flame will propagate across a foamed plastic more than two orders of magnitude faster than across a smooth plastic with the edges inhibited. Exposing of the edges on a smooth plastic sample gives perhaps a fivefold increase in propagation rate. These are results for specific materials with horizontal flame spread on an upward-facing surface in the absence of wind. Clearly the numerical results could be different under other conditions and the sharpness of an exposed edge could well be quite important if one were interested in more precise information.

Figure 1, taken from Rothermel and Anderson's report, shows the very powerful effect of another variable, the air velocity. It is seen that fire will spread across a

TABLE 1.
Effect of roughness and exposed edges on horizontal flame spread rate (O_2 at 5 psia)

Foamed plastic:	32 cm/sec
Smooth plastics, edges exposed:	0.5–0.9 cm/sec
Smooth plastics, edges inhibited: (ref. 1)	0.1–0.2 cm/sec

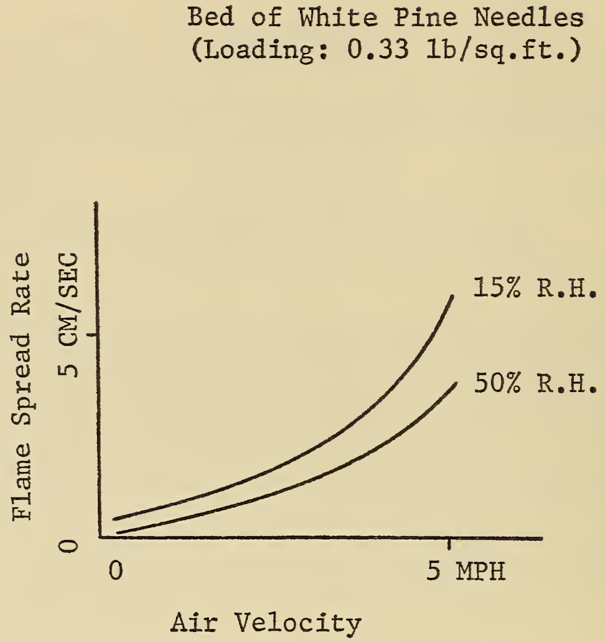

Fig. 1. Effect of wind on fire spread (Ref. 6).

bed of pine needles at least an order of magnitude faster in a five mile per hour wind than in stagnant air. It is also interesting that the rate of flame spread appears to increase exponentially with air velocity, at least over the range studied in this investigation.

Table 2 shows effects of orientation of the sample on flame spread in a stagnant atmosphere. The first results for cellulose acetate sheets with edges inhibited show that the speed of the flame creeping across the surface is not very different for

TABLE 2.
Effect of sample orientation on flame spread

(a) Cellulose acetate sheet (edges inhibited) (O$_2$, 5 psia) (Ref. 1)		
vertical upward	rapid, erratic	
horizontal	0.12–0.14 cm/sec	
vertical downward	0.12–0.15 cm/sec	
(b) Filter paper (air) (Ref. 5)		
	1 atm (cm/sec)	10 atm (cm/sec)
hotizontal	0.36	0.48
22.5° upward	0.63	1.35
45° upward	1.12	2.92
75° upward	2.92	4.20
vertical upward	4.6–7.4	5.9–8.1

horizontal propagation and for vertical downward propagation, but is considerably more rapid and is erratic for vertical upward propagation. The important conclusion to be drawn from this observation is that there is apparently a creeping mode of propagation which is relatively insensitive to orientation, as long as upward propagation is not involved and there are no free edges to burn. The table also shows some results with strips of filter paper tilted at various angles. Propagation speed is seen to increase progressively with the angle of upward tilting. The results become quite erratic when the sample is entirely vertical and these authors have suggested that a 45° upward orientation should be convenient for data-taking if one wants reproducible results which include the upward effect. Note that there is an order of magnitude difference in the upward propagation rate compared with the horizontal propagation rate, and that this difference persists at 10 atmospheres as well as at one atmosphere.

Table 3 shows effects of the chemical composition of the material on the horizontal flame spread rate. In data group (a), seven plastics are compared. The flame spread rates for the central five of the group are fairly closely bunched, ranging between 0.11 and 0.18 cm/sec for the test conditions quoted. Polyvinyl chloride, however, burns much more slowly, 0.04 cm/sec, and this is undoubtedly due to the presence of the halogen. The Tygon, which is rich in a plasticizer, burns much faster than any of the other materials and this is clearly due to the great volatility of the plasticizer compared with the other polymers which must undergo pyrolytic decomposition to produce flammable vapors.

In data group (b) of Table 3, it is seen that flame will propagate more than three times as fast over an oil-wetted paper strip as over the same dry paper. Data group (c) in this table shows that flame will propagate over warm kerosene in air at 16 cm/sec, which is two orders of magnitude faster than typical rates of propagation over smooth organic surfaces which must pyrolyze rather than phys-

TABLE 3.
Effect of material on horizontal flame spread rate

(a) PURE O_2, 5 psia (edge effect eliminated):	
	(cm/sec)
polyvinyl chloride (Ref. 1)	0.04
polyethylene (Ref. 1)	0.11
polymethyl methacrylate (Ref. 4)	0.13
cellulose acetate (Ref. 1)	0.14
polystyrene (Ref. 4)	0.16
polypropylene (Ref. 1)	0.18
"Tygon"—plasticized (Ref. 1)	0.53
(b) AIR, 1 atm (edges exposed):	
resin-impregnated paper (Ref. 3)	0.23
same, oil-wetted (Ref. 3)	0.77
(c) AIR, 1 atm (Ref. 7)	
Kerosene (3 mm thick, on water)	
Temp. = 0°C	5
Temp. = 21°C	7
Temp. = 40°C	16

TABLE 4.
Scale effects

(a) Effect of width of paper strips in air (45° upward burning) (Ref. 5)
6 mm width—1.8 cm/sec
8 mm width—2.4 cm/sec
12 mm width—3.1 cm/sec

(b) Effect of fire size on vertical downward propagation: cellulose acetate in O_2 at 5 psia (Ref. 1)
$\frac{1}{8}$ in. rod—0.37 cm/sec
1 in. diam. rod—0.23 cm/sec
1 in. × $\frac{1}{8}$ in. strip, inhibited—0.15 cm/sec

ically vaporize. The strong effect of the temperature of the kerosene on the propagation rate is also interesting.

Table 4 illustrates some effects of the scale on which the experiment is performed. In data group (a) it is seen that for 45° upward burning of paper strips, the width of the strip has a very strong effect on the rate of propagation. Indeed, over the range of experiments shown, the burning rate is almost proportional to the width of the strip. Data group (b) shows an opposite effect. Here, for downward propagation, the flame moves more rapidly down a small rod than down a large rod. In this case, apparently, the propagation rate is limited by the rate at which oxygen can arrive at the flame by diffusion from the surroundings, which is of course greater as the radius of curvature of the burning surface is reduced. These two groups of data (a) and (b) show that it is dangerous to generalize that a large fire will propagate either faster or slower than a small fire.

Table 5 shows the effect of the total pressure on the flame spread rate under conditions where the composition of the atmosphere is held constant. While these

TABLE 5.
Effect of pressure on flame spread
$V \sim p^n$

Material	Laboratory	Pressure range atm	Oxygen range (mole fraction)	n
Horizontal				
Polystyrene*	(4)	0.3–27	0.46–1	0.76
Polymethyl methacrylate*	(4)	0.3–27	0.46–1	0.82
Paper Wood	(2)	0.5–1.0	0.46	0
Paper	(5)	1–10	0.21	0.12
Paper	(3)	1–5	0.21–0.31	0.13
45° Upward				
Paper	(5)	1–10	0.21–0.5	0.46
Paper	(5)	0.2–1	1	0.38

* Edges inhibited

various authors have not necessarily claimed that a power law is the best description of their data, nevertheless for comparison the data have been forced into a power law form so that we may compare the numerical value of the power to which pressure must be raised to best represent each set of data. The horizontal propagation data show that three laboratories have found low exponents, from zero to 0.13, for paper and for wood with exposed edges. Experiments with polystyrene and polymethacrylate with edges inhibited have shown high exponents in the vicinity of 0.8. This large difference may be due to the presence or absence of edges, or it may be due to the different physical or chemical nature of wood or paper compared with smooth plastics. More data would clearly settle this question but does not appear to be available. It may be noted that for 45° upward propagation the exponent for paper is considerably larger than for horizontal propagation, suggesting that a different mechanism applies.

TABLE 6.
Effect of nitrogen dilution on flame spread
Assume: $V \sim (O_2 \text{ mole fraction})^m$ at constant P

Material	Laboratory	Pressure range (atm)	Oxygen range (mole fraction)	m
Horizontal				
Polystyrene*	(4)	0.3–27	0.46–1	2.3
Polymethyl methacrylate*	(4)	0.3–27	0.46–1	2.5
Paper	(3)	1–5	0.21–0.31	1.6
Oiled paper	(3)	1	0.21–0.31	2.7
45° Upward				
Paper	(5)	1	0.15–1	1.15
Paper	(5)	2.5	0.15–0.5	0.99
Paper	(5)	5.5	0.15–0.5	0.81
Paper	(5)	10	0.15–0.31	0.73

* Edges inhibited.

Table 6 shows the effect of varying the proportion of diluent nitrogen in the atmosphere at constant pressure. The various data are compared by assuming that the spread rate is proportional to a power of the oxygen mole fraction, although the data do not all necessarily conform precisely to such a simple law. Table 6 shows that horizontal propagation rates for various materials vary with a power of oxygen mole fraction between 1.6 and 2.7. Data for paper show that the oxygen dependency is considerably lower for 45° upward propagation than for horizontal propagation, suggesting a different mechanism. The data also suggest that at quite high pressure the dependence of upward propagation on oxygen content is less severe than at lower pressure.

Table 7 shows the effect of an equimolar substitution of helium for nitrogen on flame spread under various conditions. Such a substitution changes three properties of the atmosphere: the heat capacity, the thermal conductivity, and the oxygen diffusion coefficient. If the relative importance of these three effects on the propagation rate was the same for various materials and conditions, then the ratio of

TABLE 7.
Effect of equimolar substitution of helium for nitrogen on flame spread

Material	Laboratory	Pressure (atm)	Oxygen (male fraction)	V_{He}/V_{N_2}
Horizontal				
Paper	(3)	1	0.31	1.8
Paper	(3)	5	0.31	1.6
Paper	(2)	0.4	0.46–0.7	1.4
Cotton fabric	(2)	0.3–0.5	0.46–0.7	0.7–1.2
Cotton terry cloth	(3)	5	0.21	0.45
Cellulose acetate	(2)	0.3	0.46	1.4
Polystyrene*	(4)	0.3	0.62	1.35
Polystyrene*	(4)	27	0.62	1.55
Polymethyl methacrylate*	(4)	0.3–27	0.62	1.6
45° Upward				
Paper	(5)	3–7	0.16	0.9–1.1
Paper	(5)	1–7	0.3	1.2–1.5
Paper	(5)	1–7	0.5	0.9–1.3

* Edges inhibited.

flame speed in helium to flame speed in nitrogen should be a constant. A glance at the last column of the table shows that this flame speed ratio varies from 0.45 to 1.8. It is unlikely that this spread can be attributed to experimental error, since three different laboratories have reported cases where materials burn more slowly in helium than in equivalent nitrogen atmospheres, as shown in the table, and four laboratories have reported cases where the reverse is true for certain materials and conditions. These results are particularly striking in showing that no *simple* theory of flame spread is likely to be able to account for all experimental observed effects.

III. *Theory*

No firmly established flame-spread theory in terms of known parameter exists even for the simplest imaginable geometry. Recent theoretical investigations by Tarifa and Torralbo[7] and by McAlevy, Magee, and Wrubel[4] represent the most advanced attempts to date to describe the process of a flame steadily propagating over a combustible surface. Huggett, von Elbe, and Haggerty[2] have discussed development of an equation for "thin"materials (see below).

In considering a model for flame spread over a surface, there are at least three grossly differing geometrical possibilities: (I) the surface is that of a thick enough slab so that it may be considered to be semi-infinite in regard to the thermal wave into the slab; (II) the slab of combustible is thin in a thermal sense and is in contact with a substrate of higher thermal diffusivity which acts as a heat sink (paint on metal, oil on water, etc.); (III) the combustible is thermally thin and is burning on both sides (or all around the perimeter if cylindrical). Reference 7 treats Cases I and II, Ref. 4 treats Case I, and Ref. 2 treats Case III. Kinbara[8] has found that the rate of flame spread over a sheet of paper is inversely proportional to the thickness of the paper, over a tenfold range, a result clearly falling in regime III.

The aerodynamic behavior of the flame gas at the leading edge of the flame is clearly of potential importance. Motion of this gas may be caused by: (I) buoyant rise; (II) thermal expansion as the flame grows; (III) an external wind. All three of the theories referenced ignore all three of these possible effects. This may well be justified for propagation downward or over a horizontal surface.

The model must include at least one but may involve several modes by which heat travels from the flame to the not yet ignited material. The possibilities include: (I) conductivity through the gas phase to the not yet ignited fuel; (II) subsurface conductivity in the direction of flame spread; (III) radiation from the flame to the unignited surface. It is not easy to demonstrate that any one of these three modes is generally negligible.

The *chemistry* of the fuel volatilization and possibly ignition must be considered. A cellulosic fuel which chars while pyrolyzing is capable of subsurface exothermicity associated with the char formation. Many polymers would undergo endothermic melting and depolymerization. One theory[4] assumes that the vapors produced must rise to a chemically determined runaway temperature (ignition temperature). An alternate view is that the vapors must reach a critical concentration (lower limit of flammability), and then, regardless of temperature of these vapors, ignition will occur by spread of the adjacent flame, perhaps by radical diffusion as well as heat transfer.

Diffusion must be considered in any complete model, since the rate of flame spread can never be faster than the rate of interdiffusion of oxygen and fuel vapors (generally of complex and unknown composition if resulting from pyrolysis). Diffusion is impeded both by whatever inert gas is present and by combustion products. Representation of diffusion in any model by a single diffusion coefficient requires an assumption of what is diffusing through what (oxygen, fuel, inert gas, products).

Inasmuch as some flame spread data show substantial pressure dependence and other data show little or no pressure dependence, it is pertinent to inquire how pressure dependence would come into a theory of flame spread. First of all, aerodynamic effects described by Reynolds number or Grashof number correlations will be pressure dependent, because these involve competition between pressure-invariant viscous forces and density-dependent inertial or buoyancy forces. On the other hand, consider a steadily burning spherical oil droplet in stagnant air. In this case a spherically symmetrical flame may be assumed with no viscous effects, and the well-developed theory then shows that the rate of burning is virtually independent of pressure, except for a weak effect of pressure on the surface temperature of the droplet, which has little effect on the burning rate. Thus, theoreticians who wish to construct a flame spread model with low pressure sensitivity may feel encouraged by this analogy. On the other hand, construction of a flame spread theory showing large pressure dependence not based on aerodynamic phenomena poses a problem. McAlevy, *et al.*[4] postulate propagation based on continuous ignition governed by pressure-dependent kinetics. While this mechanism does not appeal to this reviewer as a very plausible one, it does provide a means of obtaining pressure dependency. For luminous or semiluminous flames whose radiant emissivity increases with pressure, a pressure dependence of flame spread would result if radiant energy transfer were significant.

It appears to this reviewer that basic understanding of the propagation mechanism is needed more urgently than computer solutions of the conservation equations in two dimensions, for advance in understanding of flame spread.

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Subject Headings: ***Fire spread, on surfaces and plastics; Plastics, fire spread on; Surfaces, fire spread over.***

ABSTRACTS

A. Prevention of Fires and Fire Safety Measures

Ashton, L. A. (Joint Fire Research Organization, Boreham Wood, England) "Maximum Sizes for Fire Resisting Doors and Shutters," *Joint Fire Research Organization Fire Research Note No. 662* (July 1966)

It is often necessary to protect openings in fire resisting walls of buildings by means of doors and shutters exceeding appreciably in size specimens which have been subjected to the standard fire test. An examination has been made of the factors affecting the ability of various types of door and shutter to act as barriers to the spread of fire, and how far test data may be safely extended. Recommendations for maximum heights and widths of the different types, except timber doors, have been made, and for the spacing of combustible materials of construction and contents to avoid risk of ignition by heat radiated from doors and shutters of the maximum dimensions.

Subject Headings: *Doors, fire resistant; Shutters, fire resistant; Fire resistance, of doors, and shutters.*

Old Sec. XIII Author's Summary

Institute of Defense Analyses, Washington, D.C. "Practical Experiences of Fire Protection Services, Parts I and II," *Translated from the German by C. E. Harvey and W. C. Truppner under Office of Civil Defense Work Unit No. 4315A* (June 1966)

This study is a critical presentation of the organization, technology, and tactics of fire protection as employed by a civil defense organization in Germany during World War II. The study is replete with descriptive material and personal judgments which should be of interest to professional fire fighters, research organizations concerned with the thermal effects of nuclear weapons on urban areas, and those responsible for the organization of community response to these problems.

The equipment and methods used in an attempt to control the fire effects of the overwhelming allied air raids on Hamburg are given in detail. The problems which were encountered, along with recommendations for reducing the vulnerability of large urban areas to the effects of mass fires, are also provided. It is believed that much of the information has applicability to certain of the problems involved in the protection of large cities from the thermal effects of nuclear weapons.

Descriptions of the fire storm which engulfed sections of Hamburg, as well as with the experience of the fire-fighting organizations, are of particular interest to those attempting a study of the safety of persons in large metropolitan areas subjected to the thermal effects of nuclear weapons. Comments on building density, numbers of ignitions, flammability, and above all, civil defense, should provide an insight into the solution of problems arising from efforts to increase urban protection against a fire storm.

Part II of this study is a collection of pictures of the fires and fire damage resulting from allied air raids over Germany in World War II. Notable among them are the photographs taken of the Hamburg fire storms (July 1943) and their effects.

Subject Headings: *Civil Defense, programs; Fire damage; Fire departments, German, volunteer; Fire protection, organizations and technology; Fire storms; Incendiary bomb, effects; Military fire-setting; Nuclear weapons, thermal effects of; Urban protection, against fire storms.*

Translators' Summary

Nametz, R. C. (Michigan Chemical Corporation, Saint Louis, Michigan) "Self-Extinguishing Polyester Resins," *Industrial & Engineering Chemistry* **59**(5), 99–116 (1967)

This is a literature review with descriptions of methods for making self-extinguishing polyesters and a summary of techniques most generally used for evaluating flame resistance.

Subject Headings: *Polyester resin, self-extinguishing; Self-extinguishing polyesters.*

Old Sec. XIV R. Fristrom

Shern, J. H. (Los Angeles Fire Department, Los Angeles, California) "Smokeproof Towers in Center Core Structures," *Fire Technology* **2**(4) 303–307 (1966)

Smokeproof towers are stair enclosures which are built to provide safe exits from burning buildings. They are designed to keep smoke and flame from entering the stairs and other escape routes even when the access doors are left open. They are located ordinarily on outside walls or on walls facing sizable courtyards, and are entered from open balconies. However, such exterior towers use up a great deal of desirable window space, especially in high rise buildings. If interior towers could be designed which would perform equally well, they would be preferred by both realtors and tenants.

Initial investigations carried out by the Los Angeles and San Diego Fire Departments to study the effectiveness of interior towers for keeping smoke out of stairwells showed that power ventilation could keep a stairway relatively smoke-free, but that always some smoke entered the tower. Improvement was obtained when the ventilation was designed to effect a general air movement from the stairway toward the fire floor, with exhaust provision in a vestibule separating the stairway from the fire floor.

Additional experiments by the Los Angeles Fire Department in 1965 confirmed that power ventilation was absolutely necessary, and showed that the vestibules located between the access doors and the stairways were of particular value when they were exhausted directly to the outside of the building. These experiments were conducted in an eight-story reinforced concrete building $30\frac{1}{2}$ ft wide by 66 ft long, which had been modified to present a number of typical stairway and floor arrangements. Lumber and asphalt building paper were burned to generate smoke for the tests. Thermocouples, photocells, and inclined manometers were located at strategic places to provide a measure of heat, smoke density, air pressure, and air velocity to supplement the visual observations.

The Los Angeles tests showed that vestibules on each floor of a building, plus power ventilation, could effectively prevent smoke from entering stair-shafts. These vestibules, located in the hallways at the stair landings, required a power exhaust system to an outside air shaft, independent of the stair-shaft system and the building air conditioning. The interior stair enclosures required a controlled draft system to provide a positive air pressure in the stair-shafts (relative to the vestibule pressure). When the stair-shaft and vestibule air pressures were adjusted properly, smoke could not accumulate in the stairs even when the access doors to the fire floors were left open.

The test data (not given in this paper) were used as a basis for some qualitative and quantitative specifications for the design of interior smoke-free stair enclosures. It was recommended that the stair-shaft enclosures exit into open passageways leading to public ways; that openings be limited to access and exit doors and necessary ventilating equipment; and that all doors be self-closing with a fail-safe action. Combination detectors were recommended for shutting off the comfort air conditioning and activating the emergency ventilation simultaneously, with the whole operating from an independent auxiliary power source capable of at least two hours of operation.

Additional specifications were derived for air flow, air pressure, and vestibule geometry for buildings similar to the test building.

Subject Headings: *Smokeproof towers, for buildings; Towers, smokeproof.*

Old Sec. XIII — B. Greifer

Waterman, T. E. and Salzberg, F. (IIT Research Institute, Chicago, Illinois) "Development of Fire Resistance Ratings for Shelter Components," *Final Report under Office of Civil Defense Contract N228 (62479) 68580* (February 1966)

Experiments were performed to evaluate the responses of shelter components to typical fire exposures in order to develop means for predicting these responses from the results of a minimum number of standardized tests. Exposures were provided by an infrared lampbank.

Samples included material of both high and low insulating qualities, inert materials, and those exhibiting ablative and dehydration processes. Each sample was approximately 16 in. wide, 24 in. high, and 2 in. thick.

Results indicate that fire resistance of a barrier is considerably affected by the intensity of exposure. For homogeneous combustible materials, this effect can be expressed approximately in terms of the area equivalence method suggested by

Ingberg. For homogeneous noncombustible materials, containing free water, this method produced errors ranging from 10% to 31%. This error is substantially larger for materials containing both free and chemically-combined water. In the case of nonhomogeneous materials, the error ranged from 62% to 86%.

Subject Headings: *Fire resistance, rating of; Radiative heating, of materials; Rating, of shelter components; Shelter, rating of components.*

Old Sec. XIV Authors' Abstrac

B. Ignition of Fires

Ashmore, P. G., Tyler, B. J., and Wesley, T. A. B. (University of Manchester, Manchester, England) "Experimental Investigations of Conductive and Convective Heat Transfer in Relation to Thermal Ignitions," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 1133–1140 (1967)

Temperature distributions in reacting mixtures of hydrogen and chlorine; hydrogen, chlorine, and nitrosyl chloride; and nitric oxide and oxygen were determined at various temperatures in various spherical reaction vessels. In cases where the Rayleigh number did not exceed 600, excellent agreement was found with the thermal ignition theory of Frank–Kamenetskii, for temperature rise at the center of the vessel, and for temperature profiles over a diameter.

Most experimental tests for theories of thermal ignition depend on the assumption that heat transfer to the walls of the vessel occurs only by conduction. An important criterion for the onset of convection in such experiments is the attainment of a critical value of the Rayleigh number, which is the ratio of buoyancy forces to inertial forces. The Rayleigh number (Ra) is defined by $\mathrm{Ra}=g\alpha a^3\Delta T/k\nu$, where g=acceleration of gravity, α=coefficient of thermal expansion, a=radius of vessel, k=thermal conductivity, and ν=kinematic viscosity.

Use was made of two exothermic reactions whose kinetics are well known—the combination of nitric oxide and oxygen at 70°C and the combination of hydrogen and chlorine in the presence of nitrosyl chloride at 300°C. In this manner, tests were made of the thermal theory at low values of the Rayleigh number, and the onset of convection at higher values could be demonstrated.

Experiments at 300°C were made in a Pyrex vessel with an equivalent radius of 5.4 cm, immersed in a fused salt bath. Fine-wire coated thermocouples were located at the center of the vessel, and at four other points along a diameter. Transient temperatures and pressures were measured after filling, and chlorine concentration was measured by spectral absorption. HCl concentrations could then be determined by differences. Calibrations were made to determine the heating time of the initial mixtures, which was always short compared to the reaction time.

The reactions of nitric oxide and oxygen were carried out in spherical Pyrex vessels of two different sizes, placed in an air thermostat at 70°C. In all cases, temperature profiles within the vessels could be determined by the thermocouples placed along a diameter.

In the case of equimolar mixtures of hydrogen and chlorine, with a small amount of nitrosyl chloride, at a total pressure of 106 torr, the maximum temperature rise occurred in about 100 sec, at which point the rate of formation of HCl also reached a maximum. In the cases of mixtures of hydrogen and chlorine without nitrosyl chloride, and of nitric oxide and oxygen, a maximum in temperature did not occur, but the temperatures fell steadily from high initial values.

For experiments at low values of the Rayleigh number (less than 600), the time-temperature histories at the center of the vessel, and the rate of formation of product agreed very well with values predicted by the Frank–Kamenetskii theory, particularly in the case of the hydrogen/chlorine/nitrosyl chloride mixtures. This theory also predicts that the radial temperature distribution should be parabolic, a situation also confirmed by the present experiments, again, for low values of the Rayleigh number.

At high values of the Rayleigh number, the temperature distributions, in all cases, became very asymmetric, higher at points above the center than at points below, indicating the onset of convection. A plot of the ratio of temperature rise calculated by the thermal theory, divided by the measured values, vs the Rayleigh number, shows a sharp break at a value of $Ra = 600$. This is much lower than a critical value of 10,000 as suggested by Frank–Kamenetskii.

The results shown here indicate that many previous measurements of activation energies should be re-evaluated, because such measurements are usually made under the assumption of no convection, whereas a value of $Ra = 600$ is easily exceeded. Many of the discrepancies reported may be resolved by applying the techniques of the present work.

Subject Headings: *Conductive heat transfer, effect on ignition; Convective heat transfer, effect on ignition; Heat transfer, effect on ignition; Ignition, effect of heat transfer; Thermal ignition, effect of heat transfer.*

Old Sec. III **T. K. Richmond**

Bowes, P. C. (Joint Fire Research Organization, Boreham Wood, England) "High Mean Temperatures in Ships' Holds," *Joint Fire Research Organization Fire Research Note No. 633* (October 1966)

For the purpose of assessing the spontaneous ignition hazard of a limited class of goods carried on board ships, estimates have been made of the highest time-mean temperatures likely to be encountered in the upper regions of ships' holds in some of the hottest sea areas.

Subject Headings: *Holds of ships, high temperatures in; Ignition, spontaneous, in ships' holds; Ships' holds, temperatures in; Spontaneous ignition, in ships' holds; Temperature, in ships' holds.*

Old Sec. I **Author's Summary**

Bowes, P. C. and Davey, L. D. (Joint Fire Research Organization, Boreham Wood, England) "Self-Heating and Ignition in Two-Component Systems Preliminary Experimental Study," *Joint Fire Research Organization Fire Research Note No. 643* (November 1966)

Observations have been made on self-heating and ignition of cubes of sawdust containing a fatty oil (olive oil). Preliminary comparison with a theoretical model for two-component systems (unpublished) shows that the relationship between the critical temperature rise and critical ambient temperature for ignition has the general form required by the model.

Subject Headings: *Ignition, of two-component systems; Olive oil, ignition of; Sawdust, ignition of; Self-heating, of two-component systems; Spontaneous ignition, of sawdust and olive oil; Two-component systems, ignition and self-heating of.*

Old Sec. I Authors' Summary

Chase, J. E. (Imperial College, London, England) "Evaporation and Ignition in Air of a Surface Oil Film Following Adiabatic Compression," *Combustion and Flame* **10**(4) 315–329 (1966)

The experimental investigation of the evaporation and subsequent ignition of thin surface films of oil during and immediately following adiabatic compression of air in contact with the oil is discussed in this paper. This method of compression was used in preference to compression by a surge of high pressure air through a rapidly opened valve to minimize splashing and excessive gas mixing. The results of this work and other unpublished parallel research carried out by Chase indicate that ignition is dependent on initial system temperature and compression ratio. A tentative hypothesis is proposed by which the motion of the air induced by compression causes both evaporation of the fuel and convective cooling of the mixture. Ignition is proposed to occur if the flammability limit is reached before the air-fuel mixture has cooled below the ignition temperature.

The approach used in this research is as follows. First, pressure decay data are obtained following compression with air alone. These are used to determine the gas temperature decrease in the constant volume system. From internal combustion engine theory a convective heat transfer coefficient to the walls is calculated and with the gas temperature, from above, the heat flux to the wall is calculated. This heat flux is assumed for the oil film and the oil film surface temperature is calculated from unsteady-state conduction theory. The above calculations are indicated for all compression ratios and for various times after compression. By the Reynolds analogy between heat and mass transfer, an evaporation rate and a subsequent gas-phase equivalence ratio is calculated. Experimentally, ignition and ignition delays are determined from pressure records, cine photographs, and the occurrence of soot. An attempt is made to correlate the ignition limit with such variables as compression ratio, initial temperature, film thickness, and oil type and to explain the results on the basis of the tentative hypothesis mentioned above.

Three oils were used: *n*-decane, Decalin, and Admiralty spec. (OM65) lubricating oil. Initial temperatures were varied from 17° to 180°C. Compression ratios from 9:1 to 30:1 and film thicknesses from 0.0007 to 0.003 in. were covered.

A definite correlation was found for all of the oils between the minimum compression ratio required for ignition and the initial equivalence ratio in the gas phase. (This initial equivalence ratio was obviously determined from initial temperature and the oil vapor pressure.) As expected, the lower the initial equivalence ratio the higher the compression ratio required to cause ignition. The violence of ignition, i.e., the pressure increase with oil present compared to the pressure rise with air alone, also increased with initial equivalence ratio.

For the purpose of comparison, tests were carried out to determine the ignition limit for homogeneous decane-air mixtures, i.e., without a liquid phase present. It appeared that the limit occurred at an equivalence ratio of 0.23 independent of compression ratio as long as the compression ratio was high enough to insure a mixture temperature in excess of a minimum ignition temperature.

In the oil film experiments Chase found ignition delays of 4 to 15 msec. Since, for the temperatures and pressures existing soon after the compression, these are a factor of 10 to 20 times greater than the chemical kinetic ignition delays, he postulates that the time is required to vaporize oil to raise the equivalence ratio to 0.23. As described above, he calculates the air temperature and the film surface temperature for various times after compression from pressure decay, engine theory, and unsteady-state heat transfer.

Using Spalding's[1] mass transfer model based on the Reynolds concept of flow in the neighborhood of an interface, Chase calculates the oil vaporized as a function of time and determines the instantaneous equivalence ratio based on initially pure air and the oil film. For given initial equivalence ratios he then determines the time required to achieve the ignition limit of equivalence ratio of 0.23. The agreement between his measured and calculated delays is quite impressive. Up to approximately 15 msec after compression he shows an almost one to one relationship between his calculated and experimental points. After 15 msec, he points out that the gas temperature is rapidly decreasing, eventually reaching low enough levels to require chemical kinetic delays of as much as 30 msec and more. Since his calculated delays are based only on the time to vaporize the fuel and require an essentially zero kinetic delay, the lack of agreement at long time-low temperatures is understandable.

Reference

1. Spalding, D. B.: *Convective Mass Transfer*. Arnold: London (1963).

Subject Headings: *Adiabatic compression and ignition, of oil films; Evaporation and ignition, of oil films; Films of oil, ignition of; Ignition, of oil films, by adiabatic compression; Oil films, ignition of.*

Old Sec. I F. Falk

El-Wakil, M. M. (University of Wisconsin, Madison, Wisconsin) **and Abdou, M. I.** (Higher Institute of Technology, Helwan, Egypt) "The Self-Ignition of Fuel Drops in Heated Air Streams. I. Experimental Data. II. Physical Ignition Delay. III. Chemical Ignition Delay," *Fuel* **45**(3) I. 177–188. II. 189–197. III. 199–205 (1966)

To extend previous investigations on fuel droplet combustion, where in most cases ignition was initiated by an auxiliary ignition source, the authors designed an apparatus in which an air stream could be sufficiently preheated to cause drops to self-ignite. The air was preheated in a ceramic heater using ceramic electric heating elements. The heated air stream emerges through a nozzle which gives flat velocity and temperature profiles in the experimental zone. Before an experiment the hot air stream is deflected by a solenoid-operated ceramic plate so that the fuel droplet, held on the small spherical bead of a chromel-alumel thermocouple, can be placed in position. The air temperature is measured by another thermocouple and its velocity computed using the gas laws.

The drop temperature history is recorded by a high speed potentiometer circuit. Its size was viewed and recorded using an illuminating and magnification system, in which two cameras, a low speed 16 mm camera and a Fastax were used. Camera speeds were such that flame histories could be determined to within ±0.002 sec.

The authors point out that while the drops in a fuel spray are mostly small and spherical, in this series of experiments the drops studied were large (0.055 in. and 0.065 in.) and not perfectly spherical for the whole time of an experiment. Deformations were taken into account by using an equivalent diameter for the drop equal to the diameter of a sphere of the same volume.

Two types of flames were observed depending on the air stream velocity. At low velocities a diffusion-type flame was seen, which started at the lower end of the drop and then completely surrounded it, finally persisting in most cases for a short while after the liquid had all evaporated. At high air stream velocities a detached flame was formed in a narrow plane above the drop, the distance being a function of the air stream velocity. The air stream velocity at which the flame type changes was determined for high and low volatility fuels over a range of air temperatures. The authors confine the analyses and discussion to the diffusion-type flames.

Pure straight chain hydrocarbons were used. The burning phase period increases slightly with n, the number of carbon atoms in the molecule, i.e., with decreasing fuel volatility. The increase is less marked at higher air temperatures.

The total ignition delay increases with n and the initial drop size, while it decreases with air temperature, air velocity, and initial liquid temperature.

The results obtained are represented to within ±7% by the correlation

$$\tau_t = 10.3 D_0^{0.85} \exp(A + Bn)$$

where τ_t is the total ignition delay, sec; D_0 is the initial diameter of the drop, in.; n is between 8 and 16 and D_0 between 0.05 and 0.07 in., with T_L (liquid drop temperature) between 200° and 250°F. A and B are functions of the free stream temperature, T_B in °R:

$$A = 20.5 - 35.9(T_B/1850)^2 + 13.2(T_B/1850)^4$$

$$B = 0.364(7.775 - \ln T_B)$$

It should be noted that the correlation only applies for air velocities which give diffusion flames and for air temperatures above the minimum necessary for self-ignition.

Physical Ignition Delay

A close examination of the flame photographs was made to determine what simplifying assumptions would be valid in the analysis of the physical portion of ignition delay. From other work[1] the importance of the Reynolds number in influencing the boundary layer shape was known. In both jet engines and compression ignition engines the Reynolds numbers are generally very low, ranging between 50 and 500. In this investigation the Reynolds number range was between 200 and 425 so that the patterns of boundary layers are similar.

The simplifying assumptions made were:

(a) the drop and the boundary layer surrounding it were spherically symmetrical.

(b) the flow in the entire boundary layer was laminar and heat and mass transfer occurred as simple radial molecular processes.

It was further assumed that the temperature at the surface and within the drop was uniform and equal to that measured by the thermocouple carrying the drop.

The physical ignition delay is the time it takes from the instant that the drop is exposed to the air stream for a fuel vapor-air mixture to form and diffuse to a point in the boundary layer where the temperature is at the self-ignition temperature of the fuel.

The authors develop relationships between the fuel vapor concentration, temperature, and radial position in the boundary layer. The experimental results were then used in conjunction with the analysis to obtain lean limit combustible mixture-temperature histories for various operating and ambient conditions.

An empirical correlation for diffusion-type flames was obtained,

$$\tau_p = 1.10 D_0^{0.5}[0.025 + (T_B - 1850)^{-1}]n^{0.465}$$

where τ_p is the physical ignition delay, D_0 is the initial drop diameter, T_B is the free stream temperature. This fits the results within ±7% for n between 8 and 16, D_0 between 0.05 and 0.07 in., and T_L (initial drop temperature) between 200° and 250°F.

Chemical Ignition Delay.

An Arrhenius reaction rate equation is derived for the fuel vapor-air mixture in the boundary layer. The chemical ignition delay is defined as the time elapsed from the beginning of perceptible chemical reaction to the first appearance of flame determined by the high speed photographs.

Using the temperature and partial pressure histories obtained in the physical ignition delay section, relative rates of chemical reaction can be found for the lean limit fuel vapor-air mixtures. The onset of the chemical delay period was chosen so that the relative chemical reaction rate at that moment was a fixed fraction of the relative rate at the time the first flame appears.

The results show that in general, the physical and chemical delays increase with the number of carbon atoms in the molecule, i.e., as fuel volatility decreases. The physical and chemical delays are comparable in length but the physical delays become smaller in proportion the higher the air stream temperature and the more volatile the fuel.

Reference

1. Jaeck, C. L.: "The Study of Boundary Layers around a Cylinder in Heat and Mass Transfer using a Two-Wavelength Interferometric Technique," *M. S. Thesis, University of Wisconsin* (1962).

Subject Headings: *Chemical ignition delay; Drops, ignition in heated air; Heated air, ignition in; Ignition delay, of drops in heated air; Physical ignition delay; Self-Ignition (See ignition).*

Old Sec. I M. G. Perry

Goard, P. R. C. and Mulcahy, M. F. R. (Division of Coal Research, CSIRO, Chatswood, New South Wales, Australia) "A Study of the Ignition of Graphite," *Carbon* 5(2), 137–153 (1967)

The ease with which a carbon or other combustible solid can be ignited is usually related to an ignition temperature. This is not a well-defined property of the material but depends on such factors as the size of the particle and the velocity of the oxidizing gas relative to it. The theoretical conditions for ignition of a solid particle immersed in a moving gas have been discussed by Frank-Kamenetskii and others, but the ignition phenomena of carbon seem rarely to have been examined experimentally in sufficient detail to indicate how far the theory can be applied quantitatively to an actual carbon as distinct from an idealized carbon. An outline of the basic theory of ignition as applied to the existing experimental conditions is presented.

The ignition of electrically heated rods of spectroscopic graphite subjected to transverse streams of oxygen or air at various velocities has been studied. It was found that pre-ignition combustion occurred within the pores of the graphite but did not completely penetrate the 0.6 cm diameter rod. From this it was concluded that the conditions for ignition are partly determined by the diffusion of oxygen into the pores. Ignition was found to be facilitated by oxidizing the graphite prior to testing, and hindered by depositing pyrolytic carbon in the pores by exposing the heated rods at 1000°C to a slow stream of propane.

The theory of Frank–Kamenetskii, extended to include the effect of pore diffusion on the combustion characteristics, has been used to discuss the conditions for ignition. The practicability of calculating ignition temperatures from published kinetic data and physical properties is explained in some detail. Using the calculation derived for predicting ignition temperatures from available physical and chemical data, a temperature of within ±80°C of the experimental ignition temperature is obtained.

Since this calculation has been made for the best physically and chemically characterized form of carbon available in quantity, the uncertainty in the calculation of the ignition temperature illustrates the limitations of a theoretical estimate of ignition based on kinetic data published in the literature. For less well-defined carbons—for example, impure graphites or solid fuels—the limitations are still greater.

The considerations outlined in the paper illustrate the complexity of the phenomena occurring in any process in which the rate of combustion of carbon is chemically controlled, and they emphasize the consequent uncertainties involved in extrapolating laboratory kinetic measurements. An important example of this occurs with the combustion of pulverized coal. Discussions of the possible influence of chemical control on the combustion of residual carbon particles after devolatilization have been based almost invariably on the application of kinetic data obtained with various macroscopic carbons to an impervious-sphere model of the particles. However, as with ignition, it would appear that for investigating such a process there is at present no satisfactory substitute for direct experiment.

Subject Headings: *Graphite, ignition of; Ignition, of graphite.*

Old Sec. I G. L. Isles

Grishin, A. M. (Saratov State Pedagogical Institute, USSR) "On Spark Ignition," Presented by Academician V. N. Kondrat'ev, January 21, 1966. Translated from *Doklady Akademii Nauk SSSR* **169**(5), 1115–1118 (1966)

Thermal spark ignition models up to the present do not take into account the part played by heat transfer from the reaction zone to the fresh gas in the development of ignition centers and flame propagation. Spark temperature is so high that it can not be considered the governing parameter. Spark energy is therefore the controlling parameter.

The spark ignition problem reduces to a solution of the equation

$$x^2(\partial\theta/\partial\tau)=(\partial/\partial x)[x^2(\partial\theta/\partial x)]+x^2\exp(-1/\theta) \qquad (1)$$

with the initial conditions

$$\begin{aligned}\theta(0,x)&=\infty &&\text{when } x=0,\\ &=\alpha=RT_H/E &&\text{when } x\neq 0.\end{aligned} \qquad (2)$$

Here $\theta=RT/E$ is the dimensionless temperature, $x=r(Rqk_0/\lambda E)^{1/2}$ is the dimensionless radius and $\tau=Rqk_0t/c_p\rho E$ is the dimensionless time. R is the universal gas constant, E is the activation energy, T_H is the initial temperature of the reacting gas, T is the temperature of the reacting gas, c_p is the heat capacity at constant pressure, λ is the heat conductivity, ρ the density, q the thermal effect of the reaction, and k_0 is a pre-exponent.

It is assumed that the temperature distribution in the reacting medium obeys the law

$$\theta_1=3Q\phi^3/\pi(1+\phi^6x^6), \qquad (3)$$

where Q is the dimensionless spark energy and $\phi=\phi(\tau)$ is an unknown function. If we take $\theta_0=3Q\phi^3/\pi$ (the temperature at $x=0$) as the unknown function, we may introduce the effective radius of action of the spark $l=\phi^{-1}(\theta_0/\alpha-1)^{1/6}$, where the quantity l was chosen on the basis of the condition $\theta_1(l, \tau)=\alpha$. By substituting (3) into (1) we get

$$d\theta_0/d\tau=[(\pi\theta_0)^{1/2}/2\alpha(\alpha^{-1}-\theta_0^{-1})^{1/2}][\exp(-1/\theta_0)\ \mathrm{erf}(\alpha^{-1}-\theta_0^{-1})^{1/2}-A(\alpha^{-1}-\theta_0^{-1})^{7/6}] \tag{4}$$

with the initial conditions

$$\theta_0(0)=\infty. \tag{5}$$

Here $A=4\pi^{1/6}\cdot 3^{4/3}\cdot\theta_0^{1/3}\cdot Q^{-2/3}\cdot\alpha^2$. As the limit spark energy let us take that value of $Q=Q^*$ at which a stationary temperature distribution is still maintained; this will be the case if

$$Q=[72\pi^{1/4}\alpha^{7/2}p^{7/2}\exp\tfrac{3}{2}(\alpha-p^2)^{-1}/(1-\alpha p^2)^{1/2}(\mathrm{erf}\,p)^{3/2}]. \tag{6}$$

where $p=(\alpha^{-1}-\theta_0^{-1})^{1/2}$. The quantity $Q=Q(p)$, defined by (6) has a maximum Q^* when $p=p_1^*$. p_1^* is defined on the basis of the equation

$$(1-\alpha p^2)(7-6p^2)=2p[3(1-\alpha p^2)\exp(-p^2)/\pi^{1/2}\,\mathrm{erf}\,p-\alpha p]. \tag{7}$$

Equation (7) has two roots: p_1^* and p_2^*, the first corresponding to a maximum in $Q=Q(p)$.

Since $\alpha\ll 1$ usually, we can find the smallest root of (7) by

$$p_1^*=p_0+\alpha p_1+\alpha^2 p_2+\cdots \tag{8}$$

and when we do we find that

$$Q^*=37.4126(1+0.2931\alpha)\alpha^{7/2}\exp(\tfrac{3}{2}\alpha) \tag{9}$$

Going on to dimensionless variables, we have the minimum ignition energy

$$\epsilon=235.0699\rho c_p(RT_H^{7/2}/E)(\lambda/qk_0)^{3/2}[1+0.2931(RT_H/E)]\exp(3E/2RT_H). \tag{10}$$

The effect of the various physical parameters on the magnitude of the minimum ignition energy is shown. The problem of the accuracy of formula (10) remains unresolved, since comparison with experiment is difficult due to the lack of numerical values for the physical parameters and in particular the value of the activation energy of gas ignition.

Comparisons are made with other models and other approximations.

Subject Headings: *Heat transfer; Ignition, by sparks; Minimum ignition energy; Spark ignition.*

Old Sec. I W. C. Johnston

Kumagai, S. and Sakai, T. (University of Tokyo, Tokyo, Japan) "Ignition of Gases by High-Energy Sparks," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 995–10001 (1967)

Combustion engines, which operate in excess of 10,000 rpm, depend heavily upon a short pre-propagation period and an initial or accelerating period of flame development following the passage of a spark through the combustible mixtures.

To obtain these flame qualities, it is necessary to produce rapidly an initial flame or flame kernel as large as possible. Various means were investigated to accomplish this end, as summarized below, with propane-air mixtures at about 75°F and one atm of pressure.

I. *Conventional Spark-Ignition Source*

Tests were performed in a 30 mm i.d. and 275 mm long tube equipped with eight ionization gaps along the tube length, a pair of windows for flame photography, a spark plug at one end and a conventional ignition coil. At about the 0.1 joule energy level with a conventional spark plug and one mm diam needle electrodes, the initial flame level period was essentially unaffected by the primary break current or the spark energy, except in the case of relatively low initial flame development with short gaps and mixtures of low flammability. This initial flame development period was reduced significantly with multigap spark plugs as shown in Figs. 1 and 2.

II. *Exploding-Wire Source*

Although this source of energy is not amenable for use in engines, the source is of value in determining the relation of spark energy to flame propagation. Tests were performed in a tube 66 mm i.d. and 30 mm depth with a spark source at its center and glass windows at each end for flame photography. Platinum, tungsten, copper, and constantan of 0.03 to 0.1 mm diam were used as the exploding wires. These wires were ignited by a 10-microfarad condenser charged to a maximum of 2000 volts.

It was found that:

- At equivalent, low-energy levels, the ordinary ignition-coil spark was more effective than the exploding wire,
- At energy levels of about 20 joules, the exploding wires promote, greatly, the entire course of flame propagation.

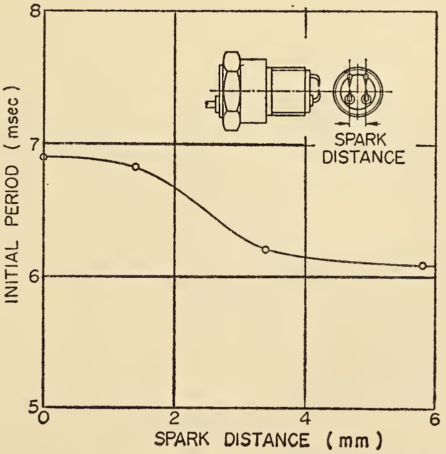

FIG. 1. Initial period of flame development vs. spark distance of an experimental twin-gap spark plug shown. Needle electrodes, 0.9-mm gap width; 6.1% C_2H_8 in air; tubular vessel.

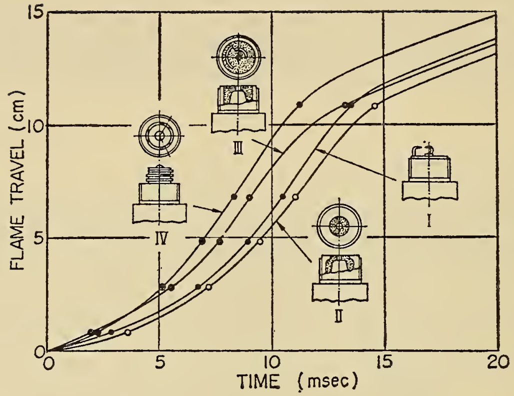

FIG. 2. Flame travel vs. time for various spark plugs shown. I: needle electrodes, 2.6-mm gap width; II: surface-discharge type, single-gap, 2.7-mm gap width; III: the same, with three-series gap, 0.95-mm width each gap; IV: the same, with 1-mm width each gap; 6% C_2H_8 in air; tubular vessel.

III. *Triggered Capacity Spark Sources*

Tests were performed with the same tubes described earlier with an electrical current designed to generate triggered capacity sparks. Capacitors (10 to 100+ mfds) at voltages below 500 volts and capacitors of 1 mfd at higher voltages were used in these tests. The data for the high capacitances and lower voltages using the 30 mm×25 mm tube showed that higher spark energies reduce the initial period of flame development (Fig. 3). This is caused by the larger mass of hot gas produced by the higher energy sparks. This is illustrated in Fig. 4 from data obtained with the 66 mm i.d.×30 mm tube. For the small capacitance-high voltage tests, the current and voltage traces were about the same as in the previous

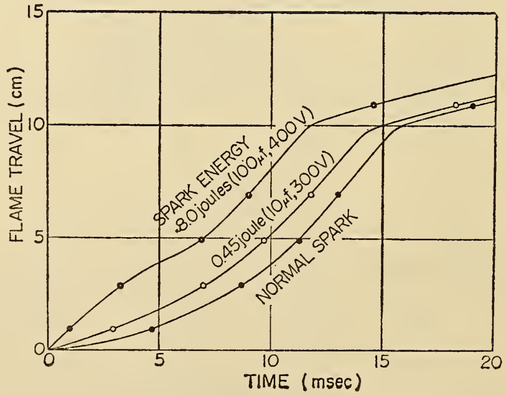

FIG. 3. Variation of flame travel vs. time with spark energy, for triggered capacity speaks and normal spark. Spark plug, 1.3-mm gap width; 6.3% C_3H_8 in air; tubular vessel.

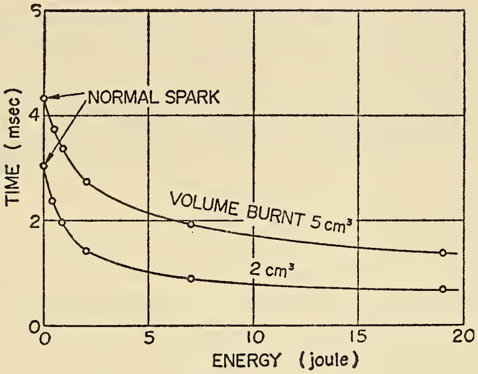

FIG. 4. Variation of time required for specified volume to burn with spark energy. Needle electrodes, 1.1-mm gap width; 6.4% C_3H_8 in air; flat cylindrical vessel.

tests, except that the discharge frequency was much higher. In addition, similar relations were developed as in Figs. 3 and 4.

These data indicated that a triggered-capacity spark of 0.5 to 1.0 joule is sufficient for engine applications with engine speeds of 10,000 rpm and higher.

Subject Headings: *Energy, influence on flame propagation; Gases, ignition of; Ignition, of gases; Propane-air mixtures, ignition of.*

Old Sec. I R. A. Gorski

Meier zu Köcker, H. and Verheesen, H. (Institut für Brennstoffchemie der Technischen Hochschule, Aachen, Germany) "The Ignition Time of Free Falling Hydrocarbon Drops in Pure Oxygen," *Erdöl und Kohle* **18**(9) 705–709 (1965) In German.

An improved apparatus has been used to measure the ignition lag and behavior of combustion of free falling hydrocarbon droplets in oxygen atmospheres at normal pressure and temperatures of 650°–800°C. Special attention was paid to the ignition properties as related to the oxygen temperatures and structural correlations of the individual hydrocarbons.

The droplet entering the combustion chamber evaporates after a short heating period. The fuel vapor interdiffuses with the surrounding oxygen and ignites after the time it takes to reach the lower fuel-oxygen burning mixture limit. The total time can be divided into three distinct periods: the heating up, the evaporation phase and mixing, and the rate-determining steps ruling the preignition reactions. Also important is the particular flow condition established within the apparatus.

The latter is designed to observe droplets of 0.7 mm or greater in size falling through a path of 3250 mm length. The oxygen is preheated in a quartz spiral and introduced into the chamber at temperatures greater than 600°C. Short chain aliphatic hydrocarbons could not be ignited below 600°C. Aromatic hydrocarbons had a lower limit of 650°C; the longer chain C_6 and C_7 aliphatic hydrocarbons do ignite at 600°C but only pass through the precombustion reactions. Photographic evidence of this blue preignition flame was difficult to obtain.

The ignition time lags that were measured increased in order—*n*-olefins branched paraffins, *n*-paraffins, naphthenes and alkylaromatics. The structures of the molecules strongly affect the ignition properties. High pressure engine tests have essentially shown the same results. Individual series of measurements are somewhat sensitive to the particular apparatus involved.

The ignition lags measured are by no means explainable by such a common property as the paraffin factor. Work by others has shown oxygen attack to occur most rapidly at the unsaturated olefin bond. Normal paraffins oxidize at decreasing rates, tertiary (10), secondary (2), and primary (1). Caution must be exercised in coming to absolute conclusions since other factors such as steric-factors, temperature, and pressure could greatly influence the rates. Some attempts have been made to correlate the number of secondary hydrogens with the ignition lag period. One very general but not binding conclusion is that self-ignition temperatures of a particular group of homologous hydrocarbons will decrease as the molecular weight increases. On the other hand the time needed to further the reaction to the point of full combustion increases as the molecular weight increases. This was pointed out earlier with reference to the C_6 and C_7 aliphatic hydrocarbons. The total ignition lag time is a sum of two factors. One is the total time needed to heat and vaporize the fuel and the second is the time needed to mix the fuel and oxygen to form an ignitible mixture. With increasing O_2 concentration the total ignition lag will decrease logarithmically, just as the over-all ignition lag time will also decrease. One additional influence is the diameter of the droplet. The time to vaporize enough fuel to form a locally combustible mixture varies linearly with increasing drop diameter. The time of mixing will decrease linearly with drop diameter. Since heating and vaporization time is somewhat longer than mixing time, the over-all ignition lag will increase linearly with increasing drop diameter assuming all environmental factors such as O_2 temperature, pressure, and flow velocity are kept constant.

A second series of experiments were performed to determine the change in the ignition lag time by adding certain substances to the hydrocarbons. Among those tested were isoamylnitrite, isopropylnitrate, and isoamylalcohol. 5% isoamylalcohol addition resulted in only a slight decrease in ignition. The nitrates and nitrites had a much larger effect. It is apparent that the mechanism sought by additive mixing is to restrict the early preignition oxidation reactions. Also the actual self-ignition temperatures are lowered. The large effects observed with the nitrates cannot be explained solely on the basis just stated.

What is obviously occurring is the initiation of chain reactions such as:

$$RONO \rightarrow RO\cdot + NO_2$$

$$RH + NO_2 \rightarrow R\cdot + HNO_2$$

$$NO_2 \xrightarrow{>400^\circ C} NO + O$$

The thermal instabilities of the additives have a major influence on their over-all capacity to alter the ignition lag time. Further work is in progress to determine the relationship of the ignition lag upon the over-all burning of the fuel drop.

Subject Headings: ***Drops, hydrocarbon, ignition of; Ignition time, of hydrocarbon drops; Oxygen atmosphere, ignition of hydrocarbon drops in.***

Old Sec. I **P. Breisacher**

Michael, M. I. and El-Wakil, M. M. (University of Wisconsin, Madison, Wisconsin) "On the Self Ignition of Hydrocarbon Mixtures," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 1027–1035 (1967)

The mechanism of vaporization and self-ignition of fuel drops of hydrocarbon mixtures was investigated. Droplets of liquid fuels were suspended on thermocouple beads and suddenly exposed to air streams at atmospheric pressure and temperatures to 1800°F. The drops self-ignited and simulated actual events in a combustion chamber. Simultaneous temperature, drop size, and flame size histories were recorded by the thermocouple and optical low-speed (32 frames/sec) and high-speed (500 frames/sec) photography, respectively.

The present work differs from previous work of these and other investigators in the self-ignition of the fuel drops, and the measurement of unsteady- and steady-state temperatures and temperature gradients together with photography, which made it possible to experimentally determine heat and mass transfer, and to obtain a heat balance on the drops at selected moments in their lifetimes.

The fuels investigated were prepared mixtures of pure hydrocarbons (*n*-octane+*n*-hexane; *n*-octane+*n*-hexadecane in various proportions); commercial mixtures such as the distillate grades 1 and 2, and the residual grades 5 and 6; six distilled fractions of grade 6 fuel (boiling ranges, °F at 760 mm Hg, were 377–676, 676–729, 729–785, 785–881, 881–1018, 1018–1078); and bottoms of grade 6 fuel, 40% by volume above 1078°F, with and without asphaltenes extracted. Drops could be formed by any of the fuels or any combination of fuels.

The drops were hung on a 0.03 in. diam. Chromel-Alumel thermocouple bead which was carefully constructed to retain a spherical drop shape during the period of regular burning behavior. They were suddenly subjected to air or nitrogen at 1800°–2000°F by a solenoid-operated ceramic deflector plate which synchronized a timing device to mark zero time of the drop histories on the photographic films and the temperature chart. The drops were illuminated by a Pointolite lamp, and optically magnified and viewed on a ground glass screen for positioning and handling. Their size was recorded by a 16 mm camera, and the flames were photographed by a Fastax camera, with the thermocouple output recorded by an Offner high-speed recording potentiometer.

Size and temperature histories of distillate fractions Nos. 3, 4, and 5 of grade 6 fuel drops in air (Fig. 1) showed a regular behavior. The heavier fractions lost mass more slowly and attained higher temperatures than the lighter fractions. The drop sizes originally increased with time because thermal expansion was

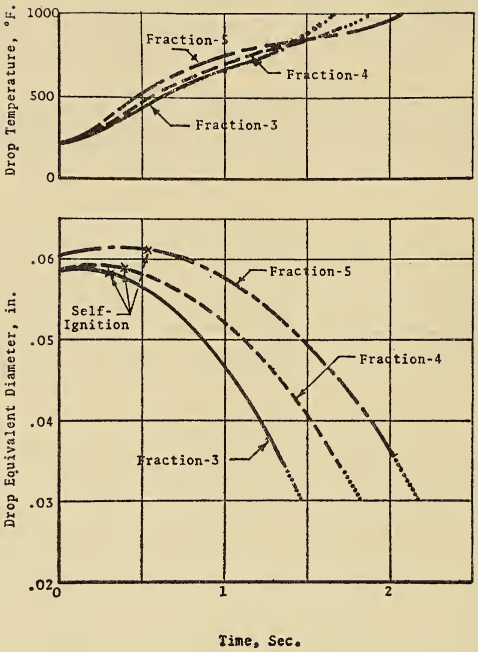

FIG. 1. Temperature and size histories of distillate fractions, numbers 3, 4, and 5 of grade 6 fuel drops in air. Air temperature 1600°F; air velocity, 1500 fpm. (Fig. 6 of original reference, p. 1033).

greater than evaporation during the low-temperature phase of the combustion. The light-distillate-type fuels such as grades 1 and 2, and the prepared mixtures of pure hydrocarbons behaved in the same regular manner.

The residual fuels such as grades 5 and 6 showed irregular behavior both in their temperature and shape histories. Two burning phases were defined, (a) the liquid phase and (b) the residue phase. Periods 1, 2, and 3 of Fig. 2 comprise the liquid phase period for a grade 5 fuel drop in 1360 fpm velocity air at 1600°F. In the liquid phase, successive swellings and contractions were observed due to thermal expansion, evolution of volatiles, and changes in liquid density and viscosity with temperature. Thermal decomposition began toward the end of the liquid phase at 800–900°F drop temperature. The end of the liquid phase occurred with the formation of a hollow-shell residue termed the cenosphere.

In the residue phase, shown by the dashed line in Fig. 2, the residual carbonaceous material was burned. This was a surface-reaction process which lasted almost as long as the liquid-phase period.

A heat and mass balance on residual fuel drops, based on experimental temperature and size data, showed that the total heat transfer from the air to the drops was greater than required in the evaporation process. The excess was equated to the energy used up in an endothermic decomposition reaction. This was represented to be 57.4% of the total heat transfer (±8%) during period 3 of the liquid phase in Fig. 2. For distillate-type fuels this endothermic decomposition heat is zero.

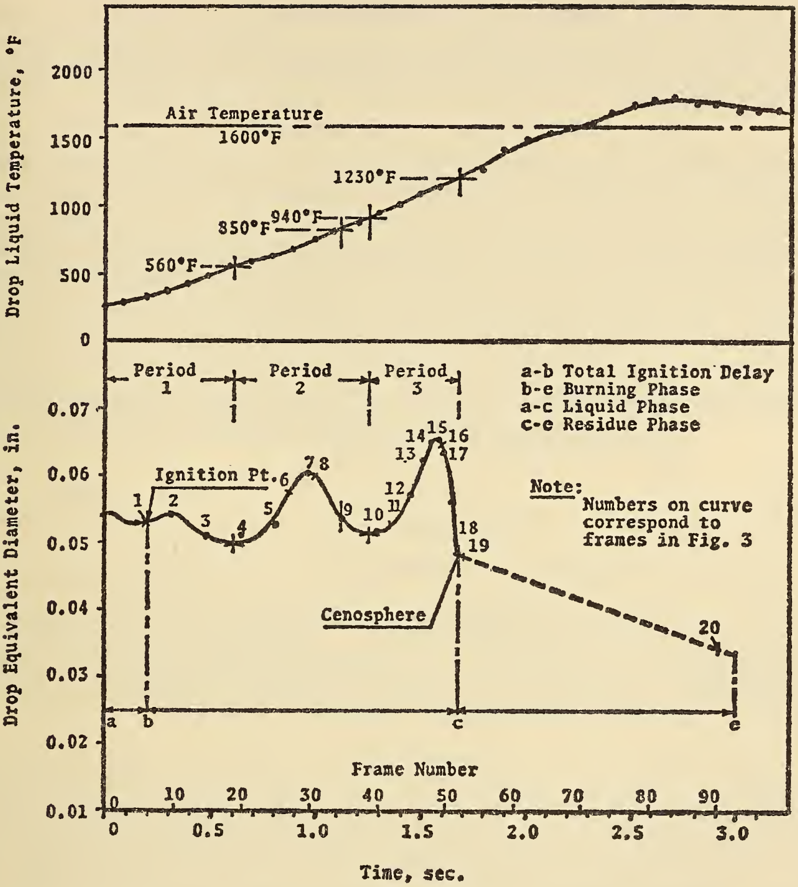

FIG. 2. Temperature and size history of a grade 5 fuel drop in air. Air temperature, 1600°F; air velocity, 1360 fpm. Numbers on size curve correspond to motion picture frames. (Fig. 2 of original reference, p. 1029).

The burning irregularity was attributed mostly to the asphaltene in the fuels, and to a lesser extent, to the heavy unstable resin components.

Ignition-delay data were obtained and correlated as a function of fuel, initial drop diameter, and operating conditions.

A motion picture of the evaporation and self-ignition of various fuels is available from the authors.

Subject Headings: *Drops, hydrocarbon, ignition of; Hydrocarbon mixtures, self-ignition of; Ignition, of hydrocarbon mixtures; Self-ignition (see spontaneous ignition); Spontaneous ignition, of hydrocarbon mixtures.*

Old Sec. I **B. Greifer**

Palmer, K. N. and Tonkin, P. S. (Joint Fire Research Organization, Boreham Wood, England) "The Explosibility of Some Industrial Dusts in a Large-Scale Cyclone Plant," *Joint Fire Research Organization Fire Research Note No. 639* (November 1966)

The explosibility of some industrial dusts in a cylone plant has been investigated. The dusts were dispersed in the turbulent air stream and ignited with a propane flame.

All the dusts which propagated explosions in the plant were in explosibility Class I. Manioc, a marginal Class I dust, and calcium citrate, a Class II dust, did not explode. Preliminary information has been obtained on the size of vents to safely relieve explosion pressures in the cyclone itself.

Subject Headings: *Calcium citrate, explosibility of; Cyclone plant, dust explosion hazards; Dusts, explosibility of; Explosibility, of dusts; Manioc dust, explosibility of.*

Old Sec. I Authors' Summary

Pavlov, B. V. (Institute of Chemical Physics, Academy of Sciences USSR) "On the Upper Limit of Autoignition in an Unbranched Chain Reaction," Presented by Academician V. N. Kondrat'ev, November 28, 1964. Translated from *Doklady Akademii Nauk SSSR* 162(4) 446–448 (1965)

In an article of less than a thousand words, B. V. Pavlov presents a scheme of an unbranched chain reaction rather than the normally assumed branched chain to explain the upper limit of autoignition. He assumes an arbitrary one-center system in which the reacting specie is generated on the surface of the reactor and terminated by a collision with an impurity and another third body. The distribution of radicals throughout the reactor is determined by diffusion and the various governing chemical reactions. The temperature distribution is found by application of a thermal conductivity equation in which the dependence of the rate constant on temperature is approximated by the first two members of the power series of $(T-T_0)$. Pavlov reduces these to a Bessel equation from which he obtains the condition for self-ignition, that is, where the temperature approaches infinity. By utilizing a reasonable boundary condition for the concentration of the reacting specie close to the wall, plus a statement of all other species being proportional to pressure, he shows the upper limit of pressure at which autoignition occurs. Finally, Pavlov transforms this limit to show that the condition for autoignition is dependent on the thickness of the reaction zone rather than the dimension of the container in which the reaction takes place, thus indicating a pressure dependence of greater than minus $\frac{3}{2}$.

Subject Headings: *Autoignition, through unbranched chain reactions; Chain reactions, unbranched and ignition limits; Ignition limits; Spontaneous ignition.*

Old Sec. I F. Falk

D. Propagation of Fires

Albini, F. A.* (Institute for Defense Analyses, Arlington, Virginia) "A Physical Model for Firespread in Brush," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 553–560 (1967)

A system of seven equations with 19 variables was set up for calculating the rate of spread of a fire in a fuel bed composed of brush with dead twigs and branches, covered with a volatile-bearing leafy layer. The results are presented in form of dimensionless rate of spread, flame depth and flame length vs dimensionless fuel loading, with wind and moisture numbers as parameters. For the sake of clarity and for facilitating the understanding of the physical conditions involved, no dimensionless numbers will be used in this review. The set of equations, after returning to physical dimensions, was:

$$L/H_t=50[U_f m_t''/H_t\rho_0(gH_t)^{0.5}]^{0.7} \tag{1}$$

$$D=U_f r^2/\alpha \tag{2}$$

$$\tan\theta=(4U_w{}^2/gD)^{0.25} \tag{3}$$

$$z_d=L\cos\theta[\tan\theta+(1-\zeta^2)/2\zeta] \quad \text{with} \quad \zeta=2MU_f m_t''/(\dot{m}_0 L\cos\theta) \tag{4}$$

$$V=\tfrac{1}{2}+L/2z_d[1-(2L/z_d)\sin\theta+(z_d/L)^2]^{0.5} \tag{5}$$

$$\begin{aligned}\Delta t_t&=\{\Delta t_d+\Delta t_h\}N\\ &=\{0.03\rho_0 C/\dot{m}_0 V+(2C/g)^{0.5}\}(g/2C)^{0.5}0.5C_h r_f/4h\end{aligned} \tag{6}$$

$$U_f=z_d/2\Delta t_t \tag{7}$$

where:

C = height of the porous leafy layer, in cm
C_h = specific heat of first, hot, glowing fuel particle, cal/(cm³ °C)
D = depth of burning zone in the direction of flame spread, cm
g = acceleration of gravity, 981 cm/s²
h = heat transfer coefficient, cal/(cm² s °C)
H_t = total height of fuel bed, cm
L = flame length, cm
$\dot{m}_0$ = characteristic flux of volatiles, g/(cm² s)
m_t'' = fuel loading in mass per unit surface, g/cm²
M = moisture mass fraction of fuel loading that has to vaporize before vaporization of combustibles starts to become important
N = number of heating cycles)
r_f = radius of first, hot, glowing fuel particle, cm
r = radius of fuel particle determining burnout time, cm
t = time; Δt_d time interval required for generation of combustible mixture in region of intermittent deflagration, s
Δt_h effective heating time before flame is lifted away by buoyancy, s)
Δt_t total time between first flame contact and flame attachment, s

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U_f=flame spread velocity, cm/s
U_w=wind velocity, cm/s
V=view factor for radiation falling on unburned fuel bed
z_d=distance ahead of flame front at which a mass fraction of moisture M has been vaporized, cm
thermal diffussivity of the solid fuel, cm^2/s
θ=tilt angle between the fuel bed normal and the flame front
ρ_0=density of air at 300°C, g/cm^3

Of these 18 variables, 9 were given fixed values, U_w and M were used as parameters and 6 were determined by solving the system of equations as a function of m_t''. Iteration was initiated by guessing a first value of U_f and then proceeding from Eq. (1) through (7). A typical set of reconstructed values of fixed variables, assuming $C=0.1H_t$ was: $\dot{m}_0=9\times10^{-5}$ gr/(cm^2 s), $C_h=0.13$ cal/(cm^3 °C), $h=2.5\times10^{-3}$ cal/(cm^2 s °C), $H_t=250$ cm, $r_f=0.1$ cm, $r=0.7$ cm, $\alpha=10^{-3}$ cm^2/s, $\rho_0=6\times10^{-4}$ gr/cm^3. The parameters were varied in between the limits $0\leq U_w\leq 500$ cm/s and $0.0075\leq M\leq 0.015$.

The system of equations was set up by arguing as follows: Depending on the distance from the radiating flame front, the top surface of the fuel bed receives energy by radiative transfer determined, among others, by a geometrical view-factor V, Eq. (5). V is also a function of the tilt angle θ, determined by the wind velocity U_w and the buoyancy of the hot gases, Eq. (3).[1] This causes the fuel bed to become partially dehydrated. At a distance z_d from the flame front the temperature and the fuel vaporization have reached conditions such that a first deflagration wave can propagate to it, Eq. (4). From this time on, fuel is vaporized more and more causing repeated deflagration waves and corresponding heating cycles. After a time Δt_t the fuel bed at the distance z_d reached a temperature high enough (about 500°C) for continuous flame attachment, Eq. (6). The velocity of flame spread could thus be approximated by a simple expression, Eq. (7). The length L of the flame as a function of fuel feed rate was taken from results obtained by Thomas,[2] Eq. (1), after some modification. The flame depth D was approximated by combining the velocity of flame spread with a time for burnout $\Delta t=r^2/\alpha$ Eq. (2), and disregarding the influence of the fuel bed height H_t. Originally,[2] Eq. (1) had the form $L/D=42[U_f m_t''/H_t\rho_0(gD)^{0.5}]^{0.61}$ which can be regarded as a more detailed description of the length of a turbulent flame than the familiar approximation of $L/D=$const. The modification leading to Eq. (1) is only valid for fires with $D/H_t\approx1$.[3] However, this restriction is unnecessary if the system had been solved by using the above original equation. Unfortunately, only a few of the eight variables can be well-defined experimentally, so that the system has a fairly wide margin of flexibility. Still, as the author points out, the dependence of flame radiation output on combustion efficiency and the influence of oxygen availability on burning time and combustion efficiency were not included in this preliminary model.

The results are plotted, at constant $H_t=250$ cm, for values of the fuel load $0.3\leq m_t''\leq 3$ g/cm^2. Velocities of fire spread were obtained within the range $10\leq U_f\leq 50$ cm/s, U_f increasing strongly with wind velocity and with decreasing moisture. U_f and D ($5\times10^3\leq D\leq 25\times10^3$ cm) were found to decrease with increasing m_t'' after a maximum at about $m_t''=0.6$ g/cm^2. The flame length, L, $2.5\times10^3\leq L\leq 10^4$ cm, increased with m_t'', U_w and with decreasing moisture. It should be interesting to compare these results with experimental data.

References

1. Putman, A. A.: "A Model Study of Wind-Blown Free-Burning Fires," *Tenth Symposium (International) on Combustion* p. 1039, The Combustion Institute, 1964.
2. Thomas, P. H.: "The Size of Flames from Natural Fires," *Ninth Symposium (International) on Combustion*, p. 844, The Combustion Institute, 1962.
3. In the original paper, on p. 557, the exponent of H_t/D should be -0.65 instead of 0.05; on page 558, C should be a function of r instead of r_f.

Subject Headings: *Brush fire spread, model for; Fire spread, in brush, model for; Model, brush fire spread.*

Old Sec. V U. Bonne

Labes, W. G. (IIT Research Institute, Chicago, Illinois) "The Ellis Parkway and Gary Dwelling Burns," *Fire Technology* **2**, 287–297 (1966)

The part which "flashover" plays in the spread of fire within buildings has always been of great interest to fire protection engineers. The author reports on two full-scale, experimental fires, the result of which suggests that fire spread through a subdivided structure can be described as a series of predictable flashovers.

The tests utilized a three-story apartment building in Chicago, and a one-story dwelling in Gary, Indiana. The timed history of both fires was described by a list of observations. These included visual, photographic, temperature, and gas analysis records.

The results indicated that the spread of fire through a building, which is subdivided into various interconnecting spaces, can be predicted through the data developed on flashover characteristics.

The ability to estimate the fire spread rate in any given structure could be of great assistance to the officer in charge during his response to an initial alarm. Further full-scale, experimental building fires, suitably instrumented and observed, will help to verify the relationships established in these tests and lead to additional applications.

Subject Headings: *Burns, at Ellis Parkway and Gary; Dwelling burns; Ellis Parkway Burn; Gary Burn.*

Old Sec. XIII J. J. Ahern

Heselden, A. J. M., Smith, P. G., and Theobald, C. R. (Joint Fire Research Organization, Boreham Wood, England) "Fires in a Large Compartment Containing Structural Steelwork. Detailed Measurements of Fire Behavior," *Joint Fire Research Organization Fire Research Note No. 646* (December 1966)

Twenty-five large-scale experimental fires have been carried out recently at the Joint Fire Research Organization in conjunction with the British Iron and Steel

Federation. This report describes the measurements made during the fires, excluding measurements of the temperature of the steelwork exposed in the compartment, and gives the results in detail. Discussion is reserved for later reports.

Subject Headings: *Compartment fires, containing steel; Fire behavior, in compartments; Structural steel, in compartment fires.*

Old Sec. V **Authors' Summary**

Roberts, A. F., Clough, G., and Blackwell, J. R. (Safety in Mines Research Establishment, Sheffield, England) "A Model Duct for Mine Fire Research," *Safety in Mines Research Establishment Research Report No. 243* (December 1966)*

This paper gives a general description of a fire propagating in the timber lining of a mine roadway. The characteristics of such fires are being studied by means of model experiments in a refractory-lined steel duct 100 ft long with a 1 ft square flow passage along its axis. Forced ventilation can be supplied at rates up to 1000 cubic feet per minute. The instrumentation of the duct is designed to give information on the rate of spread of fire along the timber lining, the composition of the products of combustion, the rate of cooling of these products, the rate of fuel emission from the lining, heat transfer rates at different stages of the fire, and reaction rate profiles along the fire. The experimental variables are the ventilation rate, the thickness and distribution of the inflammable lining, the nature of the lining, the moisture content of the lining, and the method of ignition. The paper describes the construction and instrumentation of the duct in detail and presents data for a typical fire as an example of the information which can be obtained.

Subject Headings: *Duct model; Fire spread, in mines; Heat transfer; Mine fire research.*

Old Sec. VIII **Authors' Abstract**

Thomas, P. H. and Law, Margaret (Joint Fire Research Organization, Boreham Wood, England) "Experiments on the Spread of Fire," *Report on Forest Research for the Year Ended March 1965*—Joint Fire Research Organization, Boreham Wood, England, pp. 124–130

Analysis of laboratory experiments has indicated that the rate of spread of fire in cribs of wood is due to heating of the material ahead of the fire by radiation transmitted from the surfaces of the fuel already burning. Best correlation of the

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* Report available from Safety in Mines Research Establishment, Sheffield, England. Reprinted by permission.

experimental data results from an equation of the form

$$R = k/\rho_b \qquad (1)$$

where

R = rate of fire spread, ft/sec

k = "constant," 5 to 8 mg/cm² sec

ρ_b = bulk density of fuel

Heat transfer values of 1 to 2 cal cm^{-2} sec^{-1} calculated from the rate of spread of fire in cribs were confirmed by Simms and Wraight[1] who made calorimetric measurements which were effectively correlated by the heat balance equation for thin sticks

$$R\rho_b \Delta H = i - a\alpha\theta \qquad (2)$$

where ΔH = enthalpy rise of uniformly heated wood, 180 cal/G.

i = forward flux of heat (experimental data)

α = cooling coefficient, 8×10^{-4} cal cm^{-2} sec^{-1} $°\text{C}^{-1}$

θ = temperature rise to ignition, 300°C

a = coefficient for nonuniform direction of radiant heating, $2\frac{2}{3}$.[1]

Comparison of experimental results with theoretical prediction is shown in Fig. 1, which indicates the applicability of Eq. (2). Subsequent field tests indicated a mean radiation of 1.1 cal cm^{-2} sec^{-1}, which confirmed the validity of the laboratory results.

The effect of wind velocities from 3 to 13 ft/sec was analyzed experimentally by Byram *et al.*[2] whose data are plotted on Fig. 2 against $1/\cos\phi$, where ϕ is the deflection of the flame from the local vertical. Inspection of Fig. 2 reveals that the data can be effectively correlated by the equation

$$R\rho_b \cos\phi = \text{constant} \qquad (3)$$

Quantitative evaluation of the effect of wind velocities on fire spread in deep fuel beds is facilitated by utilizing the results of the earlier experiments by Thomas, Pickard, and Wraight,[3] which show the following dependence of deflection angle on wind speed (U) and burning rate (R):

$$\cos\phi = 0.7\Omega^{-0.49} \qquad (\Omega > 1) \qquad (4)$$

where

$$\Omega = [U/(g^R \rho_b{}^h/\rho_a)^{1/3}] = [F_r/D_\text{I}]^{1/3} \qquad (5)$$

where h = height of fuel bed

ρ_a = air density

F_r = Froude number

D_I = Damköhler's Group I

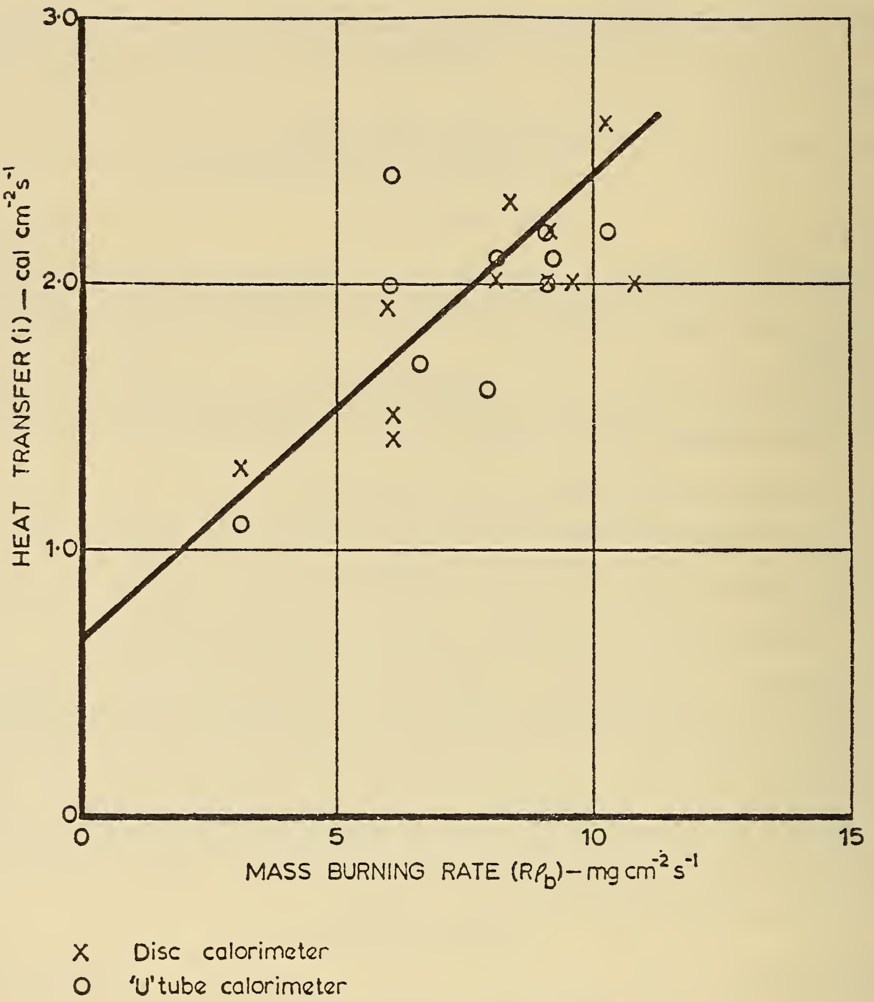
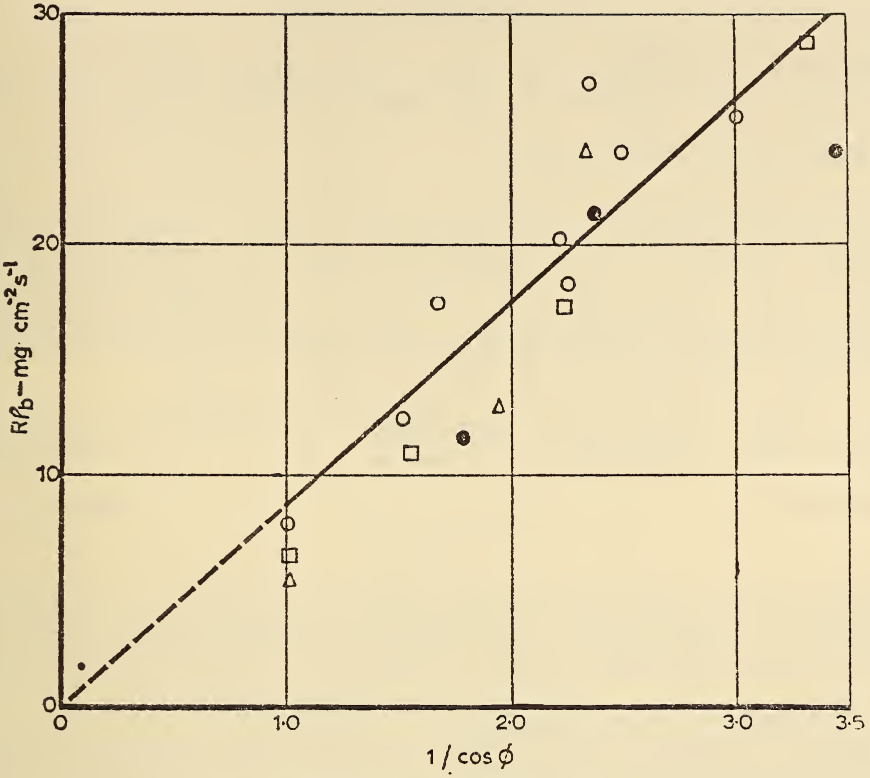


Fig. 1. Heat transfer rates in cribs.

Comparison of Fig. 2 with Eqs. (3, 4, 5) reveals that the latter analysis is not valid for wind velocities approaching zero, since zero rate of flame spreading (and infinite values for cosϕ) would be predicted for this case.

References

1. Thomas, P. H., Simms, D. L., and Wraight, H. G. H.: "Fire Spread In Wooden Cribs," *Joint Fire Research Organization. F. R. Note No. 537/1964,* February (1964).
2. Byram, G. M. *et al.*: "An Experimental Study of Model Fires," *U. S. Department of Agriculture Forest Service, Southeastern Forest Experiment Station, Technical Report No. 3,* Macon, Georgia (June 1964).



Symbol	Spacing between $\frac{1}{4}$-in sticks in
●	4·5
□	2·5
○	1·5
△	0·5

FIG. 2. Effect of wind on crib fires.

3. THOMAS, P. H., PICKARD, R. W., AND WRAIGHT, H. G. H.: "On The Size and Orientation of Bouyant Diffusion Flames and the Effect of Wind," *Joint Fire Research Organization. F. R. Note No. 516/1963* (January, 1963).

Subject Headings: ***Crib fires; Fire spread.***

Old Sec. V

C. C. Meisse

E. Suppression of Fires

Meldrum, D. N., Williams, J. R. (National Foam System, Inc., West Chester, Pennsylvania) and **Gilroy, D.** (Pan American World Airways, Inc., Patrick Air Force Base, Florida) "Foam Fire Protection of Liquid Propellants," *Fire Technology* 2(3) 234–238 (1966)

Concomitant with the rapidly advancing technology in propulsion systems is the increasing importance of providing the means to control and extinguish unplanned combustion of liquid propellant fuels. The test work described in this paper concerns protection of the fuel composed of unsymmetrical dimethylhydrazine and hydrazine (UDMH-hydrazine), such as is used in the Titan II and III C missiles and is also involved in the Saturn V vehicle.

Subject Headings: *Fire protection, of propellants, by foam; Foam, for propellant fires; Propellant fires, use of foam on.*

Old Sec. XIII **Authors' Abstract**

Narula, O. P. (Industrial Consultant, Delhi, India) "Fire Fighting Techniques in the Solvent Extraction Industry," *Chemical Age of India* **17**, 334–339 (1966)

The author presents a complete discussion of basic protection features for solvent extraction plants, with particular reference to India. Most of the features, which he describes, are done as a matter of course in most plants of this type in the United States.

He presents a good discussion of both the advantages and limitations of the use of steam in the control of fires in plants of this kind. In a similar manner he does an excellent job with carbon dioxide.

The greater part of the article, however, deals with the use of water-spray systems, sprinkler systems, and various applications of fog. A great deal of attention is given to the protection of structural steel by means of water fog.

The author also presents an excellent discussion of the potential uses of both chemical and mechanical foam, as well as a combination of sprinkler protection with foam. This should be of considerable assistance to plants of these kinds in India. He concludes the article with a discussion of sprinkler apparatus, ranging from hose reels to personal protective equipment, ending with a discussion on the type of organization best suited to handle fire fighting in a plant of this type.

Subject Headings: *Fire fighting, by solvent industry; Solvent industry, fire fighting.*

Old Sec. XIII **J. J. Ahern**

O'Dogherty, M. J. and Young, R. A. (Joint Fire Research Organization, Boreham Wood, England) "The Performance of Automatic Sprinkler Systems: Part II. The Effect of Water Application Rate and Fire Size on the Extinction of Wooden Crib Fires," *Joint Fire Research Organization Fire Research Note No. 603* (1966)

This report describes experiments on the extinction of wooden crib fires by water spray. A study was made of the effect of variations in water application rate, the rate of heat output of the fire, and crib construction. Measurements were made of fire spread, extinction time, quantity of water required for extinction, and air temperatures at ceiling level of the building used.

Subject Headings: *Automatic sprinkler systems, performance of; Crib fires, and sprinkler systems; Fire size, and sprinkler performance; Sprinkler systems, performance of; Water application rate, by sprinklers.*

Old Sec. VII — Authors' Summary

Rasbash, D. J. (Joint Fire Research Organization, Boreham Wood, England) "The Use of Liquid Gases to Extinguish Fires," *Joint Fire Research Organization Fire Research Note No. 637* (October 1966)

The theoretical basis for using liquid carbon dioxide and liquid nitrogen in place of water as a general extinguishing agent for fires has been examined. This examination indicates that there is unlikely to be a case of using liquid gases unless the fire is such that the use of water would result in a large part of the water not being vaporized. It is suggested that there may be scope for the use of liquid gases:

(a) Where the present use of water causes substantial water damage.
(b) Where the extinguishing agent cannot be made to reach the source of fire directly.
(c) Where a large flow of agent needs to be projected into a building from outside.
(d) For certain large outdoor fires, e.g., aircraft crash fires.

For the latter two applications liquid nitrogen is likely to be more effective than liquid carbon dioxide because of the inherent inability of the latter to remain a coherent liquid at atmospheric pressure. Operational problems likely to be encountered in bringing liquid gases into large-scale use at fires are outlined.

Subject Headings: *Extinguishment, by liquid gases; Gases, for extinguishment; Liquid gases, for extinguishment.*

Old Sec. XIII — Author's Summary

Richardson, D. D. (Joint Fire Research Organization, Boreham Wood, England) "The Extinction of Petrol and Solid Fuel Fires with Liquid Nitrogen," *Joint Fire Research Organization Fire Research Note No. 638* (October 1966)

This note describes an investigation of the performance of liquid nitrogen on petrol and wooden crib fires. It shows that liquid nitrogen is likely to be less effective than dry powder in the extinction of small petrol fires, but more effective than water in the extinction of small solid fuel fires.

Subject Headings: *Extinction, by liquid nitrogen; Nitrogen, liquid extinction by; Petroleum fires; Solid fuel fires.*

Old Sec. XIII Author's Summary

G. Combustion Engineering

Bakhman, N. N. (Institute of Chemical Physics, USSR Academy of Sciences) "Combustion under Conditions Determined by Diffusion in the Presence of Condensed Reaction Products," *Zh. Fiz. Khim.* **39**(8) 1890–1892 (1965) English Translation: "Diffusion Regime of Combustion in the Presence of Condensed Reaction Products," *Russian Journal of Physical Chemistry* **39**(8) 989–990 (1965)

Experimental data taken from a previous paper[1] on the combustion of $W+KClO_4$ and $Al+Fe_2O_3$ mixtures were examined. They showed that the rate of burning of the condensed mixtures, u, was strongly dependent on the particle size of the metal, d, approaching $u \propto d^{-1}$. At low values of d the rate of burning of the mixtures was weakly dependent on pressure, p; but as d increased through the range 0.1–550 microns, the pressure dependence of u became more marked.

This $u \propto d^{-1}$ dependence in systems where the fuel is relatively nonvolatile suggests a diffusion combustion regime as opposed to a kinetic regime where $u \propto d^{-0.5}$ [3,4] However the pressure dependence of the burning rates, $u(p)$ should also be examined.

The experimental pressure dependence of u at different values of d (Table 1)[1] did not agree with the theoretical dependence obtained by postulating that combustion occurred on the surface of particles suspended in free gas flow (the combustion products were regarded as gaseous and the condensed residue formed by oxidant decomposition was ignored).[3,5]

When the free gas flow assumption was removed, and the presence of condensed reaction products was considered, it was possible to obtain a relation for the rate of diffusion combustion[7] which did explain the experimental data.

$$\rho u \propto d^{-1}[\rho_{ox} D_{ox}(u/w)]^{1/2}.$$

where ρu is the mass burning rate (ρ=density of initial mixture); D=diffusion coefficient; u=rate of combustion; w=particle velocity; d=particle size.

This equation gave interesting relationships for the following conditions: (1) diffusion in free gas flow, (2) diffusion of oxidant molecules (e.g. $KClO_4$) through

TABLE 1.

Mixture, mass %	Exponent ν in the formula $\rho u = bp^{\nu}$ at values of d of					
	0.1 μm	2.7 μm	19 μm	160 μm	340 μm	550 μm
20% $KClO_4$+80% W	—	0.21	—	—	0.53	—
10% $KClO_4$+90% W	—	0.23	0.20	0.42	0.40	0.37
5% $KClO_4$+95% W	—	0.20	—	—	0.33	—
75% Fe_2O_3+25% Al	0.078	—	—	0.14	—	0.26

a layer of condensed reaction products, (3) decomposition of oxidant molecules with oxygen evolution, the latter diffusing through a layer of liquid reaction products as bubbles or in solution, (4) oxygen flowing around fuel particles but the condensed residues formed by oxidant decomposition preventing particle entrainment by the gas, (5) combinations of the above.

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Subject Headings: *Combustion, diffusion-limited, with condensed products; Condensed reaction products, and combustion; Diffusion limited combustion with solids.*

Old Sec. IV B. Greifer

Blackshear, P. L., Jr. and Murty, K. A. (University of Minnesota, Minneapolis, Minnesota) "Some Effects of Size, Orientation, and Fuel Molecular Weight on the Burning of Fuel-Soaked Wicks," *Eleventh Symposium (International) on Combustion,* Pittsburgh, The Combustion Institute, 545–552 (1967)

Experiments have been conducted on the burning rates of fuel-soaked wicks supporting flames in a quiescent environment. After the starting transients died out the burning rate of fuel was constant and was found to be nearly the same as for burning liquid fuels in horizontal pans. The wick fuel consumption rate has thus been interpreted as being controlled by the convective and radiative heat transmission to the surface.

The burning of liquid fuel in pans has been shown by Hottel[1] to correlate well with a simple expression for the conductive (or rim), convective and radiative components of the heat transfer to the surface

$$q/\tfrac{1}{4}\pi d^2 = [K_1(T_s - T_b)/d][\text{Rim heat loss}] + h(T_f - T_s)[\text{Convection to the surface}]$$
$$+\sigma F(T_f^4 - T_b^4)[1 - \exp(-\kappa d)][\text{Radiation to the surface}] \quad (1)$$

where q—heat flux to surface, cal/sec
K_1—rim conduction coefficient of proportionality, cal/cm sec °C
T—temperature, °K
d—characteristic size, cm
h—heat-transfer coefficient, cal/cm^2 sec °C
σ—Stephan-Boltzmann constant, cal/sec cm^2 °K
F—radiation viewing factor between flame and pan
κ—emission coefficient, cm^{-1}

A large amount of the data reported in the literature is consistant with Hottel's simple theory with $K_1 \approx 0$, $h \propto d^n$, $n \approx -\frac{1}{2}$ for $d < 10$, $n = 0$ for $d < 10$, and with $\sigma F T^4 = \text{const}$, and $0.0040 < \kappa < 0.040$ for most of the fuels studied. Discrepancies occur for large size and optically thick configurations. The consequences of wind speed approaching the pan fire remains to be clearly evaluated.

The use of fuel-soaked wicks gives burning rates which agree with those obtained in flowing vertical films and in stationary horizontal pools of fuel. The burning rate, expressed as a product of mass transfer rate times a driving force, yields a mass transfer coefficient that varies as $d^n M^m$ where M is the molecular weight. For vertical wicks $n = -\frac{1}{4}$ when $d < 10$ cm, $n = 0$ when $d > 10$ cm, and $m = -\frac{2}{3}$ for $d = 10$ cm. For horizontal wicks with the flame on top $n = -\frac{1}{2}$ for $d < 10$ cm, $n \simeq 0$ for $d > 10$ cm, and $m = -1$ for $d = 10$ cm. For horizontal wicks with the flame on the bottom n is estimated as $-\frac{1}{4}$ for the entire size range and $m = -\frac{1}{3}$ for $d = 10$ cm. The fuels studied were methanol, acetone, benzene, toluene, xylene, gasoline, and kerosene. It is inferred that for horizontal fuel surfaces with characteristic dimensions less than 2 cm conduction and convection are dominant, for between 2 and 20 cm convection is dominant, and between 20 and 70 cm convection and radiation are dominant. For big fires, $d > 1000$ cm, it is anticipated that an optically thick heat transfer approach will be needed to explain the phenomena.

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Subject Headings: *Burning rates, of wicks; Molecular weight, effect on burning rate of wicks; Wicks, burning rate of.*

Old Sec. IV P. Anderson

Bowes, P. C. (Joint Fire Research Organization, Boreham Wood, England) "Thermal Explosion in the Short Cylinder with a General Boundary Condition," *Joint Fire Research Organization Fire Research Note No. 642* (October 1966)

Approximate expressions are obtained for the critical explosion parameter and critical temperature rise for thermal explosion in a short cylinder of material of finite conductivity and with a finite surface heat transfer coefficient.

Subject Headings: ***Cylinders, thermal explosion in; Explosion, thermal in short cylinders; Thermal explosion, in short cylinders.***

Old Sec. V **Author's Summary**

Chung, P. M. and Blankenship, V. D. (Aerospace Corporation, San Bernadino, California) "Equilibrium Structure of Thin Diffusion Flame Zone," *The Physics of Fluids* 9(8), 1569–1577 (1966)

The authors analyze initial broadening of diffusion flame sheets using a special perturbation technique. They derive expressions for the thickness of the flame zone and the value of the maximum flame temperature. The present paper follows the work of Chung[1] who established equations for formation of a thin diffusion flame sheet using the following postulates:

1. Combustion of initially unmixed reactants chemical kinetics is represented by the simple relationship,

$$a(\text{oxidant})+b(\text{fuel}) \underset{k_b}{\overset{k_f}{\rightleftarrows}} d(\text{product}) \tag{1}$$

2. For thin diffusion flame sheets the Damköhler number

$$\left(\Gamma_f=\frac{\text{characteristic residence time}}{\text{characteristic reaction time}}\right)\rightarrow\infty$$

and at the same time the equilibrium constant $(k_b/k_f)\rightarrow 0$. For the limiting case of the thin flame sheet, combustion is completely controlled by diffusion and heat transfer characteristics of the flow field; and governing equations may be solved simply. However, when the Damköhler number or the equilibrium constant is finite and nonvanishing the diffusion flame sheet becomes a zone of finite thickness instead of a thin zone. In this case, solution of the governing equations becomes much more complicated. In previous work, Chung *et al.*[2] successfully employed a special perturbation method (the method of inner-and-outer expansions) to analyze the combustion process of Eq. (1) when flame sheet broadening was caused by decreasing Damköhler number. A similar method was used by Chung[1] when flame sheet broadening was caused by a nonvanishing equilibrium constant with the Damköhler number→∞ and for $a=b=d=1$. Results of the previous work indicated that diffusion flame sheet broadening caused by decreasing Damköhler number directly influenced the inner flame region only, whereas that due to a nonvanishing equilibrium constant directly affected both inner and outer regions.

The present work considers initial broadening of the flame sheet caused by nonvanishing equilibrium constant for equilibrium flows with arbitrary stoichiometric coefficients (a, b, and d). A simple combustion model is employed in which a jet of pure gaseous fuel is introduced into the oncoming uniform stream of pure oxidant at the stagnation region of a two-dimensional or axisymmetric blunt body. The perturbation method of inner-and-outer expansions gives closed form expressions in terms of various governing parameters for the value and location of the maximum temperature and for the thicknesses of the broadened flame zone. Van Dyke[3] describes the general method of inner-and-outer expansions. The mathematical details of the formulation and analysis are fully illustrated in the present text for the stagnant mixing layer problem. The principal governing equations are:

$$f'''+ff''=0$$

$$(H+m_1)''+f(H+m_1)'=0$$

$$(H+m_2)''+f(H+m_2)'=0$$

$$m_1{}^a m_2{}^b-\epsilon H^{a+b}[\exp(-\theta/H)]\cdot[1-(aM_1/M_3)m_1-(bM_2/M_3)m_2]=0 \tag{2}$$

where $f(\eta)$ is the standard Blasius stream function defined as $f'(\eta)=u/u_e$ with $(\ )'$ denoting differentiation with respect to the similarity variable,

$$\eta=\{[(1+\sigma)/(\rho_e\mu_e)_0](du_e/dx)_0\}^{1/2}\int_0^y \rho dy.$$

The coordinates x and y are in the lateral and normal directions respectively. The value of σ is 0 when the flow is two dimensional and one for axisymmetric flow. The subscripts e and $-e$ denote the mixing layer edges on the oxidant and fuel sides respectively, and 0 represents the stagnation points. The symbols ρ and μ are the density and dynamic viscosity of the gas mixture. H is the nondimensional temperature defined as $(c_p/\Delta h^0)T$ where c_p, T, and Δh^0 are the constant pressure specific heat of the mixture, the temperature, and modified heat of reaction per unit mass defined as $(aM_1/M_3)h_1{}^0+[b(M_2/M_3)]h_2{}^0-h_3{}^0$. M and h^0 are the molecular weight and height of formation with subscripts 1, 2 and 3 the oxidant, fuel, and combustion product respectively. The modified mass fractions m_1 and m_2 are defined as $(M_3/aM_1)\hat{C}_1$ and $(M_3/bM_2)\hat{C}_2$ where $\hat{C}$ is the actual mass fraction. θ is the normalized heat of reaction defined as $(\Delta E/R)(C_p/\Delta h^0)$ with E and R the heat of reaction and the universal gas constant per mole respectively. ϵ in Eq. (2) is the normalized equilibrium constant defined as,

$$\epsilon=(a^ab^b)^{-1}M_3{}^{a+b-1}(\Delta h^0/C_p)^{a+b}(p/R)^{1-(a+b)}K_{EO}$$

with p the pressure and K_{EO} defined by

$$(k_b/k_f)=K_{EO}T\exp(-\Delta E/RT)$$

Boundary conditions for the governing equations are:

for $\eta\rightarrow\infty$,

$$f'=1,\qquad H=H_0=(C_p/\Delta h^0)Te$$

$$m_1=M_3/aM_1=m_{1e},\qquad m_2=0$$

for $\eta \to -\infty$,

$$f' = u_{-e}/u_e = \Lambda, \qquad H = H_{-e} = H_e \Lambda^2$$

$$m_1 = 0, \qquad m_2 = M_3/bM_2 = m_{2,-e}$$

for $\eta = 0$,

$$f(0) = 0$$

The flow geometry demands that $H_{-e}/H_e = (u_{-e}/u_e)^2 = \Lambda^2$. In the analysis of the boundary value problem a perturbation solution is obtained with ϵ as the perturbing parameter. For further details of the analysis, the reader is referred to the text.

Conclusions

As a whole, it was found that varying the stoichiometric coefficients affects the flame zone and the outer regions quite differently when the flame zone is created by a nonvanishing equilibrium constant compared to the case where the zone was created by a decreasing Damköhler number. The thickness of the flame zone is much less when created by the nonvanishing equilibrium constant than by decreasing the Damköhler number. The stoichiometric coefficient of the fuel affects the oxidant side more than the fuel side and vice versa. The present findings and method of analysis may find application in analysis of combustion of initially unmixed reactants associated with hypersonic vehicles in which the initial temperatures of reactants may be extremely high. The authors suggest that the next problem worth considering may be the problem of simultaneously perturbing both the Damköhler number and the equilibrium constant from their respective limiting values.

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Subject Headings: ***Diffusion flames, structure of; Flame theory, of diffusion flames; Flame structure, of diffusion flames.***

Old Sec. IV **J. M. Singer**

Flossdorf, J. and Wagner, H. Gg. (University of Göttingen, Göttingen, Germany) "Soot Formation in Normal and Disturbed Hydrocarbon-Air Flames," *Z. physik. Chemie N.F.* **154,** 113–128 (1967) (In German)

The present paper is one of a series of papers[1–7] reporting the work on soot formation carried out by the combustion group in Göttingen. It presents a study of the temperature dependence of the final soot concentration formed in different types of flat, premixed hydrocarbon-air flames, which burned inside a glass tube in order to eliminate the influence of secondary air.

The maximum temperature for each flame vs height above the burner was obtained by the sodium line reversal method and was controlled by the velocity at which the gas mixture left the cooled burner, which acted as a variable heat sink. Although the sodium is entrained by the air to the entire burner and not to a central part of the burner only, the authors do not discuss the possible error caused by non-flat temperature profiles. Except for one reported experiment with propane in which the temperature was controlled by nitrogen addition, the variation of temperature always was linked to flow rate variations. However, the possible influence of varying flow rates,[5] e.g., of the burner surface acting as a variable radical sink was not mentioned.

The soot concentration was determined by measuring the intensity of the continuous emission of soot with a photoelectrically recording monochromator and by using the measured temperatures. Differences in gas density were taken into account so that the soot concentration from different flames could be compared.

Experimental results are presented for ethylene, ethane, propane, butane, cyclohexane, and benzene in the form of diagrams showing the logarithm of soot concentration (in g/cm^3) vs maximal flame temperature, with the ratio of carbon to oxygen (C/O) as an additional parameter.

For ethylene-air flames, the curves of constant C/O are straight lines of negative slope indicating smaller soot concentrations at higher flows and higher temperatures. An increase of 60°K at 1800°K causes the soot concentration to drop about one order of magnitude. In principle, this agrees with results obtained for flat, premixed, low pressure acetylene-oxygen flames, for which the flow rates were varied at approximately constant temperature.[5] The included curves for the visual estimation of the limits of soot formation indicate that at higher temperatures the observed limits correspond to smaller soot concentrations.

Hydrocarbons of increasing molecular weight greater than oxygen have an increasing tendency to form unstable flame reaction zone structures when burned in mixtures richer than stoichiometric.[1] In flat flames, these instabilities cause the flat flame front to break up into many small cells (cellular flames); in nozzle flames the cone-shaped flame front becomes rippled in such a way that a horizontal cross section presents a star-like pattern with 5–9 points (polyhedral flames).

With ethane and benzene, the authors were able to stabilize soot forming flames both in the unstable (high temperature) and in the stable regime (low temperature) by maintaining the C/O ratio constant and changing the flow rate. In the stable regime, as shown by Fig. 1, the amount of soot formed decreased with increasing temperature, as found with the stable ethylene flames, but it increased with temperature in the unstable regime. With propane, butane and cyclohexane flames, the observed range of C/O ratio for soot-forming stable flames was small. However, the curves log of soot concentration vs temperature were similar to those shown in Fig. 1.

Changes in flame temperature of a propane flame caused by nitrogen additions were reported to cause changes in the soot formation similar to those observed when temperature is controlled by the flow rate, i.e., in the unstable regime, the soot disappeared when the nitrogen flow was increased and became stronger upon addition of more nitrogen in the stable regime.

The observed dependence of soot formation vs increasing temperature is ex-

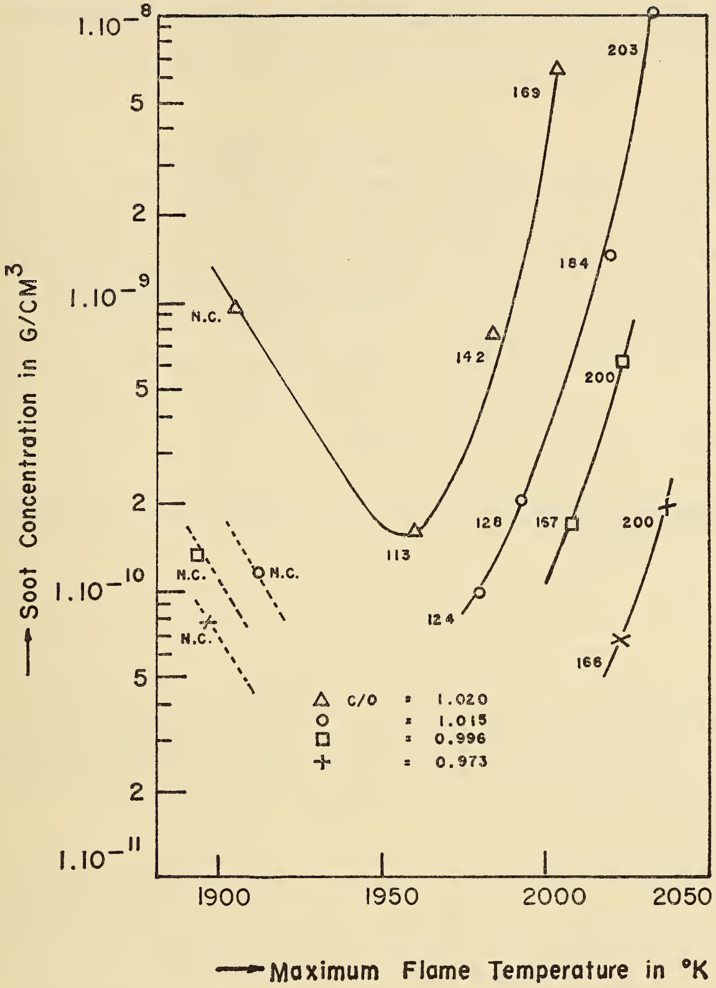

Fig. 1. Final soot concentration in flat benzene-air flames as a function of the maximum flame temperature. (The numbers refer to the number of cells on the burner surface; N.C. = no visible cell formation).

plained as follows: In the stable regime, increasing temperature decreases carbon dioxide, water, and polyacetylenes in the burnt gas, while increasing the hydroxyl radical concentration,[7,9] all of which do not favor the formation of the higher hydrocarbons that would lead to soot. When cells are formed in the unstable regime, an opposing effect causes an over-all increase in the soot formation: oxygen diffusion perpendicular to the direction of flow from the ridges between the cells (unburned mixture) into the burned gas above the cells causes the C/O ratio in the ridges to increase.[1] Increased flow and temperature enhances this process and results in the observed over-all increase in soot formation from the ridges.

This oxygen diffusion and subsequent increase of the local C/O ratios may also govern the increasing soot formation with temperature in turbulent flames of hydrocarbons with molecular weight greater than oxygen as found by MacFarlane and coworkers.[8]

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Subject Headings: ***Hydrocarbon-air flames, soot in; Soot, formation in hydrocarbon-air flames.***

Old Sec. V **U. Bonne**

Gray, B. F. and Yang, C. H. (Defense Research Corporation, Santa Barbara, California) "The Present Theoretical Position in Explosion Theory," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 1057–1061 (1967) and "The Determination of Explosion Limits from a Unified Thermal and Chain Theory," *ibid.*, pp. 1099–1106.

In reviewing the recent developments and trends in explosion theories in comparison with the classical work, the authors try to place them in perspective with respect to physical chemistry in general. The thermal theory and the isothermal radical chain theory reflect a dichotomy in physical chemistry, namely, the tendency to study chemical kinetics without considering energy conservation on the one hand and thermochemistry without kinetics on the other. As a result, many physical chemists are produced feeling that explosions and flames, two areas where the interplay between energy and species conservation is crucial, are complex subjects only amenable to treatment if one aspect or the other is omitted from consideration. The classical purely thermal theory totally ignores kinetic mechanisms and is here closely parallel to classical flame theory; in fact, the necessary conditions for a unique steady-state solution of the flame equations to exist are in fact the thermal explosion limit conditions. The authors believe future research on explosion theories must inevitably be in a direction away from this dichotomy and towards unification of the "thermal" and "kinetic" viewpoints if it is to provide more understanding in related combustion phenomena. Chemical kinetic constants in explosive systems are often determined from experimental explosion data. Some difficulties involving kinetic parameters seem to be resolvable by recent development of unified chain and thermal theories. Recent work has shown that explosion limits may be significantly modified in the presence of radiation fields for either thermal or kinetic reasons. Other progress has been made in treating the thermal theory of explosions with the consideration of fuel consumption.

Unification of Chain and Thermal Theories

Both models of the thermal and chain theories of explosion are mathematical idealizations constructed to characterize laboratory observations. They have yielded a most fruitful understanding of the explosion phenomenon in cases where physical conditions are consistent with these idealizations. Unfortunately, the attitude of regarding both as convenient models useful in particular instances has often been replaced by the outlook that real explosions are either "chain" or "thermal," thus giving rise to the setting up of criteria to decide to which class a given case belongs.

While not wishing to deny the extreme usefulness of such ideas, the authors warn that too literal an application of the distinction can lead to difficulties. For example, in the slow-reaction region between the second and third limits in the hydrogen-oxygen system, there is, in fact, measurable slow reaction, but this bounds the second (chain) limit and third (thermal) limit. If one approaches the second limit from high pressure, it would be classified as "thermal" according to the above statement, whereas it is commonly acceptable as being "chain." The conservation equations have to be satisfied for all systems and a more general theory of explosion limits should incorporate both energy and species conservation. The thermal theory can be generalized to include the influence of the kinetic scheme, not the gross heat-release rate alone, and the chain theory can be generalized to include heats of reaction. The results are not trivial; for example, they illustrate with an example discussed fully in their second paper. Consider the system

$$A \rightarrow x \rightarrow B,$$

where there is no chain reaction at all. It could only explode by a "thermal" mechanism, but even here the results are not those of the classical theory, in fact the explosion conditions are

$$(\partial/\partial T)(R-l)+(\partial R/\partial x)\cdot[(\partial \dot{x}/\partial x)/(\partial \dot{x}/\partial T)]=0$$

where all derivatives are evaluated for $\dot{x}=\dot{T}=0$, rather than the classical result

$$R-l=0$$

$$(\partial/\partial T)(R-l)=0.$$

They are of course identical if $\partial R/\partial x=0$. Similarly, it was pointed out that the equations for a linearly branched chain reaction require divergence of both radical concentration and temperature, although under some circumstances the numerical details of the limit will not be too different from the classical ones. Numerical analysis on a large computer is another way of bending the kinetic and energy equations, e.g., they cite investigators who have integrated the energy and detailed kinetic equations for the H_2–Cl_2 reaction in the presence of nitric oxide and nitrosyl chloride, using a spatially averaged temperature. They found that, without autocatalysis, the classical theory predicts pressure limits accurately. Otherwise, although obtaining the correct order of magnitude for the induction period, difficulties were experienced possibly due to incorrect rate constants. This type of approach will undoubtedly be useful, especially if coupled with qualitative insights resulting from generalization of the classical theories.

To illustrate the type of result obtainable without numerical calculations, they consider the second limit in a branched chain system, given by $P=k_b/k_t$ for fixed composition. This expression is independent of initiation rates and the slope is $\propto E_b$ which is usually a smallish number. For this same scheme, with energy conservation included the second limit condition is

$$h_t k_t k_i \cdot P^3 + h_b k_b k_i \cdot P^2 - l k_t P + l k_b = 0$$

if branching is $\propto P$ and termination and initiation are $\propto P^2$. h_b and h_t are the heats of initiation, branching, and termination. When the h's go to zero, the expression reduces to the usual one, and the theories become identical. If $k_i \rightarrow 0$, the expression is again the classical one. The main qualitative feature here is that, in the unified theory, initiation affects the second limit, whereas in the classical theory it does not. It is possible that the previously inexplicable high activation energy deduced from the data on upper limits for the $CO-O_2$ system can now be explained by the unified theory as a result of the initiation reaction appearing in the expression for the limit.

Inclusion of Fuel Consumption

Other recent work has been in the direction of generalization of the thermal theory of Semenov (spatially homogeneous) to include consumption of fuel. This is especially important in cases with a low heat of reaction, such as the burning of wood and cellulose, etc. Here the authors are talking about ignition rather than explosion. Many authors resorted to numerical integration, thus obtaining critical parameters useful in a very limited context only. An attempt to obtain general results was made by two investigators, who considered symmetrical heating of an exothermally reacting medium, replacing the spatial temperature distribution by an average value in the usual manner. They dealt with the equations

$$d\theta/d\tau = \delta \alpha e^{\theta} - A\theta$$

$$d\alpha/d\tau = -(\delta/B)\alpha e^{\theta}$$

where θ and α are the dimensionless temperature and fuel concentration, respectively, τ is dimensionless time, and $\epsilon = RT_0/E$, and $\epsilon\theta \ll 1$ was assumed. It has been common practice to take the critical temperature as that temperature at which an inflection first appears in the temperature-time curve. However, as the two above equations describe an autonomous system, it is possible to gain insight by working in the $(\theta-\alpha)$ plane simply by considering one equation

$$d\theta/d\alpha = -B + (BA\theta e^{-\theta}/\delta\alpha).$$

It is shown that an inflection in the $(\theta-\alpha)$ curve implies one on the $(\theta-\tau)$ curve, but also leads to a well-defined critical ignition temperature. It turns out to be $1+n^{1/2}$, for an nth-order reaction, i.e., 2 for a first-order reaction. A weakness of the above is the approximation $\epsilon\theta \ll 1$, i.e., $T-T_0 \ll T_0$, which restricts the analysis to systems with large activation energy. It does not appear mathematically necessary to neglect $\epsilon\theta$ to derive the critical temperature rise. At this point, the authors believe one might ask why there is a difficulty in defining critical conditions when fuel consumption is important. The answer is that the temperature in both supercritical and subcritical behavior passes through a maximum and finally falls back to T_0, the ambient temperature. Without fuel consumption the $(\theta\tau)$ curves fall into two qualitatively different well-defined classes of solution, i.e., those which remain finite and those which diverge. What is the relationship of the apparently nonphysical and somewhat arbitrary definition of criticality based on inflections in the $(\theta-\tau)$ or $(\theta-\alpha)$ curves to the obvious one without fuel consumption? As the rate of fuel consumption decreases, the inflection type definitions can be shown to be identical with the well-established classical ones.

For illustrative purposes, the authors consider a hypothetical system with fuel-proportional chain termination and branching, i.e., with kinetic equations

$$d\alpha/dt = -\epsilon(k_b)\alpha x,$$

$$dx/dt = (k_b - k_t)\alpha x,$$

where the parameter ϵ is carried so as to pass continuously over to the case without fuel consumption ($\epsilon \to 0$). Letting $\epsilon \to 0$ corresponds, at any particular time, to feeding in fuel at a rate just sufficient to maintain its concentration at a constant value whereupon it will either diverge ($x \to \infty$, explosion) or remain steady. Accordingly, the original trajectory was either supercritical or subcritical, respectively. Mathematically stated, if the exact trajectory is $x(\epsilon, t)$, $\alpha(\epsilon, t)$, the physically real trajectory being $x(1, t)$, $\alpha(1, t)$, then it is supercritical if $\lim_{\epsilon \to 0} x(\epsilon, t)$ is divergent and subcritical if not, i.e., define criticality by requiring continuous behavior as the rate of fuel consumption goes to zero. The authors ask, "Does this definition coincide with the existence or otherwise of inflections in the $x(1, \epsilon)$ curve?" The above equations can be integrated exactly, the solution goes to the usual solution when $\epsilon \to 0$. It can be shown easily that the necessary condition for an inflection in the $x(\epsilon, t)$ curve is $k_b > k_t$. In the branched-chain case then, the apparently different definitions of criticality turn out to be identical. To show their identity in the thermal and unified chain theories is difficult due to the nonlinearity of the equations.

Effect of Spatial Distribution on Explosion Limits

Turning to spatial temperature distributions in the steady state, as opposed to the time-dependent spatially averaged systems discussed above, the authors deal with the equation

$$\nabla^2 T = -\rho(R\Delta H/k)$$

where ρ is the density, R the chemical reaction rate, ΔH the heat of reaction, and k the thermal conductivity of the medium. With the exponential approximation to the Arrhenius temperature dependence, this equation was solved analytically for planar and cylindrical bodies and numerically for spherical ones. Although this equation predicts similar results to the Semenov thermal theory in its simplest form (one-step kinetics, no fuel consumption), it does not seem to be as amenable to generalization as the latter, since one is immediately faced with a nonlinear partial differential equation from which little information can be gleaned short of brute-force numerical calculation. That the introduction of the spatial variable causes such grave difficulties is unfortunate in view of experimental developments towards accurate profile measurement; however, the measurements may be useful in enabling better estimates of the mean temperature to be made for the time-dependent theories. It appears that the steady-state theory will not easily accept detailed kinetics and, in general, the spatial variables play a much less important role than the time, and hence are more easily dispensed with.

Relation of Explosion Theory to Theories of Flame and Detonation

The theory of explosions was applied to the study of another important phenomenon in combustion, detonation, by one investigator in work on detonability and chemical kinetics. Even though the kinetic scheme used does not seem to be valid under the conditions for the H_2 and O_2 system calculated, and the explanation of detonability limits is different from the more widely accepted loss mechanism of Zel'dovitch, he related the explosion theory to the initiation of detonation by a shock wave.

Other investigators showed analytically, from a mathematical viewpoint, that the flame equations have a unique solution and burning velocity only if the following conditions are satisfied:

$$\varphi=0 \quad \text{at} \quad T=T_u$$

$$\partial\varphi/\partial T<0 \quad \text{at} \quad T=T_u$$

where φ is the heat-release rate function and T_u is the temperature of the unburned mixture. Any Arrhenius type of rate function is always greater than zero at finite temperatures and is always a monotonically increasing function of temperature. However, they are quite justified physically when heat losses to the environment are considered. With heat loss, these conditions become

$$\varphi-l=0 \qquad T=T_u$$

$$\partial(\varphi-l)/\partial T<0 \qquad T=T_u.$$

It is immediately obvious that they are the conditions for explosion limits deduced by the classical thermal theory with the inequality above replaced by an equality. When $\partial(\varphi-l)/\partial T$ is equal to or greater than zero the whole system will explode homogeneously. It is quite natural that a steady-state flame cannot be supported in a gas which is unstable itself. The uniqueness condition is logically justified from physical considerations. The uniqueness theorem of Kolmogorov *et al.* for solutions of the flame equations is thus identical with the conditions of thermal explosion, or rather thermal stability.

Subject Headings: *Explosion theory; Flame theory.*

Old Sec. V E. C. Woodward

Jain, V. K. and Ebenezer, J. S. (Indian Institute of Science, Bangalore, India) "Analytical Solution of a Steady Cylindrical Flame," *Combustion and Flame* 10(4), 391–392 (1966) Letter to the Editor.

This note presents a theoretical calculation of the flame radius for a steady, cylindrical, laminar flame with a Lewis number of unity, with constant properties, and with a one-step reaction whose temperature-explicit rate vanishes below an ignition temperature and takes on a constant value above this ignition temperature. The flame radius is defined as the position at which an extrapolation of the temperature profile that is valid in the region of zero reaction rate, reaches the adiabatic flame temperature. The calculation is precisely the cylindrical analog of an earlier spherical calculation by Spalding and Jain.[1] An objective is to obtain a feeling for the effect of flame thickness on flame location, and for this purpose theoretical curves are plotted for the ratio of the calculated flame radius to the flame radius that would have been obtained if a thin laminar flame were to sit at a position where the mass flux into it equals its plane mass burning rate. The curves show that the thin-flame result is approached at high rates of injection of the combustible and that as the injection rate decreases, the calculated flame radius begins to exceed that which would have been obtained from the thin-flame approximation. The difference between the two radii increases as the ignition temperature decreases.

Reference

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Subject Headings: ***Cylindrical flame, theory of; Flame theory, for cylindrical geometry.***

Old Sec. V **F. A. Williams**

Kinbara, T. (Sophia University, Tokyo, Japan), **Endo, H.** (University of Electro-Communication, Tokyo, Japan), **and Sega, S.** (Toho University, Chiba, Japan) "Downward Propagation of Smoldering Combustion through Solid Materials," *Eleventh Symposium* (*International*) *on Combustion*, Pittsburgh, The Combustion Institute, 525–531 (1967)

The velocity of downward propagation of smoldering was studied for vertical samples of: (1) circular rods of rolled paper, (2) circular incense sticks, (3) strips of cardboard, and (4) piles of cardboard tightly bound with thread. Experimental results are presented for propagation velocities (v) perpendicular to the smoldering front as a function of sample dimension, radius (r), breadth (b), and thickness (d), and as a function of the difference between the spontaneous ignition temperature (T_i) and the ambient chamber temperature (T_a). T_i is taken as the lowest temperature of an electric furnace at which "a small sample flares up immediately after insertion in the furnace." Experimental conditions were: ambient chamber temperature from 27° to 150°C; radii of rods and incense sticks from 0.8 to 3.8 mm; breadths of rectangular cardboard samples from 5 to 15 mm with thicknesses of 0.76 to 2.28 mm.

An equation of theoretical velocity of smoldering was derived based on the following assumptions: (1) heat produced by combustion per unit time is proportional to the rate of air supplied by diffusion which is assumed proportional to (temperature of the solid body $-T_a$), (2) heat produced is inversely proportional to ($T_i - T_a$), (3) a stagnant layer of combustion gases covers the solid surface, and (4) the fresh-air supply and heat dissipation from the solid into the air occurs at the surface of the stagnant layer. The theoretical equation for v is:

$$v^2 = (4k/c^2\rho^2)(p/S)\{[q/(T_i - T_a)] - h\} \tag{1}$$

where c=specific heat, ρ=density, k=thermal conductivity, S=cross-sectional area, p=periphery of stagnant layer, h=heat transmission coefficient, and q=a constant depending on the material. Results computed from the theoretical equation and from experimental data were in excellent agreement although authors provide no information concerning the precision of T_i.

The authors note some differences between their results and those of Palmer[1] who measured horizontal velocities of smoldering through vertical board samples of larger dimension. Palmer's boards of constant thickness=13 mm varied in breadth from 13 to 90 mm. Authors compute stagnant boundary layer thicknesses of 1 to 2 mm from the theoretical equation and data; other computed values are $q \cong 0.12$ cal/cm^2 sec and $h \cong 1.5$ to 2.2×10^{-4} cal/cm^2 deg sec. The value of h was measured by means of an independent experiment to be 1.4×10^{-4} cal/cm^2 deg sec, within the limit of experimental error of the computed value.

Authors conclude that Eq. (1) is the fundamental equation for the propagation velocity of smoldering through small samples which are not affected by ascending combustion gases.

Reference

1. Palmer, K. N.: Combust. Flame *1*, 129–154 (1957).

Subject Headings: ***Combustion, of solids, by smouldering; Smouldering, combustion; Solids, smouldering of.***

Old Sec. V **J. M. Singer**

Lefebvre, A. H. and Reid, R. (College of Aeronautics, Cranfield, England) "The Influence of Turbulence on the Structure and Propagation of Enclosed Flames," *Combustion and Flame* **10**(4) 355–366 (1966)

The paper presents the results of an investigation of the effects of turbulence on the burning velocity and surface structure of the flame under conditions similar to those experienced in the afterburner systems of turbojets.

For the existing theories for turbulent flame propagation, the authors suggest the reading of a review paper by Burgess,[1] and they comment on the following concepts: the wrinkled laminar flame-front model, the influence of flame-generated turbulence, the distributed reaction zone model, and the rate of entrainment model. They also summarize, in tabulated form, the work carried out by Williams *et al.*[2] Wohl *et al.*,[3] and Wright and Zukoski,[4] and then discuss the effects of the laminar flame velocity, ft/sec (S_L), inlet flow velocity, ft/sec (U), the percentage turbulence ($T = 100u'/U$), and the fuel-air ratio on the turbulent flame velocity ft/sec (S_T). The effects of the flame-generated turbulence and the flame stabilizer are ruled out at the outset.

The apparatus used by the authors is similar to that used by Williams, Hottel, and Scurlock,[2] except the means of flame stabilization, which is now provided by a pilot burner. The test conditions, using propane-air mixtures only, are also similar except with a narrower range of flow velocities and with a higher level of percentage turbulence (2%–14%). The turbulent flame velocity is derived as the product of the inlet velocity and the sine of the angle between the flow direction and the mean surface of the flame, measured from schlieren photographs.

With a constant fuel-air ratio, the turbulent flame velocity is found to decrease with the inlet flow velocity, and the slope of the line increases with the percentage turbulence. Furthermore, the turbulent flame velocity achieves the value of the laminar flame velocity when the inlet flow velocity is extrapolated to zero. The ratio of the two flame velocities is thus established as

$$S_T/S_L = 1 + 0.43u' + 0.04U$$

The influence of the fuel-air ratio is strongly present at all velocity levels, a result conflicting with the findings on high flow velocities of previous investigations.

The surface structure of the flame is cellular and the average cell size diminishes with increase in the flow velocity. The main influence of turbulence is to lacerate and to disrupt the flame and thus to increase the specific surface area of the flame. There is no evidence of any effect of fuel-air ratio.

The findings of the present investigation support the wrinkled laminar flame-front concept of turbulent flame propagation. The results of previous investigations are also confirmed in regard to the relatively slight dependence of flame spreading rate on inlet flow velocity, especially at high velocities. However, the flame spreading rate is found to vary appreciably with turbulence and also with fuel-air ratio, a result which is consistant with the wrinkled laminar flame-front model, but which contradicts the previous findings on enclosed flames.

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3. Wohl, K. *et al.*: *Fourth Symposium (International) on Combustion*, p. 620. Williams and Wilkins, 1953.
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Subject Headings: *Propagation, of turbulent flame; Structure, of turbulent flame; Turbulence, effect on flame structure and propagation; Turbulent flame, structure and propagation rate of.*

Old Sec. V A. C. S. Ma

Peskin, R. L. (Rutgers University, New Brunswick, New Jersey) **and Wise, H.** (Stanford Research Institute, Menlo Park, California) "A Theory for Ignition and Deflagration of Fuel Drops," *AIAA Journal* 4(9) 1646–1650 (1966)

Because of the complexity of a detailed theoretical treatment of the time evolution of a fuel droplet suddenly placed in a hot oxidizing gas, these authors investigate the relevance of a *steady-state* droplet burning theory to questions of ignition and extinction. Since these questions involve homogeneous chemical kinetics in a central way, even this indirect approach to ignition/extinction phenomena requires a rational (yet tractable) theory of droplet combustion, including chemical kinetic limitations. For this purpose the authors have developed what is called a "modified flame surface" model, which indeed embodies the nonlinearity of the Arrhenius temperature dependence, but artificially confines the reactions to a zone of negligible radial thickness surrounding the droplet. At this flame surface the reactants meet in their stoichiometric ratio; but on either side of the flame surface, chemical sources (or sinks) are absent.* The quasi-steady, constant property, coupled linear ordinary differential equations governing flame location, temperature, and composition profiles, and burning rate are then solved, leading to (at most) implicit transcendental relations between these quantities and a parameter incorporating the chemical kinetics. It is this feature which renders a mathematical model suitable for parametric studies, some of which can shed light on ignition/extinction phenomena. Incidentally, the model has the necessary property of asymptotically approaching well-known quasi-steady results[1] for pure evaporation (infinitely slow reaction) and diffusion-limited (flame sheet—infinitely fast reaction) droplet combustion.

In relating these quasi-steady solutions to the more complex circumstance of ignition or extinction, the authors' present discussion is suggestive but somewhat incomplete. While significance is attached to the fact that there is a singular value of the kinetic parameter which determines whether the droplet absorbs or delivers heat to the environment, the results presented in the subject paper do not reveal the multivalued regions we have come to associate with quasi-steady analyses of ignition and extinction in related systems (e.g., surface combustion).[2,3] However, in further work on this model by Peskin and Yeh[4,5] the existence of a region of two stable steady-state solutions for fixed values of ambient temperature of oxygen concentration *has* been demonstrated, and its occurrence and location have been interpreted in terms of distinct ignition and extinction temperatures and a so-called "rich limit." Not discussed, but equally important, would be the implications regarding low pressure ignition or extinction and extinction of droplets that have become too small.[6] Indeed, further exploitation of the model and its correlation with rival treatments and experimental data will be welcome future contributions.

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* Thus, the nonlinearity is removed from the differential equations and placed in the boundary conditions on each zone.

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Subject Headings: ***Deflagration, of fuel drops; Drops, ignition and deflagration of; Flame theory, for droplets; Ignition, of fuel drops.***

Old Sec. V **D. E. Rosner**

Philpot, C. W. (Pacific Southwest Forest and Range Experiment Station, Berkeley, California) "Temperatures in a Large Natural-Fuel Fire," *U.S. Forest Service Research Note PSW 90* (1965)

Dependable temperature measurement systems for large-scale test fires are important to enable experimental values to be used as an aid to test the validity of theoretical fire models and to relate laboratory and field fires. This note describes methods used and presents some preliminary results.

Reported data were recorded from a fire involving 720 tons of fuel (95% pinyon pine and 5% Utah juniper) distributed at the rate of 20 tons per pile (oven-dry weight) in a 4½ acre plot, containing 36 piles, 47-ft-sq and spaced 25 ft apart. At ignition, the average fuel moisture content was 20%. By standard oxygen bomb calorimetry, the heat of combustion of this fuel was determined to be 9500 Btu/lb for needles and 8500 Btu/lb for twigs, branches, and stems. Ten igniters in each pile were fired simultaneously in all piles by electrical means. Zero fire-time was recorded when the wood fuel began to burn.

Three types of thermocouple towers were used: within three piles of fuel at 7 and 20 ft above the soil were bare chromel-alumel thermocouples; in the aisles at the same heights were both shielded unaspirated, and shielded aspirated thermocouples to measure gas temperatures; one aspirated thermocouple was also located at 50 ft on the tower in the aisle at the center of the fire. Tube wall temperatures of the aspirated thermocouples were not measured. Soil temperatures under piles and between piles were measured at 3 in. and 6 in. depths.

Two temperature peaks were recorded by bare and aspirated thermocouples in this fire and other fires in this study. The cause is attributed to an initial fast rate of combustion of fine fuels, followed by a period of less intense burning until the intensity of the fire in the medium and coarser fuels reaches a maximum.

Bare thermocouples over three piles of fuel failed after temperatures above 2650°F were recorded. Since the thermocouple materials melt at about 2600°F, and chromel-alumel thermocouples are not very reliable above 2300°F, the author considers values above 2600°F of questionable accuracy.

Gas temperatures in the aisle at the center of the fire were recorded with the aspirated system; these values lagged about 1 min behind those of the bare thermocouples. The first peaks in gas temperatures (uncorrected) at 7, 20, and 50 ft were

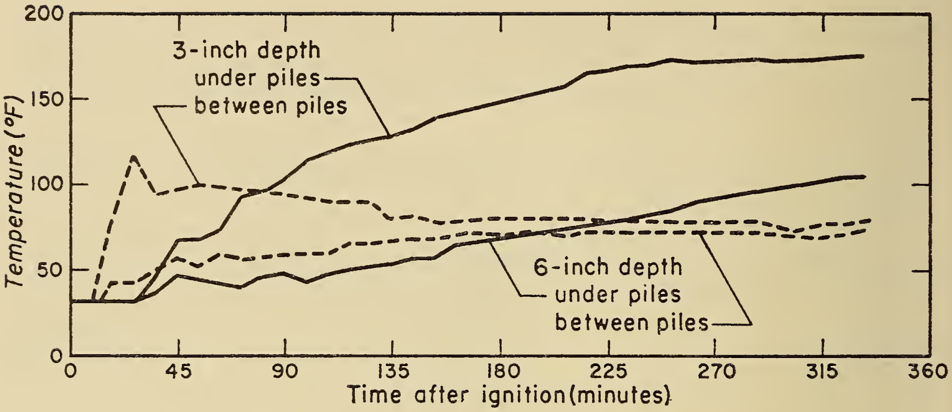

FIG. 1. Soil temperatures at two depths, under and between piles.

1250°F, 2000°F, and 540°F, respectively. Gas temperatures at the second peak were about 1500°F at 20 ft, 1300°F at 7 ft, and 1200°F at 50 ft.

The shielded unaspirated thermocouples, all of which were toward the outside edges of the plot, showed much lower temperatures than the aspirated thermocouples; also, it was found that these thermocouples produced much too great a lag time to be of value for gas temperature measurement. The large lag time corresponds to findings in earlier work.

Soil temperatures are in general agreement with past work, although comparison is difficult because of differing test conditions. The record of soil temperatures at the two depths, under and between piles, is shown in Fig. 1.

Chromel-alumel thermocouples are considered suitable for most temperature measurements on large fires. But to record temperatures above 2650°F, some other material, such as platinum-platinum rhodium junctions, must be used. An aspirated thermocouple system proved practical on this large field-test fire, but measurement of tube wall temperatures would aid correction of gas temperatures for the effects of the environment surrounding it.

Subject Headings: *Fires, large, temperatures in; Temperatures, in large fires.*

Old Sec. VII W. G. Labes

Roberts, A. F. (Safety in Mines Research Establishment, Buxton, England) "An Analogue Method of Estimating Wood Pyrolysis Rates," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 561–565 (1967)

This paper describes an experimental technique for measuring the pyrolysis or weight/time history of burning fuel elements. The technique assumes that if one ascertains the temperature distribution in a burning piece of wood, as a function of time and position, and reproduces that distribution in another piece of wood of identical properties, then one will reproduce the chemical reaction distribution, hence total weight/time curve, of the original piece of wood.

In particular, the author is interested in studying and simulating the pyrolysis of burning wooden planks placed in good thermal contact with a semi-infinite noncombustible wall. To simulate the pyrolysis of the planks, it is necessary to reproduce the same temperature distribution in the sample. Heat conduction theory requires that the test samples have identical thickness, moisture content, physical properties, temperature dependence of physical properties, heat source, and sink distributions as the original burning planks. These conditions were approximately met by taking samples from one of the original planks. The test samples had to have the same initial temperatures, and also had to be placed in good thermal contact with a noncombustible backing thermally equivalent to the plank backing. Then it only remained for the author to reproduce the same temperature/time curve on the exposed surface.

The planks of interest to the author were simulated by cutting circular discs (1.5 in. diam) of wood from the planks from areas free of visual defects. This insured the same thickness, physical properties of the wood, and moisture content. The edges of the discs were sealed with sodium silicate to prevent the radial outgassing of volatiles. Next the discs were placed in a sample holder whose thermal properties were similar to the plank, thus simulating thermal effect of the much larger plank of wood by minimizing radial heat losses. In addition, an appropriate noncombustible wall was placed in good thermal contact against the back face of the sample and its holder.

Thermocouples were placed on the sample surface. Then a controlled blast of hot gas was blown against the exposed disc face. The heating was regulated so as to maintain a prescribed temperature/time curve at the exposed disc face. This control was accomplished by a servomechanism which required that the surface thermocouple output voltage follow a prescribed voltage/time curve generated by a cam-operated rheostat. By means of this device, the author was able to keep the temperature of the sample within 5°C of the prescribed temperature/time curve.

While being heated, the sample was continuously being weighed by suspending both the sample and its holder from a load cell of the unbonded-strain gauge-type. Using 0.5 in. thick samples, with weights of 13–14 grams, the weight record could be interpreted to the nearest 0.1 gram.

The reproducibility of the experiments was such that, for correctly heated samples, individual weight/time curves were kept to within ±0.2 grams of the mean weight/time curve for the particular heating condition. The differences in these curves led to larger differences in the differentiated curves, i.e., the rate of weight loss/time curve. These larger differences could be significantly reduced by considering the mean curve for three runs, using the same heating conditions.

The over-all experimental technique was verified by first burning some samples in front of a gas-fired radiant panel with their weights and surface temperatures continuously being recorded. Other samples were then made to obey the same surface temperature variations. The resulting weight/time curves for the two sets of samples agree quite well. They are within 5% of each other, except for a 10% variation during a short period toward the end of the run when the hot gas-heated samples lost more weight than the radiant panel samples. The reviewer speculates that this larger variation might be attributed to the different chemical atmospheres that the two sets of samples were subjected to. On the one hand, the radiant panel samples had combustion taking place above the surface, thus depleting the available oxygen at the surface. On the other hand, the hot gas-heated sample might have had more oxygen blown directly onto its surface thus causing a more rapid oxidation on the sample surface. Of course, it would be possible to produce the same chemical atmosphere by mixing an appropriate amount of nitrogen or other gas with the air used in the hot blast heater. Perhaps when these surface chemical effects are investigated, it will be proven that they play only a minor role in the over-all pyrolysis.

This experimental technique has two primary applications. First it can be used to predict the fuel pyrolysis or weight loss in an experimental fire just by duplicating the same surface temperature (and atmospheric?) conditions. This will permit one to relate the effects of pyrolysis to the over-all combustion problem. Second, upon determining the heating condition of a fuel element in a particular type of fire, the effects of impregnation with different levels and formulation of fire retardant treatment could be assessed by subjecting samples of impregnated wood to the same heating conditions.

Subject Headings: *Analog computation, of pyrolysis; Pyrolysis, of wood; Wood, pyrolysis of.*

Old Sec. II **J. de Ris**

Schaffer, E. L. (Forest Products Laboratory, U.S. Forest Service, Madison Wisconsin) "Review of Information Related to the Charring Rate of Wood," *U.S. Forest Service Research Note FPL 0145* (1966)

This review indicates that information on the charring rate of wood has been limited to special experiments resulting in empirical relationships for predicting char depth or rate of char. However, experiments and proposed models of the rate of char in other polymers have been prolific during the last decade, thereby providing a good foundation for the analysis of the rate of char in wood.

A comparison of the limited models developed for the rate of char in wood with that of other polymers suggests that the principle of conservation of mass, coupled with Arrhenius-type temperature dependence, may be appropriate in the physical description of the charring rate of wood. For example, Vorreiter[1] and Lawson[2] found that the char depth in wood can be expressed as:

$$s = Kt^n$$

If K is the Arrhenius rate constant given by:

$$K = A \exp[-E/RT]$$

where T would be a characteristic temperature, equation

$$s = At^n \exp[-E/RT]$$

by Barker *et al.*[3] is generated.

Other models for defining the charring rate of polymers depend upon such parameters as the charring temperature, the temperature difference between the char surface and decomposition temperature of the material, thermal coefficients, mass, and applied heat flux. These models exhibit promise of application to the charring rate of wood.

It appears that the significant wood properties that affect its rate of char will be mass density, moisture content, thermal properties k, α, C_p, annual ring orientation with respect to the heated surfaces, charring temperature, and combustible volatile content.

Blackshear's and Murty's[4] observations of temperature-dwell at the boiling point of water, even in initially dry cellulose, indicate that moisture may delay the rise to the charring temperature of the wood. An excess of moisture, however, is shown by Shorter[5] to have a disastrous spallation effect on concrete under fire exposure. This phenomenon could have the same effect in the wood char layer, thereby decreasing the insulative thickness of the char.

The charring temperature of wood appears to lie in the range of 540° to 600°F (280° to 320°C) as estimated by the degradation zones in wood (Hawley[6], Jakob[7], and Tang[8]) and the temperature at the base of the char layer pointed out by Truax.[9] Ignition temperatures of wood also appear to lie in this range (Bamford[10] and Tang[8]).

It also appears that the heat liberated in the combustion of wood species to various stages of char can be determined from the total heats of combustion for the species (Klason, Heidenstam, and Norlin,[11] Parr and Davidson,[12] and Salisbury[13]) and the per cent of the total heat contained in the volatiles as a function of volatilization.

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Subject Headings: Charring, of wood; Wood, charring of.

Old Sec. II Author's Summary

Tarifa, C. Sanchez and Torralbo, A. Muñoz (Instituto Nacional de Técnica Aeroespacial, "Esteban Terradas," Madrid, Spain) "Flame Propagation along the Interface between a Gas and a Reacting Medium," *Eleventh Symposium* (*International*) *on Combustion*, Pittsburgh, The Combustion Institute, 533–544 (1967)

A two-dimensional analysis was applied to a two-phase system, involving the propagation of flame over the surface of a solid or liquid fuel (or oxidizer) in contact with a gaseous oxidizer (or fuel).

It was assumed that no reactant atmosphere existed far ahead of the flame, and that flame propagation took place through the following sequence of events: heating of the fuel ahead of the flame, vaporization of this fuel and mixing with the oxidizer, and finally, ignition and combustion of this gaseous mixture. The ambient atmosphere was assumed to be quiescent. Heat transfer from flame to fuel ahead of the flame front was assumed to take place through radiation, exclusively; whereas heat transfer from flame to fuel behind the flame front was assumed to take place through both convection and radiation. Flame velocity is given by the condition that the flame reaches a certain location when the temperature of the fuel surface at that location reaches a given ignition temperature.

An equation was set up, involving the heat balance, and boundary-layer solutions obtained, involving heat transfer through the fuel as well as through the vapor. The flame was assumed to have a rectangular shape. Convective heat transfer was assumed to be laminar and dependent on the densities and flame speed. Radiant heat transfer was taken to be constant close to the flame front, and dependent on the fuel surface temperature and emissivity. The boundary-layer approximation is valid only if a thin layer of fuel experiences a temperature rise as a result of the flame propagation. This condition is generally met. Results were obtained, in which the dimensionless flame velocity was found as a function of the dimensionless ignition temperature, and the dimensionless combustion temperature. Two separate classes of solutions were found, depending on whether the convective heat transfer was large or small compared to the radiative heat transfer. For small values of ignition temperature, it was found that the combustion temperature did not influence the process, and the influence of convection was negligible. A different set of results is obtained if the convective heat transfer behind the flame is much larger than the radiative heat transfer (such as a flame with low emissivity).

A theoretical and experimental study was conducted for the case of flame spreading over the surface of hydrocarbon fuels burning in air. The ignition temperature in this case was assumed to be the flashpoint temperature, so all fuel initial temperatures were taken equal to or less than the flashpoint temperature. The study was intended for rather large flames, in which radiative heat transfer is predominant; this condition does not hold, however, for very small propagation velocities. An additional condition was that the ignition temperature not be large compared to the initial temperature, so that temperature gradients parallel to the fuel not be large; so such gradients were neglected, compared to gradients perpendicular to the surface. Flame propagation velocities were obtained as a function of fuel thickness, for certain values of ignition temperature. Above certain values of fuel thickness, flame propagation velocity did not depend on the former. On the other hand, flame velocity decreased for smaller values of fuel thickness and high thermal conductivity of the supporting medium.

An accompanying experimental study was conducted, involving the steady flame propagation in a channel. In order to study the effect of fuel depth and fuel initial temperature, a large channel was set up, 16 ft in length and 20 in. wide. The channel was filled with water to the desired initial temperature, and the fuel (JP-1) was spread over it. Flame propagation velocities were measured by means of a movie camera or a chronometer. By measuring the flame emissive power with radiometers, it was possible to calculate the flame propagation speed, according to the theory. The experimental results were found to agree reasonably with the theory. The flame speed was found to vary between about 0.5 to 20 cm/sec, as the fuel initial temperature varied from 275° to 320°K, and the fuel depth from 0.05 cm to 0.3 cm. The flashpoint was taken to be 325.5°K and the emissive power 0.09 cal/cm^2 sec.

Subject Headings: *Flame propagation, two-phase; Flame theory, two-phase; Interfacial flame propagation.*

Old Sec. V **J. K. Richmond**

Tsuji, H. and Yamaoka, I. (University of Tokyo, Tokyo, Japan) "The Counterflow Diffusion Flame in the Forward Stagnation Region of a Porous Cylinder," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 979–984 (1967)

This paper presents the results of an experimental study of the properties of a laminar diffusion flame established in the forward stagnation region of a cylinder. Air with a flat velocity profile was forced past the cylinder while fuel was ejected uniformly through the porous cylinder wall. This flow pattern will yield a laminar diffusion flame a short distance from the surface of the cylinder under a certain range of conditions. The distance of the flame from the surface and the blowoff limit were found for various uniform air stream velocities, V, surface fuel velocities V_w, cylinder diameters, D, and fuel compositions. The temperature distribution through the flame and the flow pattern were examined in detail.

For a particular fuel composition the blowoff limit was found to be a unique function of the nondimensional ejection parameter, $-f_w = (V_w/V)(\mathrm{Re}/2)^{1/2}$ and the velocity gradient, $2V/R$ ($\mathrm{Re} = VR/\nu$ being the Reynolds number, and ν the mean kinematic viscosity across the boundary layer with flame in the stagnation region). The criteria for blowoff appeared to change from the normal thermal instability at low velocity gradients to a chemical reaction instability at high gradients. This interpretation is supported by temperature distributions measured with a very fine thermocouple. It is suggested that the latter limit can be used to study the over-all chemical reaction rate in various flames.

Subject Headings: *Counterflow diffusion flames; Diffusion flames, cylindrical; Porous cylinder, diffusion flames; Stagnation region, combustion in.*

Old Sec. IV **F. R. Steward**

Welker, J. R. and Sliepcevich, C. M. (University of Oklahoma, Norman, Oklahoma) "Burning Rates and Heat Transfer from Wind-Blown Flames," *Fire Technology* 2(3) 211–218 (1966)

A study has been made of the effect of liquid fuel burning rates, flame lengths, wake gas temperatures, and flame radiation on the flame heat transfer and fire spread for wind-blown flames from liquid pool fires. Both circular burners, 4 in. to 2 ft in diameter, and channel burners, 5 ft long and 2 in. to 8 in. wide, were used. Five fuels were studied; methanol, acetone, *n*-hexane, cyclohexane, and benzene.

With the exception of the methanol fires, the burning rates for circular burners showed a decrease with increasing wind velocity (measurements were made with wind velocities up to about 6 ft/sec) and an increase with increasing burner size. Methanol burning rates tended to be constant. The decrease in burning rate can be attributed to a change in the geometrical view factor with changing wind velocity. The geometrical view factor represents the radiant energy returned to the surface of the pool, expressed as a fraction of the total radiant energy released by the flame. An increasing flame tilt caused by the increasing wind velocity thus decreases the rate of heat feedback to the pool, with a more noticeable effect on the larger fires since they receive a greater portion of their energy feedback from radiation than from convection. The increasing burning rates for increasing burner diameters is in agreement with the results from other investigations.

Flame lengths, taken from photographs and normalized with respect to an equivalent burner diameter (defined as four times the ratio of burner area to burner perimeter) were essentially constant for a given fuel, although the channel burner values were less consistant than the circular burner values.

Shielded thermocouples were used to measure the temperature in the convective plume downwind from the fires. A single dimensionless position was used for the data presented which is plotted as a dimensionless temperature rise vs a dimensionless wind velocity as suggested by Thomas.[1] The fair amount of scatter in the data indicates the need for further refinement in the technique.

A ground-level radiometer, located five burner diameters (or 15 burner widths) downstream from the fires was used to measure the intensity of the flame radiation. For circular burners the radiation intensity increased slightly with increasing wind velocity, except for methanol flames which showed a decrease. For channel burners the radiation decreased with increasing wind velocity for all fuels. All of these results can be attributed primarily to changes in the view factor from the radiometer. The radiant energy release from methanol fires was measured as about one-fifth of that from acetone fires. Radiant energy released from hydrocarbon fires was measured as about five times that from acetone flames.

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Subject Headings: *Burning rates, of wind-blown flames; Heat transfer, from wind-blown flames; Wind-blown flames, burning rate of.*

Old Sec. V T. P. Anderson

H. Chemical Aspects of Fires

Baldwin, R. R., Norris, A. C., and Walker, R. W. (University of Hull, Hull, England) "Reactions of Methane in Slowly Reacting Hydrogen–Oxygen Mixtures," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 889–897 (1967)

Small quantities of CH_4(ca 1%) have been added to slowly reacting $H_2O_2–N_2$ mixtures in aged boric-acid-coated vessels at 500°C. The pressure change has been used to determine the amount of H_2 oxidized, and conversion of the products HCHO and CO to CO_2 has given the amounts of CH_4 consumed. By examining how the relative rates of consumption of CH_4 and H_2 vary with mixture composition and total pressure, values for the ratio

$$k(OH+CH_4)/k(OH+H_2) \quad \text{and} \quad k(H+CH_4)/k(H+O_2)$$

have been obtained. Strong evidence has been provided that the reaction CH_3+H_2 competes effectively with CH_3+O_2, and some indication has been obtained that the latter proceeds by both bimolecular and termolecular paths.

Subject Headings: *Hydrogen-oxygen flames, reactions of methane on; Methane, reactions of; Reactions, of methane.*

Old Sec. V Authors' Abstract

Bennett, J. E., Mile, B., and Thomas, A. ("Shell" Research Ltd., Chester, England) "Studies of the Formation, Structure, and Reactivity of Peroxyl Radicals at Low Temperatures with a Rotating Cryostat," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 853–859 (1967)

The reaction $R\cdot+O_2(+M)\rightarrow RO_2\cdot(+M)$ has been studied directly at very low temperatures for a wide range of trapped radicals with a rotating cryostat used in conjunction with electron spin resonance (ESR) spectroscopy. All the radicals investigated react with oxygen to form peroxyl radicals with great facility, even at 77°K, indicating that the reaction is highly efficient and has a low activation energy. Therefore, the reaction is likely to be the main process by which hydrocarbon radicals are consumed during combustion at moderate temperatures, but the high efficiency will also result in the reaction being too fast to be rate controlling.

The ESR spectra of the various peroxyl radicals, $RO_2\cdot$, are almost identical, being independent of the nature of the group R, indicating that the orbital occupied by the free electron is located almost entirely in the O–O region and is unaffected by the substituent group. Since the reactivity of a radical in terms of activation energy must be determined principally by the orbital of the free electron, this in turn implies that the reactions of all peroxyl radicals in bond-forming reactions will have similar activation energies and any differences will be due mainly to steric or configurational effects.

When the deposits containing trapped peroxyl radicals are warmed slightly, the radicals decay at rates similar to those of the decay of alkyl radicals of roughly the same size and shape in the same matrix, indicating that the mutual termination reactions of peroxyl radicals are like those of alkyl radicals in possessing low activation energy.

Subject Headings: *Peroxyl radicals, formation, structure, reactivity; Rotating cryostat, for radicals.*

Old Sec. V Authors' Abstract

Benson, S. W. and Spokes, G. N. (Stanford Research Institute, Menlo Park, California) "Application of Very Low Pressure Pyrolysis to Combustion Kinetics," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 95–103 (1967)

A new technique has been developed for the study of individual steps in chemical reactions. Molecular pyrolysis is performed at very low pressure in a fused silica vessel in which a uniform temperature is maintained. The products are examined directly with a mass spectrometer. Controlled amounts of oxygen or other gases can be added in order to study oxidations or other reactions.

Results are presented on the pyrolysis of 1,1,1-trichloroethane and of chloroform. The former compound decomposes through a simple unimolecular elimination of HCl. The observed low-pressure-pyrolysis data are in accord with a high-pressure rate law, $k_\infty = 10^{13.8} 10^{-51.7/\theta}$ sec^{-1}. Chloroform pyrolysis has proved to be dependent on the gas-flow rate; in addition, wall catalysis modifies the decomposition rate. Products of chloroform pyrolysis are HCl plus, variously, C_2Cl_4, Cl_2, CCl_4, solid carbon, or at the highest temperatures (~1000°C), $SiCl_4$. Decomposition is greater in the presence of C_2Cl_4. Evidence is presented that the activation energy for the molecular elimination exceeds 56 kcal. Oxygen added to the products of pyrolysis of $CHCl_3$ yields a new pair of mass peaks at 63 and 65 AMU, possibly due to $COCl^+$ from phosgene—an expected product of the reaction of dichlorocarbene with O_2.

The solid-carbon film produced by pyrolysis of chloroform was removable by oxidation with a flow of molecular oxygen at low pressures at 1000°C.

Subject Headings: *Chloroform; Kinetics, of combustion; Pyrolysis, at low pressure; Trichloroethane.*

Old Sec. II Authors' Abstract

Fish, A. ("Shell" Research Ltd., Thornton Research Centre, Chester, England) "The Non-Isothermal Oxidation of 2-Methylpentane. II. The Chemistry of Cool Flames," *Proceedings of the Royal Society* **A298,** 204–237 (1967)

The oxidation of 2-methylpentane has been studied in detail with respect to the general temperature-pressure ignition limits and the nature of the intermediate and final products found during the course of each stage of combustion. Five distinct regions of oxidation have been identified. Area one shows slow oxidation occurring prior to ignition. No cool flames are formed. In another region it is found that up to three cool flames are consecutively formed prior to ignition. In some cases it is possible to choose a particular temperature and pressure when ignition never occurs subsequent to cool flame formation. Above 307°C no cool flame ever occurs, no matter what the pressure. Below 307°C it is shown that ignition pressure rises with a decrease in temperature. This fact reveals that chemical factors must play a significant role in determining the mode of combustion since simple thermal explosion theory would not adequately explain this inverse temperature dependence upon the pressure of ignition. It is the purpose here to elucidate in detail the array of species found in each region and to determine from this the significant branching or chain breaking reactions which would most likely influence the course of oxidation at any temperature and pressure.

A 2:1 oxygen-2-methylpentane mixture was used in a static reactor. Analysis of products was by gas liquid chromatography. Products formed in the slow combustion include alklyperoxides, O-heterocycles, and low molecular weight alkanes. The total amounts of products increase in the pressure range 150–250 mm and in the temperature range 235°–249°C.

At very low pressures (<39 mm) and temperatures higher than the singly defined region just described the products formed are much more diverse. This is the area of the ignition plot where a cool flame would occur if the pressure were raised. The induction period for slow combustion decreases rapidly with rise in temperature.

The region just below the first cool flame appearance features the gradual decrease in yield of peroxides and condensable organic compounds as the temperature of oxidation is increased.

Above the cool flame limit temperature of 307°C there is an extensive region of flow combustion. Between 310° and 350°C the normal alkane and alkene species increase at the expense of the oxygenated derivatives. Above 350°C very few oxygenated compounds are found, except acetaldehyde and certain peroxides.

Studies of the non-isothermal combustion were performed at six temperatures from 259°C to 455°C. Careful temperature measurements were accompanied with pressure increases as observances were made of discontinuities in the temperature as the combustion proceeded from one region to another. Analysis of products is followed at each inflection point or passage from one cool flame to another. At ignition the predominant nonoxygenated species is shown to be C_6H_6. The general trend is as indicated already. With increase in pressure at a constant initial temperature the oxygenated species decrease while the higher alkanes or aromatics increase in concentration. At each initial temperature the yield of products varies considerably in amount and type of product.

Some attempt was made to determine the effect of additives upon these non-isothermal reaction paths. Each additive was added in place of 2% of the initial fuel concentration. Induction periods were measured with and without additives.

One additive, *t*-butyl hydroperoxide did have a very significant effect upon the normal induction time to ignition. At −291°C the *t*-butyl hydroperoxide lowered induction period for the appearance of the first and second cool flames so much that static reaction condition in the vessel was not attainable.

The wide diversity of products formed in the oxidation of 2-methyl-pentane is greatly influenced by the temperature at which the reaction is conducted. The variety of products formed in the temperature range 250°–307°C is lower than outside of this temperature range. The radical responsible for attack upon the 2-methylpentane is probably OH in the 250°–307°C range.

$$RH+OH\cdot \rightarrow R\cdot +H_2 \text{ (Cool flame attack)}$$

At other temperatures, below 250°C or above 307°C, hydroperoxy or alkoxy radicals determine the chain propagating steps,

$$RH+R\dot{C}OOR \rightarrow RCOOHR+R\cdot \text{ (below 250°C)}$$

Further propagation of the chain occurs when the hydroperoxide degenerates to $\cdot OH$ and $R\dot{C}OR$ radicals, the OH reacting once again with an alkane molecule.

$$RCOOHR \rightarrow OH\cdot +R\dot{C}OR$$

$$R\dot{C}OR \rightarrow RC{=}O+RH$$

$$RH+OH\cdot \rightarrow R\cdot +H_2O$$

Within the cool flame one major contributing factor to the high peroxide concentration is the isomerization of the alkylperoxide radical itself.

$$ROO\cdot \rightarrow \cdot ROOH$$

The hydroperoxides themselves decompose by simple decomposition resulting in ring closure to yield a O-heterocycle and OH radical. Or, cleavage of the C–O bond to yield an alkene and $\cdot HO_2$ radical. Thirdly, the $\cdot ROOH$ may decompose by cleavage of the O–O bond followed by intramolecular transfer of hydrogen to yield a ketone and an OH radical. Fourth, simultaneous cleavage of an O–O and C–C bond to yield an alkene, ketone or O-heterocycle plus an $\cdot OH$ radical. Two more modes of decomposition involve the simultaneous breaking of one O–O bond and one or more C–C bonds to yield a variety of alkehydes, alkenes, unsaturated ketones, and alkyl radicals.

This great array of isomerization and decomposition reactions found in the cool flame region qualitatively can explain the origin of each compound found. It has been argued that the alkylperoxy reaction occurs on the walls of the vessel rather than in the gas phase. This question has been answered by observation of many of these products under low surface area, high pressure, and extremely short cool flame induction times.

At temperatures above that of cool-flame existence (307°C) oxygen is more likely to attack alkyl radicals by abstraction than addition.

$$R\cdot +O_2 \rightarrow R+\cdot HO_2$$

$$RH+\cdot HO_2 \rightarrow H_2O_2+R\cdot$$

$$R\cdot \rightarrow \text{cracked to lower hydrocarbons}$$

A study of the areas where maximum yields of different products occur suggests that each combustion region must in some way favor particular paths of isomerization or decomposition of the active alkylperoxide or hydroperoxide radicals. Thus it is pertinent to distinguish energetically the relative rate of H-abstraction as to whether it originates from the α or β or γ position of the molecule. α–H abstraction is seen to be more important in the second and third cool-flame region than in the low temperature or first cool-flame combustion zone. At temperatures too high for cool flame propagation intramolecular α–H atom transfer is the sole process. Similar demarcations can be applied to the rest of the isomerization processes.

The identity of each of the three cool flames analyzed here indicates that the oxidation or pyrolysis of a given specific group of products is responsible for the particular cool flame involved. Passage to the next cool flame will accompany a marked reduction in the concentration of the compounds responsible for the establishment of the first flame. In the case of 2-methylpentane the three cool flames (259–261°C, 261–275°C, and 275–307°C) are propagated mainly by alkylperoxy and alkylhydroperoxy branching reactions which in each case produce a series of intermediates leading to the establishment of the next cool-flame. Aldehydes also play a role in all the processes.

Finally, one stage ignition is probably due to H_2O_2 as a chain branching agent,

$$R\cdot + O_2 \rightarrow R + \cdot HO_2$$

$$RH + \cdot HO_2 \rightarrow R\cdot + H_2O_2$$

$$H_2O_2 + M \rightarrow 2\ OH\cdot + M$$

Large quantities of aromatics and C_2 hydrocarbons are produced.

Subject Headings: *Cool flames, of 2-methylpentane; Ignition, spontaneous, of 2-methylpentane; 2-methylpentane, oxidation of; Oxidation, of 2-methylpentane; Spontaneous ignition, of 2-methylpentane.*

Old Sec. V **P. Breisacher**

Hardy, W. A. and Linnett, J. W. (Cambridge University, Cambridge, England) "Mechanisms of Atom Recombination on Surfaces," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 167–179 (1967)

There are two mechanisms by which atom recombination might occur at surfaces. The first, often called the Hinshelwood mechanism, supposes that two atoms, absorbed separately, recombine on the surface and then desorb as a molecule. The second, often called the Rideal mechanism, supposes that an atom adsorbed on the surface recombines with an atom from the gas phase which strikes it. The Rideal mechanism more readily explains the very wide prevalence of first-order kinetics. In this paper, the various possible mechanisms are analyzed in general terms and it is found that certain general conclusions can be drawn.

In the first section dealing specifically with results, the behavior of insulators, in particular glass and silica, is considered. Such surfaces are more active after treatment with alkali, and usually surfaces of this kind show a greater activity the more alkaline their character. It has been concluded that oxygen and hydrogen atoms which are loosely attached to surface sites (perhaps valency saturated oxygen atoms) are the ones involved in recombination.

Perhaps the most interesting group of catalysts is that of semiconductor oxides. It is concluded that, for oxygen-atom recombination, *p*-type oxides are the most effective, indicating that the formation of O^- (or O^{2-}) on the surface is important. The possible significance of ligand field effects is discussed.

Finally metal and alloy surfaces are considered. With oxygen atoms, a surface layer of oxide is formed; this is sometimes more active than the simple oxide, indicating that the metal backing may have an effect. Hydrogen-atom recombination on palladium-gold alloys has been studied. In these cases, the presence of *d*-band vacancies in palladium seems to favor a higher activity. These holes are filled by adding gold, or by absorbed hydrogen.

In the final section, the need for more detailed knowledge of the surface is stressed.

Subject Headings: *Atom reactions, on surfaces; Catalysis, of atom recombination; Reaction of atoms, on surfaces; Surface reactions.*

Old Sec. V Authors' Abstract

Hoare, D. E., Li, Ting-Man, and Walsh, A. D. (Queen's College, Dundee, Scotland) "Cool Flames and Molecular Structure," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 879–887 (1967)

To show the effect of molecular structure upon the low temperature combustion of a variety of ketones and esters, the slow combustion, cool flame limits, and ignition limits have been studied. No cool flames or associated combustion characteristics were found with methyl acetate, methyl propionate, *t*-butyl acetate, or methyl-*t*-butyl ketone; however, cool flames and the associated combustion characteristics were found with ethyl acetate, *n*-propyl acetate, *i*-propyl acetate, methyl-*n*-butyrate, acetone, methyl ethyl ketone, di-ethyl ketone, methyl *n*-propyl ketone, and methyl *i*-propyl ketone.

The methods available for studying the relation between ease of "low-temperature" oxidation and fuel molecular structure include (1) the plotting of limiting hot-flame ignition curves, (2) the plotting of limiting cool flame ignition curves and (3) the plotting of the maximum rate of slow combustion (ρ_{max}) as a function of temperature at a fixed pressure below the minimum pressure of the cool flame boundary curve. All these methods have been used in this study.

Only 1:1 fuel-oxygen mixtures were used. Pressure limits were obtained for the occurrence of cool (and/or hot) flames within the temperature range 240° to 450°C. Total pressures up to 600 mm Hg were used. The occurrence of a cool flame and/or a hot flame was determined either by a direct observation through a thermally insulated slit in the furnace or by observation of a pressure pulse on the spiral gauge.

The cool-flame limit curves for the ketones and esters studied were plotted and from them the temperature [T(tip)], pressure [P(tip)] and the induction period [τ(tip)] were found for the tip of the cool-flame pressure-temperature boundary for each fuel.

TABLE 1.

The tips of the cool-flame-limit curves of ketones and esters.

Ketone	T(tip) (°C)	P(tip) (mm Hg)	τ(tip) (sec)	Ester	T(tip) (°C)	P(tip) (mm Hg)	τ(tip) (sec)
Acetone	330	380	25	Methyl acetate		no cool flame	
Methyl ethyl ketone	310	133	7500	Ethyl acetate	315	285	67
Di-ethyl ketone	310	78	29	Methyl propionate		no cool flame	
Methyl *n*-propyl ketone	310	88	133	*n*-Propyl acetate	320	110	12
Methyl *i*-propyl ketone	310	228	1500	Methyl *n*-butyrate	310	260	264
Methyl *t*-butyl ketone		no cool flame		*i*-Propyl acetate	310	270	65
				t-Butyl acetate		no cool flame	

It was found that methyl-*t*-butyl ketone, methyl acetate, methyl propionate, and *t*-butyl acetate did not yield cool flames. It might be supposed that these fuels would yield cool flames had it been possible to use pressures greater than 600 mm Hg. This would seem improbable because the $\log \rho_{\max}$ vs $1/T$ plot for these fuels shows no negative temperature coefficient region. A negative temperature coefficient region in the $\log \rho_{\max}$ vs $1/T$ plots was observed with all the other fuels.

Comparison with other work shows the results obtained fit in well with previous observations and the summary of results is shown in Table 1.

Several significant features are to be noticed in the table:

(1) Where cool flames are observed with the ketonic fuels, T(tip) is remarkably insensitive to fuel molecular structure; only acetone has T(tip) significantly different from 310°C. Similarly, where cool flames are observed with the esters, T(tip) is also remarkably insensitive to fuel molecular structure. T(tip) is to be associated with the interplay of chain branching and termination reactions. Its approximate constancy suggests that the processes concerned must be similar in over-all activation energy, whatever the fuel.

(2) The values of T(tip) differ only slightly from ketones to esters. This observation is the more remarkable since, among the ethers, although dimethyl, diethyl and di-*i*-propyl ethers each have in their cool-flame-limit diagrams a lobe with a T(tip) value around 300°C, the latter two also have a more prominent lobe with a T(tip) value considerably less than 300°C.

(3) Within either the ketone or the ester class, the P(tip)—in contrast to the T(tip)—values vary sensitively with fuel molecular structure. Thus, one notes the big effect of isomerism on the P(tip) values; ethyl acetate and methyl propionate, *n*-propyl ketone and methyl *i*-propyl ketone, supply examples. The usual effects of lengthening the hydrocarbon chain [lowering P(tip)] and branching the hydrocarbon chain [raising P(tip)] are evident.

(4) Insertion of an O atom into a ketone molecule to make a carboxyl group always causes a rise in P(tip). Table 1 gives six examples of this; there are no exceptions.

(5) Change of a CH_2 group (adjacent to a carbonyl group) to the isoelectronic

O atom always causes a big rise in P(tip). Table 1 gives three examples of this; there are no exceptions.

(6) The most striking feature of the data is the failure of methyl-*t*-butyl ketone among the ketones, and of the following esters, to yield any cool flames at all.

The methyl esters of formic, acetic, and propionic acid yield no cool flames; the ethyl esters (and the *n*-propyl esters of at least formic and acetic acids) produce cool flames. Although methyl formate, acetate, and propionate produce no cool flames, methyl *n*-butyrate produces cool flames. Although *n*-propyl and *i*-propyl acetate produce cool flames, *t*-butyl acetate produces no cool flames; although methyl *n*-propyl and methyl *i*-propyl ketones yield cool-flames, methyl *t*-butyl ketone produces no cool flames.

It is generally agreed that the oxidation of any particular fuel molecule (R—H) starts with the step.

$$X\cdot + R{-}H \rightarrow X{-}H + R\cdot \tag{1}$$

where X· is some free radical; R· is thus the original fuel molecule minus one H atom.

It is also generally agreed that the second essential step for low temperature combustion to occur is

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{2}$$

Step 2 has a considerable exothermicity. The peroxy radical produced may therefore be pictured as initially twisting, bending, and generally contorting vigorously. Isomerization, by intra-molecular transfer of an *H* atom to the free valency of the O_2 group, is therefore likely

$$RO_2\cdot \rightarrow R'\cdot OOH \tag{3}$$

R'· is thus the original fuel molecule minus two H atoms and possesses a free valency. Because of the latter, one step that may follow (3) is the addition of a second O_2 molecule.

$$R'\cdot OOH + O_2 \rightarrow (RO_4)\cdot \tag{4}$$

The exothermicity of (2) will make not only isomerization but also decomposition of $RO_2\cdot$ likely, so that (3) will compete with (5)

$$RO_2\cdot \rightarrow \text{molecules} + \text{radicals} \tag{5}$$

Addition of (5) to (1) and (2) will result either in a straight chain cycle or even, if the single radical produced is sufficiently inert, in chain ending. Similarly, the additional exothermicity of (4) will make decomposition of $(RO_4\cdot)$ particularly likely as will also the presence in $(RO_4\cdot)$ of an O–O single bond.

$$(RO_4\cdot) \rightarrow \text{molecules} + \text{two or more free radicals} \tag{6}$$

Eq. (6), unlike (5) is a branching reaction step.

The general scheme is therefore.

$$\begin{tikzcd}
& & & R'\cdot OOH \arrow[r, "(4)", "O_2"'] & \text{branching chain} \\
X\cdot \arrow[r, "(1)", "RH"'] & R\cdot \arrow[r, "(2)", "O_2"'] & RO_2\cdot \arrow[ur, "(3)", "\text{isomerization}"'] \arrow[dr, "(5)", "\text{decomposition}"'] & & \\
& & & \text{free radical} \arrow[r] & \text{straight chain.}
\end{tikzcd} \tag{7}$$

Many other reactions must complicate the full picture but in view of much evidence for the crucial importance of the isomerization step Walsh has suggested (7) represents a part of what is kinetically essential for the occurrence of the branching process known as "low" temperature combustion.

It should be noted that the branching scheme involves H abstraction from two different C atoms in the oxidizing fuel molecule. This happens in the case of the ketones. Since methyl *t*-butyl ketone does not give a cool flame while acetone and the others listed in Table 1 do give cool flames, it must be concluded that the crucial steps are not confined to one C atom but involve as would be expected from (7), H atoms on two C atoms.

Turning now to esters, it may be argued that since ethyl and *n*-propyl acetate yield cool flames, but *t*-butyl acetate does not, the presence of at least one H atom on the C atom that is α to the ethereal O atom is apparently essential for cool flame formation. Further, since the methyl esters of formic acetic and propionic acids do not yield cool flames but the ethyl esters of these acids and the propyl esters of formic and acetic acids do, the presence of a βC atom (probably bearing at least one H atom) directly linked to the C atom that is α to the ethereal O atom is also essential for cool-flame formation.

Whether an ester yields cool flames is therefore determined by whether the ester molecule contains two C atoms directly linked and each bearing at least one H atom. This is in agreement with the esters which do and do not produce cool flames. In addition it is worth noting that the failure of CH_4, HCHO, CH_3OH to yield cool flames, in contrast to the appearance of cool flames with C_2H_6, CH_3CHO, $(CH_3)_2CO$ and $(CH_3)_2O$ must provide strong evidence that one of the conditions for a cool flame to appear is the presence in the fuel molecule of at least two C atoms, each bearing at least one H atom. This provides strong evidence for a two center theory.

Subject Headings: *Cool flames, and molecular structures; Molecular structure, and cool flames.*

Old Sec. V G. L. Isles

Homann, K. H. and Wagner, H. Gg. (University of Göttingen, Göttingen, Germany) "Some New Aspects of the Mechanism of Carbon Formation in Premixed Flames," *Eleventh Symposium* (*International*) *on Combustion*, Pittsburgh, The Combustion Institute, 371–379 (1967)

Hydrocarbons of molecular masses up to 500 mass units have been sampled from the gas phase of carbon-forming flames of acetylene and benzene, premixed with oxygen burning at a pressure of 20 mm Hg. These hydrocarbons which originate from the burned gas some centimeters behind the oxidation zone are identical with those evaporating from soot samples when heated under high vacuum conditions in a mass spectrometer. They are mainly polycyclic aromatic hydrocarbons. Their concentration profiles in acetylene flames show that they are by-products rather than intermediates for carbon in this case. In benzene flames, these polycyclic aromates appear during the oxidation of the fuel so that their concentration is much larger in the region where solid carbon is formed.

In contrast to polycyclic aromates a great many other hydrocarbons, mainly those of molecular masses greater than 200 mass units, do not survive in the burned gas. Not yet being identified, they can be detected only in the gas phase close behind the oxidation zone, where carbon formation begins. Similar hydrocarbons can be evaporated from very "young" soot, sampled from the same region of the flame. These hydrocarbons which appear in the region of carbon nucleation are considered to be important intermediates or nuclei for carbon formation. The role of polyacetylenes and of polycyclic aromates as "building bricks" for active nuclei with radical character is discussed. The rate of carbon formation in acetylene-oxygen flames agrees with the amount of carbon gained by the addition of C_6H_2 and C_8H_2 to small carbon particles. The hydrogen content of the solid carbon, which has been determined as a function of the height in the flame, is also compatible with this mechanism.

Subject Headings: *Carbon formation, in flames; Flames premixed (see Premixed flames); Premixed flames, carbon formation in.*

Old Sec. V Authors' Abstract

Mayer, S. W., Schieler, L. (Aerospace Corporation, El Segundo, California) and **Johnston, H. S.** (University of California, Berkeley, California) "Computation of High-Temperature Rate Constants for Bimolecular Reactions of Combustion Products," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 837–844 (1967)

A procedure is presented for using available molecular data to compute the activation energies and rate constants of bimolecular transfer reactions for the halogen atoms. This computational method is also applied to calculating the kinetics for transfers of O, N, C, B, Be, and Al atoms bonded to univalent atoms. The procedure is based on modifications of the Johnston-Parr method of predicting kinetic data for hydrogen-atom transfer reactions. Potential energies of repulsion are calculated by using a reduced variable treatment of the Sato function. The procedure and results are also presented for computations of high-temperature rates of hydrogen-atom transfer reactions in which molecules containing a total of four atoms are involved. Computed rate constants are compared with experimental kinetic data when available, and agreement is generally satisfactory. Less than 0.1 minute of electronic-computer time per reaction is required to calculate the activation energy, vibrational parameters of the activated complex, rate constants at 25 temperatures (primarily in the 1000° to 4000°K range), and Arrhenius rate equation constants. Results are summarized for bimolecular atom-transfer reactions involving combustion, products such as HF, HCl, HBr, HI, CF, CCl, BF, BCl, BeCl, ClO, AlCl, CH, OH, NH, AlH, BH, BeH, CH_2, NH_2, BH_2, BeH_2, H_2O, HCO, HBO, HCN, AlOH, and NaOH.

Subject Headings: *Bimolecular rate constant, computation of; Computation, of rate constants; Rate constants, computation of.*

Old Sec. V Authors' Abstract

Jenkins, D. R. and Yumlu, V. S. ("Shell" Research Ltd., Thornton Research Centre, Chester, England) and **Spalding, D. B.** (Imperial College, London, England) "Combustion of Hydrogen and Oxygen in a Steady-Flow Adiabatic Stirred Reactor," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 779–790 (1967)

The stirred reactor is considered to be a unique method of determining currently unknown reaction-kinetic constants. The experimental data are obtained quickly in the numbers required for subsequent statistical analysis. Furthermore, algebraic rather than differential equations describe the system, and the transport properties of the mixture or its components are not required.

This article forms the first report of a long-term project at Thornton Research Centre. It describes the apparatus developed for the work, reports some measurements made on hydrogen–oxygen-steam mixtures, and presents some of the preliminary conclusions concerning the more important rate constants of that system.

From a theoretical standpoint, it is possible to formulate equations to describe conservation of mass and energy, reaction rates, rate constants, partial pressures, and the relations of enthalpy with absolute temperature. The resulting equations are nonlinear, and special procedures have been adopted to solve them. The temperature and composition of the exhaust gases can therefore be predicted when the reaction-kinetic and thermodynamic data together with the experimental conditions are given. Reaction-kinetic data were obtained from a literature survey and are subsequently termed standard values because better values eventually obtain from systematic adjustments to the analysis in bringing the calculated results closer to the measured values of temperature and composition. Reactions involving HO_2, H_2O_2, and O_3 have been considered to be unimportant in the present experiments which are confined to the temperature range 1330° to 1560°K. Nine possible reactions have been considered, and it is shown that six of these are important and their rate constants can be checked experimentally.

The reactor developed for the project is a quartz hemisphere, $\frac{1}{2}$ in. radius, joined to a truncated cone. The input gases are injected into the reactor by means of a nozzle, and the burnt gases leave through the annular space around the nozzle, approximately $\frac{1}{8}$ in. wide. Both the input gas temperature and the temperature of the gas in the reactor are measured by thermocouples. The input gases are heated by the exit gases passing around the outside of the nozzle, and the inlet temperature can be controlled at different levels by the amount of cooling applied to the nozzle and by heaters in the gas supply lines. All gas flows are metered to an accuracy better than 0.5% before mixing in a swirl chamber, and the hydrogen/oxygen ratio is further controlled by a calibrated katharometer.

For each experiment, the reactor is made adiabatic by adjusting the power supplied to its surrounding heating coils until no temperature gradient, as indicated by thermocouples, exists between the reactor wall and the coils. A correction for radiation losses to the surroundings through the annular gap in the reactor inlet is applied to the enthalpy of the gas.

Preliminary experiments indicated that input gas velocities greater than 100 m/s and different surface-to-volume ratios had no effect on the temperature-enthalpy curve, implying that the gas mixing rate and the quartz surface had no effect on the gas phase reactions. The reactor temperature was uniform over 80–85% of the reactor volume, and the effective or ideal reactor temperature is taken as the mean of the maximum temperature and the value at the end of the reactor opposite the nozzle. The maximum difference in these two latter temperatures was 40°C which could create a maximum error of 20% in the value of the rate constant.

The maximum difference between the observed and predicted temperatures amounted to 45% of the difference between the observed temperature and the equilibrium temperature for a given inlet condition. When the adjusted values of the rate constants were used, the ratio of the differences of temperature referred to previously was reduced to 2%. Future work will investigate the combustion of hydrogen at lower temperatures, check whether the reactions of HO_2, H_2O_2, and O_3 are really important, and then study the combustion of mixtures of carbon monoxide and hydrogen.

Subject Headings: ***Combustion, of hydrogen and oxygen; Hydrogen, combustion of; Oxygen, combustion of; Stirred reactor, for hydrogen and oxygen.***

Old Sec. V **P. L. Start**

Murty, K. A. and Blackshear, P. L., Jr. (University of Minnesota, Minneapolis, Minnesota) "Pyrolysis Effects in the Transfer of Heat and Mass in Thermally Decomposing Organic Solids," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 517–523 (1967)

The authors of this paper present measurements for local temperatures and densities in a pyrolyzing cylindrical specimen of α-cellulose and use these to (1) estimate the heat of reaction throughout the sample, (2) to correlate density changes with the heat of reaction to obtain volumetric heat sources or sinks, and (3) to map the regions in which various processes are important. For many details of the experimental technique and the analysis of the kinetics, which are not discussed in this report, reference is made to a previous paper.[1]

This report deals with the pyrolysis of a cylinder with a 1.750 cm diameter, an initial density of 0.605 gm per cc, and a char density of 0.120 gm per cc. The experiment itself was continued for 16.0 min, by which time the char extended inward for 40% of the radius. The remainder of the cylinder was, by that time, less than twice as dense as the char, approximately a third the original density. The surface first exhibited a fully established char at 10 min.

By assuming that the rate of change in density was equal to the rate of efflux of pyrolysis products, i.e., that the gases formed passed instantaneously through the char layer, the mass flow rate was determined. A slight maximum in flow rate occurred at four minutes near the surface probably due to the flow of moisture vapors. The major maximum occurred at 10 min, just as the surface became fully charred, with the flow rate falling rapidly from that time on. Also at 10 min the surface temperature began to drop rapidly, reaching a value of 440°C at 12 min and remaining constant throughout the remaining four minutes. While not explicitely stated, the surface temperature must have been rising slowly throughout the first 10 min to the indicated maximum of 600°C at 10 min.

Utilizing the measured densities and temperatures an energy conservation equation was set up involving conduction, convection, chemical reaction, and change of temperature. With an assumed knowledge of thermal conductivities and specific heats of gases and solids and an assumption that they remained constant throughout the process, the authors determined the chemical heat release. This heat release, of course, included all unidentified physical or chemical processes involving evolution or exchange of energy. For most conditions of reaction occurring in the interior, the heat of pyrolysis was negative. Only for reactions which occurred at temperatures above 350° to 400°C was the heat positive. Near the surface once a temperature of 350°C was exceeded, a strongly exothermic reaction was indicated. The authors explained this latter point as being due to either cracking reactions of the outflowing pyrolysis products or an oxidation process in which inward diffusing oxygen reacted with outflowing cracked products. The latter explanation seems more reasonable to this reviewer.

A differential thermal analysis of the data indicated an endothermic well near 300°C. Such wells have been attributed in the past to the unzipping process of the cellulose molecules.

In estimating the apparent kinetic constants the activation energy for an assumed one-step, first-order reaction was found to vary from 22 kcal/mole near the surface to 13 kcal/mole near the center. The variation in the frequency factor was stated to be much more unsystematic. Clearly, as the authors state, "because the kinetics are so affected by incubation and vapor migration, the temperature-time history will not be really useful in predicting pyrolysis rates until the process is better understood."

Reference

1. Murty, K. A., and Blackshear, P. L., Jr.: Paper 19 Western States Section, The Combustion Institute, Denver Colorado; Proposed for publication in the "Pyrodynamics."

Subject Headings: *Kinetics, of pyrolysis; Organic solids, pyrolysis of; Pyrolysis, of organic solids.*

Old Sec. II F. Falk

Wilson, W. E. and Westenberg, A. A. (Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland) "Study of the Reaction of Hydroxyl Radical with Methane by Quantitative ESR," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 1143–1150 (1967)

The study referred to in the title was conducted in a flow tube at pressures of 0.7 to 1.3 torr. A microwave discharge cavity surrounding the flow tube was used to dissociate H_2. The H-atoms thus produced were reacted with NO_2 downstream of the discharge to produce OH radicals, which in turn were allowed to react with one of several hydrocarbons, the most extensively studied of which was methane. The concentrations of H and OH along the tube were quantitatively monitored by an electron spin resonance (ESR) spectrometer with a movable cavity. After the appropriate calibrations and corrections, a rate constant for the disappearance of OH in a large excess of CH_4 was determined. The measurements were straight-forward and unambiguous. The problem, as in a great many other such studies, is to ascertain to what mechanism the measured quantities are related.

In the absence of CH_4, the decay of OH down the flow tube occurs via

$$OH+OH\rightarrow H_2O+O \qquad (2)^*$$

and

$$O+OH\rightarrow O_2+H \qquad (3)$$

Since Reaction (3) is faster than Reaction (2), a steady-state O-atom concentration is established. The mechanisms for reaction of CH_4 under the various conditions of these experiments were assumed to be comprised of the appropriate reactions within the following list:

$$CH_4+OH\rightarrow H_2O+CH_3 \qquad (6)$$

$$CH_3+OH\rightarrow H_2CO+H_2 \qquad (7)$$

$$CH_3+O_2\rightarrow H_2CO+OH \qquad (8)$$

$$H_2CO+OH\rightarrow HCO+H_2O \qquad (9)$$

$$H_2CO+H\rightarrow HCO+H_2 \qquad (10)$$

$$HCO+OH\rightarrow CO+H_2O \qquad (11)$$

$$HCO+H\rightarrow CO+H_2 \qquad (12)$$

Under conditions of low $[H]_0$ and $[O]_0$ obtained by titrating the H-atom stream with NO_2 to the "end-point" and with only that O_2 produced in Reaction 3, the limiting mechanism consists of Reactions (6), (7), (9), and (11). Thus, four OH radicals are consumed for each CH_4 reacted. If all the reactions subsequent to Reactions (3) and (6) are fast the OH decay equation is

$$-d[OH]/dt=3k_2[OH]^2+k_{ESR}[CH_4][OH]$$

in which k_{ESR} is the experimentally determined OH decay rate constant due to CH_4 and is equal to nk_6 where n is the number of OH radicals consumed by each CH_4—in this case, four. k_2 had been determined by Dixon-Lewis, Wilson, and Westenberg[1] in a similar study in the same apparatus to be $1.55\pm0.12\times10^{12}$ cm^3 mole^{-1} sec^{-1}. Solution of the above equation gives

$$\ln\frac{1+k_{ESR}[CH_4]y/3k_2[OH]_0}{1+k_{ESR}[CH_4]/3k_2[OH]_0}=k_{ESR}[CH_4](z/v)$$

where $y=[OH]_0/[OH]$, z is the distance down the flow tube, and v the linear flow velocity. The equation was solved for k_{ESR} by iteration.

The predominant reactions in the presence of large H-atom concentrations, i.e., when $[H]_0/[OH]_0=15$ to 20, are (6), (7), (10), and (12). This leads to a value $n=2$. Similarly when $[O_2]_0/[OH]_0$ is made high ($\sim$30) through addition of O_2, Reactions (6), (8), (9), and (11) dominate, again yielding $n=2$ since, despite the fact that four OH radicals are consumed, Reaction (8) regenerates one OH. All of the reactions (6–12) participate to some extent under all conditions but the

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* The author's number sequence for reactions has been retained throughout.

assumptions above lead to limiting values for k_6 at 300°K of $6.5 \pm 1.5 \times 10^9$ cm^3 mole^{-1} sec^{-1}.

A check on the rate constant determined above was obtained by a mass spectrometric determination of the amount of CH_4 reacted far down-stream of the CH_4 injection point. The products, after analysis, were converted to the equivalent amount of CH_4 reacted and compared to the change in [OH] over the same time (flow) interval. Thus, $n = \Delta[OH]/\Delta[CH_4]$ and $k_6 = k_{ESR}/n$. This technique is more approximate than the point-to-point analyses by ESR but nevertheless, in most cases, yielded values of k_6 within the previously established limits.

There are several values for k_6 in the literature, the most recent of which is one determined by Greiner[2] via kinetic spectroscopy. Greiner's measurements give $5.30 \pm 0.2 \times 10^9$ cm^3 mole^{-1} sec^{-1}, well within the limits established in this work. Nearly all of the other available values for k_6 are reported in terms of the ratio k_6/k_5 where Reaction (5) is

$$CO + OH \rightarrow CO_2 + H \qquad (5)$$

When the room temperature value of k_6/k_5 obtained via the technique employed in this study* is put on an Arrhenius plot with the prior data from the literature a good straight line is obtained intersecting points from H_2/O_2 inhibition,[3] flame studies,[4] and this work. Slow oxidation studies[5,6,7] yield values which fall below the line by roughly a factor of three but which, if taken by themselves would give about the same activation energy. The authors of this paper have reviewed this work quite thoroughly and give what appear to be good reasons for the observed discrepancies. The best fit of the data gives the following expression for k_6:

$$k_6 = 6.5 \pm 1.5 \times 10^9 \exp[(5000 \pm 600)/R][(1/300) - T^{-1}]$$

Measurements of the kinetics of OH attack on C_2 hydrocarbons were also made but in these cases only the over-all rate constant, k_{ESR} could be determined. Not enough is known of the mechanisms of attack to ascertain the number of OH radicals consumed by each molecule of hydrocarbon. Moreover, reactions of H-atoms with C_2H_2 or C_2H_4 may be fast enough to further obscure the results.

References

1. Dixon-Lewis, G., Wilson, W. E., and Westenberg, A. A.: J. Chem. Phys. *44*, 2877 (1966).
2. Greiner, N. R.: J. Chem. Phys. *46*, 2795 (1967).
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7. Blundell, R. V., Cook, W. G. A., Hoare, D. E., and Milne, G. S.: *Tenth Symposium (International) on Combustion*, p. 445, The Combustion Institute, 1965.

Subject Headings: ***C_2 hydrocarbon, reaction with hydroxyl radical; ESR studies, of hydroxyl radical reactions; Hydroxyl radical, reactions of; Methane reaction, with hydroxyl radical.***

Old Sec. V **W. J. Miller**

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* k_5 was taken from Reference 1.

I. Physical Aspects of Fires

Batiyevskiy, A. L., Mosse, A. L., and Tarasevich, L. I. "Convective Heat and Mass Transfer in the Combustion of Chemically Active Substances in the Boundary Layer on a Porous Surface," *Akademiya nauk Belorusskoy SSR*, 168–175 (minsk, 1965) Translation by B. Poplawski—ATD Report 66-26 (17 March 1966)

In several applications, particularly in high speed aerodynamics, heat loads of the order of 10^7 kcal/m^2 hr (10 Btu/inch^2 sec) or higher must be accommodated. In recent years special consideration has been given to the possibility of protecting surfaces against such a heat load by injecting a coolant through the surface, which is made porous for this purpose. The coolant may or may not react with the main stream.

Several attempts to analyze the shear, heat and mass transfer under these conditions have been made. Most of the relevant papers are concerned with laminar flow, but there are several authors who consider the problem involving turbulent flow.

The governing differential equations may be written as follows:

continuity equation

$$(\partial/\partial x)(\bar{\rho}\bar{u})+(\partial/\partial y)(\bar{\rho}\bar{v}+\bar{\rho}'\bar{v}')=0$$

momentum equation

$$\bar{\rho}\bar{u}(\partial\bar{u}/\partial x)+(\bar{\rho}\bar{v}+\bar{\rho}'\bar{v}')(\partial\bar{u}/\partial y)=(\partial/\partial y)[E_v(\partial\bar{u}/\partial y)]-(\partial p/\partial x)$$

diffusion equation

$$\bar{\rho}\bar{u}(\partial\bar{C}_i/\partial x)+(\bar{\rho}\bar{v}+\bar{\rho}'\bar{v}')(\partial\bar{C}_i/dy)=(\partial/\partial y)[\bar{\rho}E_{D,i}(\partial\bar{C}_i/\partial y)]+\bar{w}_i$$

energy equation

$$\begin{aligned}\bar{\rho}\bar{u}(\partial/\partial x)(\bar{H}+\tfrac{1}{2}\bar{u}^2)&+(\bar{\rho}\bar{v}+\bar{\rho}'\bar{v}')(\partial/\partial y)(\bar{H}+\tfrac{1}{2}\bar{u}^2)\\ &=(\partial/\partial y)[E_\lambda\sum_i(\partial/\partial y)(\bar{h}_i\bar{C}_i+\tfrac{1}{2}\bar{u}^2)+\sum_i\bar{\rho}E_{D,i}(1-\mathrm{Le}_\tau^{-1})\\ &\quad\times\bar{h}_i(\partial C_i/\partial y)-E_\lambda(1-\mathrm{Pr}_\tau^{-1})(\partial/\partial y)(\tfrac{1}{2}\bar{u}^2)]\end{aligned}$$

In these equations each term has been averaged in respect to time, and E_v, E_D and E_λ designate the total exchange coefficients for momentum, mass, and heat transfer, respectively. Similarly Le_τ and Pr_τ are the Lewis and Prandtl numbers based on the total exchange coefficients. A particular simplification is obtained if these two numbers are assumed to be equal.

Approaches to the solution by various authors are then discussed with emphasis on the special assumptions made in each case.

Special attention is given to the experimental results by Kulgein[1] who conducted one of the few experimental studies of the problem. In these experiments a porous cylinder 1.5 in. in diameter was exposed to a flow of air, the velocity being in the direction of the cylinder axis. The upstream end of the cylinder was fitted with a rounded nose piece. During operation methane was injected through the pores of the cylinder. The principal reaction is given by the equation

$$CH_4+2H_2O\rightarrow CO_2+2H_2O$$

The concentration distributions for CH_4, CO_2 and O_2 were measured and the corresponding graphs are reproduced. In addition the coefficients for the transfer of mass (j_D) and heat (C_H), and the friction coefficient (C_F) were measured as a function of Reynolds number (based on the length along the cylinder) and the results are reproduced in graphical form. The three coefficients show similar trends and may be estimated within an accuracy of ±30% by the relation

$$\tfrac{1}{2}C_F = C_H = j_D = 0.038\ \mathrm{Re}_x^{-0.2}.$$

No direct comparisons between the theoretical and experimental results are given. The need for further experimental work is stressed.

Reference

1. Kulgein, N. G.: Journal of Fluid Mechanics *12*, 3, 1962.

Subject Headings: ***Boundary layer combustion; Heat transfer, in boundary layer combustion; Mass transfer, in boundary layer combustion.***

Old Sec. III **R. H. Sabersky**

Becker, H. A., Hottel, H. C., and Williams, G. C. (Massachusetts Institute of Technology, Cambridge, Massachusetts) "Concentration Fluctuations in Ducted Turbulent Jets," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 791–798 (1967)

This paper presents experimental studies of furnace mixing patterns which are simulated by a cold jet of oilfog-marked air issuing axially into a cylindrical duct fed by a uniform stream of clean air. The duct was a transparent plexiglass cylinder 125 cm long and 19.7 cm inside diameter. The jet source was a nozzle of 0.635 cm throat diameter and 2.41 cm upstream inside diameter. The surrounding air entering the duct was ambient air drawn in by the nozzle's jet. The rate of surrounding air flow was limited by sieves and perforated plates fitted over the duct inlet. A rounded entry section was provided, with the duct outlet opening abruptly to the atmosphere. Experiments were conducted at a nozzle Reynolds number of 54,000.

Oilfog droplets were used to trace the flow patterns of the air from the jet nozzle. The oilfog droplets were small enough to follow the turbulent velocity fluctuations faithfully. A scattered light technique was employed to measure the oilfog particle location. Since the diffusivity of fog droplets in air is 5 orders of magnitude less than the diffusivity of air in air, care must be taken to assure the fog particles are indeed indicative of air motion. In this experiment the use of small control volumes, ranging from 0.5 to 2 mm, permitted accurate measurement of the mean oilfog concentration.

The total mean-square fluctuation in concentration appropriate to gas–gas jet mixing was effectively measured even though the molecular aspect of the mixing process was not simulated.

A single parameter, the Craya-Curtet number (C_t) governs the flow and mixing patterns when the ratio of the duct and nozzle diameters is large, the nozzle Reynolds number is large, and the nozzle Mach number is small. These conditions were all fulfilled in the experiment. The Craya-Curtet number is defined as

$$C_t = U_k / (U_d^2 - \tfrac{1}{2} U_k^2)^{1/2}$$

where U_k is the kinematic-mean velocity of streams entering a confined jet system and U_d is the dynamic-mean velocity of streams entering the confined jet system. U_d is that uniform entering velocity which produces a force equal to the excess of the true stream thrust at the jet area over the stagnation pressure-area force of the induced stream.

Since recirculation is virtually absent at Craya-Curtet numbers above 0.65, the concentration fluctuation intensity field of the ducted jet of $C_t > 0.65$, up to the point where the jet reaches the duct wall, is negligibly different from that of a free jet. Data for a value of $C_t = 0.673$ show that the fluctuation intensity profile becomes nearly self-preserving in shape about 50 nozzle radii downstream of the nozzle mouth. For full self-preservation the ratio of fluctuation to nozzle flow concentration at the centerline is 0.21, similar to the value of 0.22 obtained for a free jet.

At Craya-Curtet numbers of 0.345, 0.212 and 0.140 recirculation is clearly evident. At the lowest C_t number the fluctuation intensity is everywhere as high as at the jet core, from recirculated fluid.

Centerline concentration fluctuation intensity is a function of axial position and C_t. For regimes with recirculation, the decay of the intensity with increasing distance from the nozzle begins roughly at the leading edge of the recirculation eddy; beyond this point the jet receives an increasing proportion of its entrainment fluid by recirculation. The decay process is virtually exponential in the recirculatory zone: at C_t values of 0.14 and 0.212 the fluctuation intensity decays 50% per 1.4 duct radii increase in distance from the nozzle. When fluctuation intensity is scaled to the excess of mean concentration over its value in the free stream a different result is seen. The excess concentration decays toward zero with axial distance from the nozzle exit. A rapid increase in fluctuation intensity divided by the excess of mean over free stream concentration with distance from the nozzle results from the nonuniform composition of the entrainment fluid in zones of recirculation. The free stream there fluctuates between fresh secondary fluid from upstream and recirculated jet fluid from downstream.

The concentration fluctuation intensity is nearly radially uniform in the free stream and varies only in the axial direction. This variation is a function of C_t. The fluctuations at any axial position result from surviving turbulent fluctuations in the recirculated jet fluid and the intermittency associated (in the free stream) with the alternating presence of fresh secondary feed and recirculating jet fluid. The greater part of the mean-square fluctuation is accounted for by the intermittency term.

Data are shown on the one-dimensional spectrum of concentration fluctuations at a particular axial position for C_t with little recirculation.

Lateral correlation coefficients were measured for conditions of little or no recirculation. The following observations were derived from these measurements:

1. The lateral correlations are similar at small separation distances.
2. The lateral correlations are strongly negative at large separation distances, while the longitudinal correlation is always positive.

3. The lateral scale of the concentration fluctuations is smaller than the longitudinal scale.
4. Symmetrical correlation about the jet centerline is the smallest lateral correlation at all separation distances.

Subject Headings: *Concentration fluctuations, in ducted jets; Jets, ducted concentration fluctuations in; Turbulence, and concentration fluctuations.*

Old Sec. V **A. E. Noreen**

Chigier, N. A.* and Chervinsky, A. (Israel Institute of Technology, Haifa, Israel) "Aerodynamic Study of Turbulent Burning Free Jets with Swirl," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 489–499 (1967)

A series of turbulent swirling free flames studied both theoretically and experimentally are described. In the experiments the burner was designed in such a way that gaseous fuel and air were premixed and fed into the burner axially; fresh air was supplied tangentially through four slots. The degree of swirl was varied by varying independently the axial and tangential flow rates of air. The fuel was an evaporated petroleum gas (51% propane, 34% butane, 15% ethane). The swirling jets issued from a round orifice with exit velocities of the order of 60 m/sec. No visible flame existed near the burner exit, and it is only at some 20 cm from the orifice that the velocity magnitudes had been sufficiently reduced by entrainment to allow an annular flame front to be stabilized there. For a distance of 150 cm the flame was unconfined and air was entrained from the surroundings. Downstream of the free-flame region the combustion gases entered a cylindrical exhaust chamber and after passing through an ejector were exhausted to the atmosphere.

Mass flow rates of the axial air, tangential air, and gas were measured with sharp-edged orifice plates. Measurements of the time-mean values of velocity and static pressure were made with a 5-hole hemispherical water-cooled inpact probe. Temperature was measured with a platinum/platinum rhodium thermocouple and with the aid of the velocity measurements, corrections were made for radiation losses as recommended by Dr. Fristrom.[1]

The measurements of radial distributions of velocity and temperature were made for three different degrees of swirl at seven axial stations out to 120 cm from the burner exit. The radial distributions of axial velocity are found to be of Gaussian profile. The radial distributions of swirl velocity have the form of a combined vortex with an almost linear inner region corresponding to free vortex flow. The temperature distributions show that the maximum temperature occurs in the reaction zone, the temperature is lower in the core of the jet, and decreases rapidly outside the flame. Reasonably good similarity is found for the profiles of axial and swirl velocity and only in the outer region of the jet for the temperature profiles. The large effect of temperature changes in the jet causes a slower decay of velocities than found previously in the case of a cold swirling jet.

From the flame stabilization it was observed that the turbulent burning velocity

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and the velocity gradient in the outer region of the jet where the flame was stabilized was 250 sec.^{-1}

In the theoretical analysis the turbulent equations of motion, energy, and state have been integrated. With the assumption of similarity, theoretical expressions are obtained for the decay of the maximum of axial velocity, tangential velocity, and temperature along the axis of the jet. The theoretical results match the experimental data fairly well. However, one thing that disturbs the reviewer very much in this theoretical treatment is that the authors completely ignored the term of combustion energy in the energy equation. Since the missing term is very important in studying the combustion problem, it is rather surprising that the theoretical results still match the experimental data.

In the Comments on this paper one point may be briefly mentioned here for better understanding the difference between the fire whirl and the swirling jet flame. Dr. N. A. Chigier pointed out that the experiments of fire whirls carried out by Dr. Emmons and Dr. Ying[2] had shown that the introduction of swirl to the surrounding atmosphere led to a large increase in flame length and a reduction in the rate of entrainment. On the other hand in their work, they found that the introduction of a swirling motion to the air supply led to a reduction in the flame length and an increase in the rate of entrainment. To explain these contradictory effects, the reviewer believes that Dr. H. W. Emmons gave the best explanation. He said "The dominating difference is the difference in radial stability of the two cases. The whirl has a free vortex surrounding a rotating core. The angular momentum has a positive or zero radial gradient everywhere. The swirling jet on the other hand, has stationary air outside of the jet. Thus, at the jet boundary there is a strong negative angular momentum radial gradient. The jet boundary is therefore unstable." In addition, the reviewer feels that the different effects in the two experiments are partially due to the fuel supply. In Dr. Emmons' and Dr. Ying's experiments, liquid fuel-acetone was used as the fuel which was kept at a constant level. The burning rate was controlled entirely by the fire whirl. The evaporating rate of acetone increases with the circulation strength. On the other hand, in this paper the fuel was in a gaseous form and it was controlled by a metering system. The circulation strength could not affect the amount of fuel supplied into the flame.

References

1. Fristrom, R. M.: "Experimental Techniques for the Study of Flame Structure," *Report No. 300, Applied Physics Lab., The John Hopkins University*, Jan., 1963.
2. Emmons, H. W., and Ying, S. J.: "The Fire Whirl," *Eleventh Symposium (International) on Combustion*, pp. 475–488, The Combustion Institute, 1967.

Subject Headings: *Free burning jets, with swirl; Jets, burning of; Swirling jets, with flame; Turbulent flames.*

Old Sec. V S. J. Ying

Eisenklam, P., Arunachalam, S. A., and Weston, J. A. (Imperial College, London, England) "Evaporation Rates and Drag Resistance of Burning Drops," *Eleventh Symposium (International) on Combustion,* Pittsburgh, The Combustion Institute, 715–728 (1967)

An experimental study has been made of the mass-transfer rates and drag coefficients for evaporating and burning spherical drops falling freely in air atmospheres at temperatures of up to 1000°C and burning drops in pure oxygen at 20°C. The liquids studied were methyl alcohol, ethyl alcohol, benzene, heptane, pentane, and water. The drops were between 2 mm and 25 μ in diameter, and the Reynolds number range was between 0.01 and 400 based on the properties of the undisturbed atmosphere.

The chamber for the high temperature studies was 18 in. long with a $2\frac{1}{2}$ in. by 2 in. cross section; it had two opposing quartz-glass windows 12 in. by $1\frac{1}{4}$ in. The chamber for combustion in oxygen was 3 ft long with a 3 in. by 4 in. cross section and two opposing glass windows. Single falling drops were photographed repeatedly at an accurately measured rate with the use of intermittant illumination and a moving-plate camera. The diameter and the position of each drop were measured from the photographs. Thus the mass-transfer rate (i.e., the evaporating rate or burning rate of the drop) and the drop velocity and acceleration were determined as a function of time. The maximum acceleration experienced by a drop was 600 cm/sec², a value small enough to insure negligible influence on drag and mass transfer.

The following dimensionless parameters based on mean physical properties for the system were employed in the correlations of the data:

Nusselt number:

$$\mathrm{Nu}^* = -(\rho_L L/4k\Delta T)(dD^2/dt)$$

Drag coefficient:

$$C_d^* = \tfrac{4}{3}(\rho_L/\rho)\,\frac{D\{g[1-(\rho/\rho_L)]-a\}}{V_\infty^2}$$

Reynolds number:

$$\mathrm{Re} = V_\infty D/\nu$$

Transfer number:

$$B = c\Delta T/L \qquad \text{(for evaporation)}$$

$$B = \frac{[c\Delta T + m_{O_2}(H/S)]}{L} \qquad \text{(for combustion)}$$

where D = the drop diameter at time t,
V_∞ = the velocity of the falling drop at time t,
a = the acceleration of the drop at time t,
g = the acceleration due to gravity,
m_{O2} = the oxygen concentration in the surrounding atmosphere,
H = the heat of combustion of the fuel,
S = the stoichiometric ratio of O_2,
ΔT = the difference between the drop surface temperature T_d (wet bulb temperature in the case of evaporation; boiling point in the case of combustion) and the temperature T_s of the surrounding atmosphere,

L = the latent heat of evaporation of the liquid at T_d,
ρ_L = the density of the liquid at T_d,
k = the mean thermal conductivity (gas field),
ν = the mean kinematic viscosity (gas field),
c = the mean specific heat (gas field),
ρ = the mean density (gas field).

For evaporating drops the mean values of k, ν, c, and ρ were taken as the arithmetic mean of the vapor at T_d and the surrounding atmosphere at T_s. For burning drops the mean k was the arithmetic mean of vapor at T_d and surrounding atmosphere at the adiabatic flame temperature T_F, the mean c was the arithmetic mean of the surrounding atmosphere at temperatures T_d and T_s, and both ν and ρ were taken at the mean of the vapor at T_d, the surrounding atmosphere at T_F, and the surrounding atmosphere at T_s, weighted in the proportion 1:2:1.

The mass-transfer data for heptane drops (diameter 25–500 μ) for both evaporation and burning in air are reported in a plot of Nu* vs Re. The family of curves obtained for evaporation in air at temperatures 200°, 400°, and 600°C ($B=0.68$, 1.71, 3.00, respectively) and the two curves obtained for combustion in air at 800° and 1000°C ($B=11.65$, 12.30, respectively) all fall below the curve for heat transfer without mass transfer ($B=0$) where the standard Nusselt number is $\mathrm{Nu}=2+0.63\ \mathrm{Re}^{1/2}$. The magnitude of the difference between the standard Nusselt number Nu and the Nusselt number with mass transfer Nu* increases with increase in B.

Three theories are discussed relative to the problem of evaporation and combustion of drops. The following groups emerge:

$\mathrm{Nu}^*[B/\ln(1+B)]$ from the stagnant film theory,

$\mathrm{Nu}^*(1+B)$ from the boundary layer theory,

and

$\mathrm{Nu}^*(2+B)-4$ from the slow viscous-flow theory.

The applicability of each theory was tested by plotting the relevant group vs Re. For both evaporating and burning drops, the group $\mathrm{Nu}^*(1+B)$ was considered to correlate the results best.

For the evaporation of fuel drops (in air at temperatures 200°–600°C) and water drops (in air at temperatures 200°–1000°C), the data can be represented by $\mathrm{Nu}^*(1+B)=2+1.6\ \mathrm{Re}^{1/2}$. The numeral 2 is included to represent the condition of the stationary sphere under heat transfer by conduction and no mass transfer (i.e., when $B=0$ and $\mathrm{Re}=0$). The ranges of Reynolds numbers and transfer numbers (both based on mean properties) are Re: 0.02–20 and B: 0.092–3.00.

In the burning tests two types of flames were noted: side flames and envelope flames. The data for envelope flames are more reproducible; they are represented by the following: $\mathrm{Nu}^*(1+B)=4.9\ \mathrm{Re}^{0.4}$ ($\pm 18\%$). Here the ranges of Reynolds numbers and transfer numbers (both based on mean properties) are Re: 0.1–3 and B: 3.52–12.30. All of the fuels were burned in air at 800°C; two, ethyl alcohol and heptane, were also tested at 1000°C. Owing to the scatter of the data for burning drops, extrapolation is not recommended.

The effect of mass transfer on the drag coefficient was considered in an analagous manner. Again the boundary layer theory was applied successfully; i.e., $C_d^*(1+B)$ plotted vs Re produced rather good correlations for both evaporating and burning drops in air. Both sets of data fall astride the standard curve for the drag coefficient C_d for spheres in steady flow under non-evaporating conditions ($B=0$). These drag data are companions to the mass transfer data discussed above; hence, the liquids, temperatures, and ranges of Re and B are the same. In addition, however, drag data were obtained for heptane and pentane drops burning in pure oxygen at 20°C ($B=36$). The drag coefficients found do not correlate with those obtained for burning in air; the points fall considerably below the standard curve (Re range: 2–10).

The slow viscous-flow theory is outlined, yielding both the mass transfer rate $\dot{m}^*$ and the drag coefficient C_d^* as a function of Re and B:

$$C_d^*=24/\mathrm{Re}\{[(2+B)/2+\tfrac{3}{4}B-\tfrac{3}{16}\mathrm{Re}(2+B)]-\tfrac{1}{3}B[(4+\mathrm{Re}/(2+B)]\}$$

$$\dot{m}^*=-\pi D\mu B[(4+\mathrm{Re})/(2+B)]$$

where μ is the absolute viscosity. This theory is applicable only when the Re is low ($\mathrm{Re}<1$). The equation for $\dot{m}^*$ was utilized in developing the group $[\mathrm{Nu}^*(2+B)-4]$ mentioned above.

The drag coefficient C_d^* can be represented generally as follows: $C_d^*=C_d'^*-C_d''^*$, where $C_d'^*$ is the coefficient due to forces on an enclosing control surface far from the drop and $C_d''^*$ is the coefficient due to the vapor momentum leaving the control surface. In the case of slow viscous flow it is readily shown that C_d^* decreases with increase in B and that $C_d'^*$ increases comparatively slightly. This suggests that here the major cause of reduction in drag is the momentum of the vapor from the surface and that the streamline pattern far from the drop is not altered much even at high mass transfer rates.

The drag data for heptane drops burning in oxygen were examined further. Calculations of $C_d''^*$ were made using a published value of the evaporation constant and $C_d'^*$ was then obtained by difference from C_d^*. The values of $C_d'^*$ plotted vs Re fall below the standard curve for C_d. Evidently the presence of flame has a marked effect on the pressure and viscous forces (altering the streamline pattern) such that $C_d'^*$ is reduced. It is likely also that for the combustion data the physical property distribution peculiar to the gas field containing a flame envelope is inadequately represented by the mean property values employed. It is concluded that the slow viscous-flow theory (and the boundary layer theory) cannot be applied generally to the burning of drops without appropriate consideration of the role of the flame envelope. The equations for C_d^* and $\dot{m}^*$ can however be applied to evaporating drops when the Re is low and to special situations such as spray combustion where small drops can often be considered as being under "evaporating" rather than "burning" conditions.

Subject Headings: *Drag, of burning drops; Drops, burning, evaporation and drag of; Evaporation, of burning drops; Mass transfer, from burning drops.*

Old Sec. X G. A. Agoston

Elder, J. W. (University of Cambridge, Cambridge, England) "Steady Free Convection in a Porous Medium Heated from Below," *Journal of Fluid Mechanics* 27(1) 29–48 (1967)

In this paper the author considers free convection in a porous medium. Although some experimental results are reported, the principal content of this paper concerns numerical solutions of the governing equations. The appropriate equations for convection in a porous medium are very similar to the equations for a viscous fluid with large Prandtl number. It is expected that the solutions should be qualitatively similar.

Numerical solutions of the finite difference form of the partial differential equations are obtained using Leibmann's extrapolated method with alternating direction of scan. A number of flow and temperature fields are presented for natural convection with mass discharge. The author considers both the cases of forced discharge where flow is injected with a prescribed velocity and natural discharge where the flow is the result of the buoyancy force.

Subject Headings: *Convection, in porous media; Porous media, convection in.*

Old Sec. X **D. L. Turcotte**

Emmons, H. W. and Ying, Shuh-Jing (Harvard University, Cambridge, Massachusetts) "The Fire Whirl," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 475–488 (1967)

This paper reports the results of a series of experiments on the fire whirl. The fire whirl was generated by introducing an external circulation to a fire burning over a pool of liquid fuel. The external circulation induced a rotation in the buoyant fire plume. The fire was fed by a 4 in. diameter pool of acetone. A flame holder over the pool was used to anchor the base of the flame. A 12-mesh cylindrical screen with a diameter of 88 in. and a height of 10 ft was mounted with the fire plume on its axis. Circulation was introduced by rotating the cylindrical screen at from 0.8 to 10 rpm. It was found that the induced circulation had a profound effect on the structure of the fire plume. As the circulation was increased the radius of the fire plume decreased and the height increased, a fire whirl was generated as the circulating ambient air became entrained in the buoyant combustion zone.

The authors present measured temperature profiles. Reduction of the data was made difficult by a persistent wander of the fire plume. In addition to the wander, large turbulent fluctuations were present. The temperature measurements indicated a maximum temperature away from the axis of the plume. It is concluded that the core of the fire whirl was fuel rich with maximum heat generation taking place in a cylindrical region.

Obviously any analysis involving a turbulent flame is very difficult. The authors introduce the appropriate conservation equations for mass, momentum, and energy. Using standard methods for turbulent plumes the equations are averaged and a mixing coefficient is introduced. Many approximations are required before a solvable set of equations are obtained. Some agreement between theory and experiment is found. The theory fails to predict the observed increasing rate of growth of the plume radius with height. The authors introduce the Rossby number as a nondimensional measure of the induced circulation and the Froude number as a nondimensional measure of the buoyancy.

This research is to be commended for adding to the literature a controlled experiment on a fundamental combustion problem of considerable practical importance. The dependence of the plume structure on circulation and the associated temperature profiles will be of interest to anyone working on fire research. The results should also contribute to the understanding of the turbulent mixing process.

However, the theoretical approach of the authors would seem to be subject to some criticism. It is not surprising that the application of the turbulent mixing theories which have met limited success in natural convection should be in poor agreement with the experimental results. With the additional complications of fuel evaporation and turbulent combustion in the presence of circulation any agreement would be indeed surprising. However, further efforts to obtain scaling of the results should shed light on the important scaling parameters. Are the Rossby and the Froude numbers adequate scaling parameters and what role does the combustion process play?

Subject Headings: ***Fire whirls; Plumes; Pool fires, whirls above.***

Old Sec. X **D. L. Turcotte**

Forstrom, R. J. and Sparrow, E. M. (University of Minnesota, Minneapolis, Minnesota) "Experiments on the Buoyant Plume above a Heated Horizontal Wire," *International Journal Heat Mass Transfer* **10,** 321–331 (1967)

The temperature field within the buoyant plume arising from a heated wire in air was explored for the laminar flow case. The experiment also provided information on the transition to turbulent flow and on the tendency of the plume to execute a slow oscillatory motion.

Because free convection flows are very sensitive to fluid motions and temperature fluctuations in the surroundings, the work was done in a test room or cell which had been designed as a thermally insulated environmental control chamber. However, preliminary experiments showed that an additional isolation enclosure was needed. It was also found that the presence of personnel affected the plume so the traversing apparatus was controlled from outside the test room.

The heated horizontal wire was 0.04 in. in diameter and 34 in. long although only the central 10-in. space of this length was used. The wire was located 12 in. above the bottom of the isolation enclosure. Its resistance was 0.5406 Ω/ft, and it was given an electroplated gold film to reduce radiant heat transfer to a negligible value. The final isolation enclosure was 44 in. high, 34 in. long, and 24 in. wide. The sides and top consisted of finely woven brass screen and the ends (perpendicular to the direction of the wire) were constructed of glass and plywood for observation.

The temperature probe consisted of a 0.001-in. chromel and constantan thermocouple suspended between the ends of the tines of a stainless steel fork. The accuracy of the probe was at least 0.1°F. Its horizontal travel could be controlled to within 0.001 in. and its vertical position could be determined to within 0.002 in. in 100 cm.

Although the isolation enclosure reduced the swaying motion of the plume, some sway continued to persist. Considering the favorable environment for the plume, it was felt that such motions could be regarded as a characteristic of buoyant plumes. The flow was fully laminar for all heat output rates at elevations up to 6 in. above the wire. For the lower heating rates, laminar flow existed at higher elevations as well. At higher heating rates the flow was no longer fully laminar. Periodically the passage of a turbulent burst would cause a rapid change in the temperature sensed by the thermocouple probe. At higher elevations and higher heating rates the frequency of the turbulent bursts increased, thus indicating the onset of turbulent flow.

The temperature field was investigated at 8 different heights ranging from $\frac{1}{4}$ in. to 15 in. above the center of the heated wire. At each height the centerline temperature was measured for 12 different heating rates ranging from 0.26 to 5.1 w/ft of wire length. Temperature profiles were determined at each height for three heating rates. Owing to the flatness of the temperature profile in the neighborhood of the centerline, temperature oscillations induced by plume sway were always small. Off the centerline the oscillations were much larger and it was assumed that the temperature was best represented by the long-time average. This period was about 60 sec.

The experimentally determined relationships between centerline temperature, elevation above the heated wire, and the heating rate are in very good agreement with the theoretical relationships given by the work of Fujii.[1] This is also true of the experimental and theoretical temperature profiles except the profile for the 15-in. elevation and highest heating rate, in which case the flow was predominantly turbulent. As computed from the experimental data, the position of the virtual line source of the plume was 0.083 in. below the center of the heated wire.

The onset of the transition to turbulent flow was related to a modified Grashof number which had a value of 5×10^8 for the experimentally determined transition point. For the fully developed state it was assumed that the value of this number would be equal to or greater than 5×10^9.

Reference

1. Fujii, T.: "Theory of the Steady Laminar Natural Convection above a Horizontal Line Heat Source and a Point Heat Source," International Journal Heat and Mass Transfer *6*, 597–606 (1963).

Subject Headings: ***Convection fields; Plumes, above heated wire.***

Old Sec. V **G. M. Byram**

Kremer, H. (Gaswärme-Institut e. V., Essen, Germany) "Mixing in a Plane Free-Turbulent-Jet Diffusion Flame," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 799–806 (1967)

This paper deals with a study of plane free-turbulent-jet diffusion flames. The theoretical analysis is based on Reichardt's similarity hypothesis which is extended to the plane case. Using solutions for the spread of momentum and nozzle gas-mass fluxes, expressions for the location of the flame front were derived. These results can be used to calculate density, velocity, temperature, and concentration fields in the flame.

Experimental results obtained for plane, isothermal turbulent air jets and a vertically burning, plane turbulent city-gas flame are reported. The measurements include momentum and nozzle gas-mass-flux distributions with air and flame jets. The results served to evaluate momentum and mass transfer coefficients appearing in the theory. Comparing the results with earlier investigations of round jets and diffusion flames it was similarly found that—though generally having higher values—the transfer coefficients of plane jets decrease with growing ratio of nozzle and ambient gas density.

The different behavior of isothermal and burning gas jets seems to be caused by the fact that the nozzle fluid of the latter almost spreads in combustion products at flame temperature.

If one introduces the density, when plotting the measured transfer coefficients versus the ratios of nozzle and ambient gas densities, it is observed that the empirical curve connecting the transfer coefficients continually declines towards greater density ratios.

From the experiments the validity region of the theory was determined, and a comparison of calculated and measured flame contours was made.

Subject Headings: ***Diffusion flames, turbulent, mixing in; Mixing, in turbulent flames; Turbulent flames, mixing in.***

Old Sec. V **Author's Abstract**

Lee, Shao-Lin (State University of New York, Stony Brook, New York) "Axi-symmetrical Turbulent Swirling Natural-Convection Plume. Part 1. Theoretical Investigation. Part 2. Experimental Investigation," *Journal of Applied Mechanics, Transactions of the ASME* **33**(3) Part I, 647–655. Part II, 656–661 (1966)

This pair of papers presents a theoretical and experimental investigation of a swirling turbulent plume. In the theoretical analysis the author applies the integral-similarity techniques which have been used successfully to predict the behavior of nonswirling turbulent plumes. The same entrainment hypothesis is also used. The flow is assumed to be fully turbulent and the boundary layer approximation to be valid. The Boussinesq approximation is also used. The author assumes similar velocity profiles for both the axial and swirling components of velocity. After integrating out the radial dependence, the set of total differential equations for the axial dependence of the variables is integrated numerically. The results are found to depend only on the source Froude number and the source Rossby number. The results do not differ greatly from the results for non-swirling plumes.

The author also presents measurements carried out on a swirling turbulent plume. The swirling plume was obtained by entraining the hot gases from a bunsen burner into a swirling mass of cold air from a set of tangential jets. After mixing the hot, swirling gas was emitted from a 2 in. diameter orifice into a 6×6×12 ft screened cage. Velocity and temperature profiles in the resulting swirling plume were obtained using a resistance velocity probe and a thermocouple to measure the temperature. The dependence of the plume radius, maximum buoyancy, maximum swirling velocity, and axial velocity on the height above the orifice is in good agreement with the theory.

This research is an important contribution to the understanding of turbulent phenomena. Although the results are not spectacular, they add to the list of turbulent flows which are reasonably well understood.

Subject Headings: ***Convective flow, in plumes; Plumes, turbulent convection; Turbulent convection plumes.***

Old Sec. X **D. L. Turcotte**

Lee, Shao-Lin (State University of New York at Stony Brook, New York) and **Ling, Chi-Hai** (Christian Brothers College, Memphis, Tennessee) "Natural Convection Plume above a Circular Ring Fire," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 501–506 (1967)

This study concerns the flow field of the turbulent natural convection plume above a circular ring fire. A ring of fire often develops when wildland fuels of uniform kind are ignited at one point on level ground during calm weather and are allowed to burn freely. Spread of such fire is thought to be related to convective air movements in and above the fire. The only previous study of a plume above a region bounded by thin flames was one in which two parallel lines of small flames were simulated by using one line of flames and the method of images in which a wall was placed at the plane of symmetry between the flames and a hypothetical line of flames.

In expressing a theory of the fully turbulent convection plume having small relative variations in density over a circular ring fire the governing differential equations presented are: (1) continuity, (2) vertical momentum, (3) horizontal radial momentum, (4) energy. These are integrated with respect to a radial length from the center of the ring and are transformed to eliminate constant coefficients. For the fluid inside the plume flow field, they relate vertical velocity, radial velocity, temperature, and pressure with the independent variables of vertical and radial distance. The functional relationships of velocity and temperature with the independent variables were determined experimentally.

A ring burner 29 in. in diameter containing 32 evenly spaced inlets for a propane-air mixture was placed flush with a horizontal asbestos platform and was doubly shielded to avoid disturbances from surrounding air. Temperature and velocity were measured with a thermocouple and hot-wire probe at various heights above the burner and at various radial distances from the center to beyond the fire ring.

Dimensionless graphs of experimental measurements at three heights and eight radial distances are given for temperature, vertical velocity, and radial velocity. At the highest level measured, vertical velocity was a maximum at the center of the convection plume, but at the lowest level the velocity flattened off at some distance from the center. At all levels radial velocity was zero at the center, a maximum at some distance from the center, and a low value at the outer limit of measurement. At the highest level, temperature was a maximum outside the center, but at the lower levels it was a maximum at the center. Velocities increased with height, but temperatures decreased.

Subject Headings: *Fire, ring, plumes above; Plumes, above a ring fire; Ring fire (see Fire, ring).*

Old Sec. X **W. G. Morris**

Smith, R. K. (University of Manchester, Manchester, England) "Radiation Effects on Large Fire Plumes," *Eleventh Symposium (International) on Combustion*, Pittsburgh, The Combustion Institute, 507–515 (1967)

The radiative transport of heat above very hot fire plumes in both the lateral and vertical direction has been modeled in an attempt to describe the course of air flow above the immediate combustion zone.

The air flow above such a fire is driven by strong buoyancy forces. Close to the fire radiative heat transfer is the dominant field force. At higher levels the immediate heating effects are not due to direct combustion, since rapid radiative cooling and cold air containment has already occurred. The work here is mainly confined to the dynamics of the radiative field and a study of the combustion zone itself with reference to its effect upon the flow processes occurring at higher levels.

The flow model is represented in the cylindrical coordinate system. The input velocities are modified by turbulent fluctuation terms where the latter is assumed to be zero on the axisymmetric line. The swirl component of velocity about this axis is also denoted as zero up to any height. This boundary condition is open to restudy. Pressure throughout the vertical and lateral field is assumed to vary insignificantly. The turbulent velocity fluctuation term is small as the radius of the plume increases, and is taken as zero at $R=\infty$. Viewing an actual plume we see a rather slow lateral expansion with respect to the vertical enlargement. Thus we can assume a constant cross section for the velocity or dimensional profiles throughout the total height of the fire plume. The rate of ambient air containment is defined in terms of a weak plume edge entrapment surface with the assumption that there exists a predictable density profile of the enshrouding air.

The radiation field is divided into the lateral and vertical components. The plumes are divided into three classes: opaque, intermediate, and transparent. This division refers to the opacity of a plume to the direct burning radiation and is defined as the rate of the local mean radius to the mean free path of the radiation. The first involves the case where solid particles of combustion almost completely block the radiation from emission. This type of plume is characterized by the appearance of tongues or eddies of hot gases bursting through the opaque envelope of the cloud. They result from bulk convection of very hot gases into the surface of the plume. These often appear to be the tips of tongues of flame at great heights but really are just hot gases. These eddies of radiation contribute a major proportion of the total radiative heat loss in opaque plumes.

The intermediate case is characterized by a more uniform radiative penetration of the plume.

The lateral radiation is defined as the mean radiative temperature of an emissive surface on a mean radiating edge. The net heat loss of the defining surface follows the normal Stefan law. A small correction is made to account for the radiation received by the plume itself from the environment.

The vertical radiation loss is directly related to the relative opacity of the plume. The more transparent to radiation the higher will the plume become. The stronger the buoyant forces near the combustion zone are, the greater will the initial accelerations of the gases become. If the vertical radiation penetration is large, then those buoyant forces will be present to a greater distance above the fire itself. The deceleration of the gases will occur more slowly. It must be remermbered that the most important plume height determiner is the maximum tempetature of the actual fire, with radiative factors contributing about 5% of the nec effect. The greatest radiative contribution occurs in hot, transparent conflagrations.

Subject Headings: *Fire plumes (See Plumes); Plumes, effect of radiation on; Radiation, effect on plumes.*

Old Sec. VI **P. Breisacher**

Tewari, G. P. and Weinberg, F. J. (Imperial College, London, England) "Struty ture of Flame Quenched by Cold Surfaces," *Proceedings of the Royal Socie-* **A296**(1447) 546–565 (1967)

Weinberg is well-known for his elegant investigations of the structure of laminar flames using optical techniques. In this paper an investigation of the structure of a near-burnt premixed ethylene-air flame in contact with a cooled body is reported.

The flame used was produced on a flat flame burner of the type devised originally by Powling and was free from contact with any surface except those deliberately introduced in the investigation. Two types of cooled surface were introduced. The first was a water-cooled cylindrical body introduced at the periphery of the flame disc. This had the disadvantage that the flame lacked radial symmetry, and hence, although the authors made some measurements (described below) the system was soon abandoned and replaced by a water-cooled cylinder around which the burner was constructed. It therefore lay at the center of the flame disc so that an essentially two-dimensional flame was generated. Both heat sinks had a horizontal slit on the upstream side of the flame so that by applying suction to the slit the flow pattern could be altered in the region in which the interaction between the flame and the cooled body occurred.

Measurements of local flow velocities were made throughout the flame zone using the particle track method, distance resolutions down to under 1 mm being obtainable. A schlieren system was used to define the flame front, except sometimes in the vicinity of the cold body when the flame shape made the use of schlieren impracticable. In these cases the surface corresponding to the isotherm $T=T_0[(a+2)/(a+1)]$ was employed, when T_0 is the initial temperature and a is the exponent in the dependence of the ratio of the thermal conductivity to specific heat on temperature. This surface corresponds well to the schlieren surface; it was located by the use of the continuity equation in conjunction with the particle track results. From these observations local flame speeds were calculated.

Flame speed measurements made with the peripheral heat sink with no applied suction showed, as might be expected, that the flame speed was reduced in the vicinity of the sink. More curiously, however, when the flow pattern was modified by suction, the flame speed was found to increase close to the surface, passing through a maximum greater than the unperturbed value, and then to diminish again nearer to the surface. This result the authors' are inclined to attribute to the importance of radical diffusion in the quenching process (see below), but they noted that the flame had a marked curvature when suction was applied and thought that the increase might well be due to the known effect of curvature on flame speed. Hence they abandoned the use of the peripheral heat sink. Their scepticism appears to have some justification for the result was not repeated with the axisymmetric heat sink which did not give a flame curved in this way.

In order to link flame speed measurements using the axisymmetrical heat sink with the heat loss pattern, a detailed investigation of the flame temperature was made using a thermocouple which could be traversed throughout the flame zone. The heat lost from the stream lines was calculated and the result was correlated with the local flame speed. The trend, as might be expected, was that increasing heat loss produced a decreasing flame speed. However a comparison of results with and without suction showed that the flame speed was not a unique function of heat loss but depended on the orientation of the flame front to the heat sink. This the authors interpret as clear evidence that the heat sink is not partly thermal in its effects and that the diffusion of active species is important in the problem. Certainly it is hard to see otherwise why equal heat loss should not produce equal flame speed.

The conclusion is supported by calculations based on measurements of local temperature and velocity of local heat release rates. These show that high heat release rates are encountered even at small distances from the heat sink, though the zone in which heat release occurs is appreciably narrowed. The existence of these high heat release rates in a region in which the temperature is very low is explained by the authors as due to the diffusion into the region of species effective in promoting reaction.

In order to examine in more detail the diffusion processes which are taking place the authors carried out a composition survey in which samples were withdrawn from the flame by a probe and analyzed by gas chromatography.

The results suggest that the narrowing of the reaction zone near to the heat sink is due to the suppression of the conversion of CO into CO_2. More important, they suggest that there is a net diffusion of hydrogen towards the heat sink in the vicinity of the reactor zone. This hydrogen does not appear to be in combination with oxygen and is most probably in atomic form. Thus, in the vicinity of the surface there must be a sink for this species and the authors argue that the disappearance of the hydrogen, or something formed when it disappears, is responsible for the high reaction rates observed there. In fact the authors suggest that the reaction

$$H+O_2 \rightarrow OH+O$$

is replaced near the surface by

$$H+O_2 \rightarrow HO_2$$

This reaction has been thought to be important by a number of authors and the suggestion receives support from some spectroscopic investigations by Gaydon which are referred to in this paper.

The paper is interesting and well written. It suggests that the phenomenon of quenching is extremely complicated and that theoretical models of considerable complexity will be needed to produce accurate predictions of quenching phenomena. It should be read by anyone concerned with the theory or practice of flame quenching by surfaces.

Subject Headings: *Flame structure, near surface; Quenching, near surface; Surface, effect on flame structure.*

Old Sec. VII **D. G. Martin**

J. Meteorological Aspects of Fires

Plate, E. J. (Colorado State University, Fort Collins, Colorado) "Diffusion from a Ground Level Line Source into the Disturbed Boundary Layer Far Downstream from a Fence," *International Journal Heat Mass Transfer* **10,** 181–194 (1967)

This is a report of experiments on the diffusion plume, performed in a low speed wind tunnel with the air velocity of about 2.7 m/sec in the free stream. A two-dimensional diffusion plume was produced by a line source of ammonia which was emitted continuously parallel to the leading edge of a smooth flat plate at ground level. On the downstream of the source, the boundary layer was obstructed by an impermeable and sharp-edged fence which extended over the whole width of the plate. Fences with four different heights were studied.

The flow field has been well described by the author. At some distance upstream from the fence, the boundary layer is unaffected by the presence of the fence and behaves like an undisturbed boundary layer along a smooth flat plate. At a short distance in front of the fence, the boundary layer separates and a separation bubble with a closed circulation is formed. The separation streamline reattaches on the front of the fence, at a point close to the fence edge. On the fence edge behind the fence, the flow separates again. This time the separation zone is much longer. Reattachment takes place at certain horizontal distance, $N=L$, away from the fence. Along the plate for $N>L$ a new inner boundary layer is developing and gradually thickens. The outer portion of the boundary layer in this region remains essentially unchanged, except for an outward displacement.

The vertical distributions of velocity and concentration were measured at different distances behind the fence. The velocity was measured by a pitot static tube in conjunction with an electronic micromanometer. The concentration is determined by a neutralization process with hydrochloric acid and by using Nessler's Reagent as an indicator. Empirical formulas were obtained for the velocity and concentration profiles. Because the formula for concentration was misprinted in the paper, the correct form of the formula (to the reviewer) is written here for convenience.

$$C(x, y)/C_{\max}(x) = \exp\{-(\ln 2)(y/\lambda)^{1.6}\}$$

where C is local concentration, $C_{\max}$ is maximum or ground level concentration, y is vertical distance from the wall, and λ is vertical distance at which $C = \frac{1}{2}C_{\max}$.

Subject Headings: *Boundary layer, diffusion in; Concentration and velocity, of diffusion plume; Diffusion plume, in disturbed boundary layer; Disturbed boundary layer, with diffusion plume; Plumes, two-dimensional.*

Old Sec. X **S. J. Ying**

Slawson, P. R. and Csanada, G. T. (University of Waterloo, Waterloo, Ontario, Canada) "On the Mean Path of Buoyant, Bent-Over Chimney Plumes," *Journal of Fluid Mechanics* 28(2), 311–322 (1967)

Faulty assumptions and lack of careful, objective observation have caused confusion regarding the mean paths of chimney plumes under varying ambient conditions. Theoretically plume behavior consists of three phases in each of which mixing is dominated by turbulence from a different source.

1. Initial—self-generated turbulence
2. Intermediate—environmental turbulence
3. Final—energy-containing eddies of environmental turbulence

After theory is developed, three questions remain to be answered through experimentation.

1. How far downstream does the $z \sim x^{2/3}$ law hold? (z = plume height, x = downstream distance).
2. How significant is the intermediate phase in the "leveling off" of the plume?
3. What is actual plume behavior in the final phase?

Plumes from the 493 ft stack of an electrical generating station were observed and measured on eight occasions by means of a single-camera technique. Conditions during observation were:

Cloud cover, %	0–100
Ceiling height, ft	2500 to unlimited
Atmospheric stability	neutral to very unstable
Wind speed, ft/sec	
At plume height (U)	25–49
2m above ground	5–25
Gustiness	
Vertical	0.079–0.160
Horizontal	0.133–0.331
Ambient temperature, °R	490–526
Exit gas temperature, °R	640–683
Mass flow of gas, lb m/hr $\times 10^6$	2.04–4.19
Gas exit velocity, ft/sec	30.4–67.0
Chimney radius at exit	9.75
Bouyant acceleration at chimney, ft/sec	9.86–11.96
Flux of bouyancy at chimney, $\mathrm{ft}^4/\mathrm{sec}^3 \times 10^3 (F)$	28.5–72.0

In a neutral environment plume shape during the initial phase followed the dimensionless equation $z/\ell = 2.3(x/\ell)^{2/3}$, in which $\ell = F/U^3$. The transition point occurred approximately at $x/\ell = 1200$, $z/\ell = 280$. The intermediate phase was insignificant, and the final phase had a constant slope (differing between experiments) as predicted by theory.

Near the source, plume shape in unstable air was similar to that in stable air, indicating the existence of an initial phase dominated by self-generated turbulence. Height and shape of the final phase varied between and within experiments because of the interaction of varying gustiness and lapse rate. Increasing gustiness increases dilution rate, hence decreases buoyancy and retards upward movement. Increasing instability increases the excess temperature of the plume, which therefore acquires greater buoyant acceleration and rises higher.

Subject Headings: *Buoyant plumes; Chimney plumes; Plumes, buoyant chimney.*

Old Sec. X G. E. Fahnestock

K. Physiological and Psychological Problems from Fires

Banks, W. G. and Holt, F. E. (Northeastern Forest Experiment Station, U.S. Forest Service, Upper Darby, Pennsylvania) "Who Starts Forest Fires in Maine and How?" *U.S. Forest Service Research Note UE-51* (1966)

One hundred seventy one fires were studied. In 51% of them the cause was positively identified. In 39% the probable cause was identified. The Table refers to these 154 cases where the cause was identified.

TABLE 1

Classification of the people responsible for starting fires investigated in Maine (1964)

Category	Item	Percent
Sex	Male	88
	Female	12
Age	Under 12 years	24
	12 to 20 years	9
	21 to 50 years	47
	Over 50 years	20
Residence	Out of state	3
	Within state	97
	Within town	85
Occupation	Students[1] and pre-school	31
	Farmers	16
	Woods workers	11
	Service employees	7
	Housewives	6
	Retired	6
	Truckers	5
	Unskilled	5
	Miscellaneous other: commercial fishermen, managerial law enforcement, disabled, unemployed	13
Activity when fire started	Debris-burning	49
	Playing (children under 12 years)	22[2]
	Cutting, yarding, and hauling wood	11
	Fishing	4
	Parking in secluded areas	2
	Miscellaneous other: walking or hiking, joyriding, camping, driving truck, berry-picking, shooting fireworks, repairing a cottage.	12

[1] Includes students more than 12 years old.

[2] This figure does not include fires started by children while engaged in other than strictly play activities.

Subject Headings: *Forest fires, in Maine; Maine, forest fires in; Sources of forest fires in Maine.*

Old Sec. XIV

Authors' Table with Editor's Note

Chambers, E. D. (Joint Fire Research Organization, Boreham Wood, England) "Fire Education: The Apparent Effectiveness of a Wall Chart," *Joint Fire Research Organization Fire Research Note No. 636* (September 1966)

Children who had seen an educational poster about fire were questioned about its contents, and their answers compared with those of a group who had not seen it.

Subject Headings: *Charts, and fire education; Children, and fire education; Fire education, by wall chart.*

Old Sec. XIV Author's Summary

Chambers, E. D. (Joint Fire Research Organization, Boreham Wood, England) "Fire: The Personal Experience of a Sample of Fire-Conscious Adults," *Joint Fire Research Organization Fire Research Note No. 680* (September 1966)

Persons working at an establishment concerned with fire research were asked for particulars of fires they remembered in their houses.

Subject Headings: *Adults, fire experiences of; Fire experience, of fire-conscious adults.*

Old Sec. XIV Author's Summary

Saint, C. E. and Fry, J. F. (Joint Fire Research Organization, Boreham Wood, England) "Children with Fire," *Joint Fire Research Organization Fire Research Note No. 632* (September 1966)

Subject Headings: *Children, and fire; Fire, and children.*

Old Sec. XIV

Fry, J. F. and Saint, C. E. (Joint Fire Research Organization, Boreham Wood, England) "General Knowledge of Fire Protection among Householders in London," *Joint Fire Research Organization Fire Research Note No. 612* (September 1966)

Subject Headings: *Fire protection, knowledge among householders; Householders, knowledge of fire protection; London householders; Knowledge of fire protection.*

Old Sec. XIV

Keller, J. A. (The Dikewood Corporation, Albuquerque, New Mexico) "A Study of German World War II Fire Fatalities," *Report under Office of Civil Defense Contract OCD-PS-65-53* (April 1966)

Ranges for estimated fire fatalities are developed for firestorms and group fires initiated by conventional weapons in German cities during World War II. Firestorm fatalities are estimated to vary between 4% and 20% of the population-at-hazard. Group fire fatalities are estimated to include up to 4% of the population-at-hazard.

Limitations on extension of these estimates to the nuclear case and to U.S. cities are discussed.

Subject Headings: *Fatalities, fire in World War II; Fire fatalities; Fire storms, casualty estimation; German fire fatalities; Incendiary raids.*

Old Sec. XV **Author's Summary**

L. Operations Research, Mathematical Methods, and Statistics

Chambers, E. D. (Joint Fire Research Organization, Boreham Wood, England) "Incendiarism Statistics," *Joint Fire Research Organization Fire Research Note No. 631* (1966)

Deliberately started fires probably account for a larger proportion of the United Kingdom fire loss than published statistics suggest. Methods of improving the collection and interpretation of these statistics are put forward.

Several lines of research into factors associated with the occurrence of incendiarism are outlined.

Subject Headings: *Incendiarism, statistics; Statistics, of incendiarism.*

Old Sec. XIV **Author's Summary**

Cohn, B. M. (Gage-Babcock & Associates, Inc., Westchester, Illinois) "The Confrlagration Potential in San Jose and Albuquerque," *Final Report under Office of Civil Defense Contract OCD-PS-64-74* (October 1966)

For the purpose of field testing its methods and procedures, the "System for Conflagration Assessment of Urban Areas" was applied to establish the relative conflagration potential of the various sections of two metropolitan areas and to delineate firebreaks therein. The communities used for test purposes were the San Jose, California, and the Albuquerque, New Mexico, metropolitan areas. Analysis from Sanborn maps and aerial photographs was supplemented to a large extent by field surveys. Several problems and discrepancies were encountered, and recommendations are made for modifications to alleviate them. Over-printed topographic maps showing potential conflagration areas and firebreaks in the two communities are included with the report.

Subject Headings: *Albuquerque, conflagration potential; Conflagration potential, of San Jose and Albuquerque; Firebreak; Fire spread; San Jose, conflagration potential; Urban fire potential.*

Old Sec. XIV **Author's Abstract**

Labes, W. G. (IIT Research Institute, Chicago, Illinois) "Fire Department Operations Analysis," *Interim Report under Office of Civil Defense Contract N228(62479)69032* (July 1965 to June 1966)

This is an interim report on a study designed to evaluate public fire fighting operations. Information is developed on how fire fighting operations are performed under a variety of field conditions. The primary body of data consists of information extracted from reports on seventy-three (73) fires. Useful correlations between the following parameters are presented:

(a) Water Application Rate Density for Control vs Fire Area
(b) Water Application Rate for Control vs Fire Area
(c) Fire Control Time vs Fire Area
(d) Man-Hours Expended for the Complete Fire Fighting Operation vs Fire Area

In this case the fire area represents the maximum floor area of the space involved in the fire.

Significant Findings

1. Within each category, residential and non-residential, it is possible to represent the frequency of occurrence versus fire area in terms of statistical parameters. However, the sampling procedure used eliminated both very large and very small fires from consideration, and any conclusions drawn from statistical analysis would not necessarily be valid for the overall situation.
2. Correlations have been obtained between maximum floor area involved in fire and the following variables:
   —Water application rate density for fire control
   —Water application rate for fire control
   —Fire control time
   —Man-hours expended for complete fire-fighting operation
3. The water application rate density for control of fire (P—GPM/100 ft^2) is linearly related to maximum fire area (A_2—ft^2) according to the following:

For residential fires of 300 to 5000 ft^2,

$$P = -0.006A_2 + 46$$

For non-residential fires of 2500 to 30,000 ft^2,

$$P = -0.0009A_2 + 40$$

4. Water application rate densities used by fire departments to control real fires are about twice those reported by various investigators for control of experimental fires.
5. Satisfactory correlation has not yet been found between total water usage and fire area.
6. Averages of manpower usage for the 70 fires indicate the following distributions of effort.

Operation	Percentage of total effort	
	Residential	Non-residential
Rescue	3	1
Forcible entry	9	3
Ventilation	3	2
Extinguishment	21	37
Salvage	5	3
Overhaul	55	49
Exposure protection	4	5

Subject Headings: *Equipment, fire fighting; Fire department operations; Fire extinguishment; Fire fighting, manpower, equipment, water usage, and time; Time, in fire fighting; Water usage, fire fighting.*

Old Sec. XI

Author's Summary

Nash, P. (Joint Fire Research Organization, Boreham Wood, England) "Research on Aircraft Fires," *Joint Fire Research Organization Fire Research Note No. 641* (December 1966)

Subject Headings: *Aircraft fires, statistics of; Statistics, of aircraft fires.*

Old Sec. XIV

Spencer, V. H., Price, H. E., Siciliani, F. A., Howard, W. J., and Korn, B. (Serendipity Associates, Chatsworth, California) "Trans-Attack and Post-Attack Communications Requirements for Fire-Fighting Operations and Control," *Final Report U. S. Naval Radiological Defense Laboratory Contract N228(62479)69222* (June 1966)

A systems analysis was conducted to determine the trans-attack and post-attack communications requirements for fire-fighting operations and control during a hypothetical nuclear attack on a metropolitan area. Communications functions within the metropolitan fire department were derived and, insofar as possible the interdepartmental communications functions with interacting agencies in the disaster network. The types of information communicated, and the volume and frequency of messages were delineated. From these data a traffic model was developed and queuing theory was applied to evaluate the effects of specific communications and organizational parameters against traffic criteria.

It was concluded that (1) for large attacks the communication requirements are a function of the number of fire-fighting units rather than the number of fires; (2) three channels of communication are adequate to serve approximately 200 fire-fighting units if only significant information is communicated, and if the through channels are shared; (3) redundant communications can be reduced by decentralizing decision centers in the fire department organizational structure.

Subject Headings: ***Communication, of fire departments; Control, of fire departments; Fire departments, communications; Nuclear attack, effect on communications; Operations, of fire departments.***

Old Sec. XI **Authors' Summary**

M. Model Studies and Scaling Laws

Baldwin, R. (Joint Fire Research Organization, Boreham Wood, England) "Some Tentative Calculations of Flame Merging in Mass Fires," *Joint Fire Research Organization Fire Research Note No. 629* (1966)

A simple model of flame merging in mass fires is examined for fuel beds placed in a regular array. The model leads to an estimate of the critical conditions at the onset of merging which is in agreement with the scanty data available.

The theory indicates that the critical conditions expressed in terms of the flame height, fuel bed separation and size, are independent of the number of fires except insofar as the number determines the flame height, and a simple means of visualizing the effect of increasing numbers is given.

Subject Headings: ***Flame merging, and mass fires; Mass fires, and flame merging.***

Old Sec. VIII **Author's Summary**

Brown, A. M. (Gas Council, London, England) "The Investigation of Large Flames by Scaled-Down Hot Models," *Fuel Society Journal, University of Sheffield, England* **17,** 24–38 (1966)

The aerodynamics of burner design in burners employing pressure-jet oil atomizers without supporting air or steam jets was studied by modeling. Laboratory models were developed capable of reproducing a full-scale flame well enough to be used as the basis for investigations on improved combustion.

Scaling criteria were chosen to suit the objectives of the study and the available laboratory facilities. Since the available laboratory facilities required that all experiments be performed at atmospheric pressure, it was necessary to see how analyses such as Stewart's[1] for a pressure jet in a gas turbine combustion chamber could be modified. Objectives were to follow the combustion process, velocity distribution, and mixing conditions downstream from the burner. Aerodynamic similarity and similarity in fuel distribution were maintained. The important characteristics considered for scaling were:

(a) Physical
   1. Degree of turbulence
   2. Relative momentum between oil and air
   3. Spray distribution
   4. Penetration of oil droplets
   5. Evaporation time for droplets
   6. Temperature
   7. Residence time in combustion chamber

(b) Chemical
   1. Ignition delay
   2. Reaction kinetics
   3. Turbulent flame speed

Similarity in all of these characteristics simultaneously could not be maintained and various dimensionless groups had to be considered in such combination as to provide reasonable compromises. Combustion chamber pressure was kept constant as were air/fuel ratios and fuel properties. The various characteristics were grouped into parameters which included

1. Spray air momentum capability
2. Reynolds number
3. Spray-cone angle
4. Ignition delay
5. (a) Simultaneous evaporation and combustion
   (b) Droplet Reynolds number
6. (a) Reaction time/residence time
   (b) Turbulent flame speed/air velocity
7. Spray penetration

Keeping spray momentum and spray angle constant, scaling was considered based on similarity in (1) Reynolds number, (2) residence time (or ignition delay), and (3) velocity—a compromise between (1) and (2). Reynolds number similarity could not be accomplished since velocity would vary inversely with length scale and the high velocity at small scale would be incompatible with flame speeds and reaction times. The Reynolds number was thus kept well into the turbulent region at all times but was otherwise allowed to vary. Residence time similarity was achieved by adjusting the input mass flow rate to maintain similar residence times. Alternatively, velocity similarity could also be achieved. In the experimental work flames were modeled both ways, comparing a full-scale boiler with a one-third-scale model. Results for different models of flames compared with full size were obtained by comparing and plotting velocity profiles and velocity decay results. Gas composition data were obtained by sampling from the flame from which equivalence ratio (ratio of actual air to fuel ratio to stoichiometric) and combustion efficiency were calculated. Plots of equivalence ratio show good agreement between model and prototype. Combustion efficiency was usually 10% to 15% higher in the model than the prototype.

Both scaling methods gave reasonable representations on the model of full-scale conditions and it was concluded that

(1) Geometric and spray similarity are required
(2) Reynolds similarity is not necessary
(3) The system is sensitive to air-fuel momentum ratio
(4) Changes in fuel reactivity affect the results more than differences in the ignition delay time.
(5) Changes in droplet size do not appear to change reaction rates in flames significantly.

The author also states that while the one-third-scale model was the smallest that could be conveniently used in this case, modeling below about one-quarter-scale in any hot model would probably introduce too many errors to be reliable. Provided the general form of the burner does not change too drastically, hot modeling can provide a useful means of investigating burner variables.

Reference

1. Stewart, D. G.: *Selected Combustion Problems*, Vol. II, Butterworth's 1957, p. 384.

Subject Headings: *Flame modeling; Hot-scale models, of flames; Scaling, of flames.*

Old Sec. VIII A. Strasser

N. Instrumentation and Fire Equipment

Bol'shakov, G. F. (Baku, Russia) "Instrument for Studying the Oxidizability of Petroleum Hydrocarbons at High Temperatures," *Vysshie Uchebnye Zavedeniya, Neft' i Gaz* (*Higher Education Institute Bulletin, Oil and Gas*) No. 9, pp. 61–63 (1964) Translated by A. I. Schidlovsky, The Johns Hopkins University Applied Physics Laboratory under Naval Ordnance Systems Command Contract NOw 62–0604-c (October 1967)

A method for determining the oxidizability of fuels and lubricants by measuring the absorption of oxygen at high temperatures is described. The instrument used enables readings to be taken at constant pressure, thus avoiding errors due to fluctuations in atmospheric pressure.

Subject Headings: *Fuel test, for oxidizability; Hydrocarbons, petroleum, oxidizability of; Oxidizability, of fuels.*

Old Sec. XII Author's Abstract

Kuznetsov, I. L., Trokhan, A. M., Baranova, G. R., and Ignatenko, Yu. V. (Institute of Chemical Kinetics and Combustion and Institute of Theoretical and Applied Mechanics, Siberian Branches, Academy of Sciences of the USSR) "Investigation of Flame Turbulence by the Photoelectric Method," Translated from *Doklady Akademii Nauk SSSR* **171**(2), 327–330 (1966). Published in *Soviet Physics-Doklady* **11**(11), 984–987 (1967)

An accurate technique involving the use of tracers is applied to the measurement of turbulent intensity and average flow velocity both in a flame and in the products of combustion. Tracer particles of aluminum or magnesium oxide particles are entrained in the gas stream. In high temperature fields the particles are luminous; in cold streams they are illuminated by an external source. The image of a particle falls upon a shield having two parallel slits. When the image crosses one slit, a voltage pulse is generated which results in triggering the oscilloscope beam. When the image crosses the second slit, a bright flash appears on the screen of the oscilloscope. Long-exposure photographs are made of the screen, and are analyzed photometrically to yield the flight-time spectrum of the tracer particles and the spectrum of the longitudinal pulsations of the flow velocity.

It is imperative that the particles follow the local flow motion with sufficient precision. The suitability of a given sample of tracer powder is determined as follows: The maximum sedimentation velocity of the particles in air is measured experimentally. This velocity is used to calculate the diameter of an equivalent sphere of the tracer material. The sphere diameter and the estimated values of the intensity and scale of the turbulence in the flow in question are then used to calculate the motion of the particle relative to that of the gas. For this purpose equations are provided applying to particle motion in a harmonically vibrating fluid.

The above tracer method for turbulence measurement was tested in a burner system without combustion (isothermal flow). The intensity of turbulence ϵ_0 and the mean velocity V_0 were obtained at various points along the chamber axis downstream of the swirling grid. A comparison of the results was made with those obtained with a constant temperature hot-wire anemometer. The tracer method yielded slightly higher results.

The same information was obtained under combustion conditions (tracer technique): intensity of turbulence ϵ and mean velocity V. The flame-generated turbulence U'' was then calculated: $U''=\epsilon V-\epsilon_0 V_0$. In addition, a record of combustion luminosity along the axis was obtained to show progress of combustion in the burner.

The observations show clearly that as combustion progresses both the difference $\epsilon-\epsilon_0$ and U'' increase. At a point where the combustion intensity begins to subside, these begin to diminish owing to the dissipation of turbulence energy. The difference $\epsilon-\epsilon_0$ ultimately reaches zero downstream in the zone of burned gases.

The dependence of the maximum value of U'' on the isothermal flow turbulence U' is presented graphically for different mixtures of propane and hydrogen in air. These dependencies being based on time-averaged values within a flame do not conform to the theoretical relation for flame-generated turbulence at the flame surface.[1]

In conclusion, it is reported that there is satisfactory agreement between the amplitude spectrum of the pulsations in the presence of combustion and a Gaussian distribution, as in the isothermal case.

Reference

1. Karlovitz, B., Denniston, D., and Wells, F.: J. Chem. Phys. *19*(5), 541 (1951).

Subject Headings: *Flame turbulence, by photometry; Photometric method, for studying turbulence; Turbulence, in flames, by photometry.*

Old Sec. XII **G. A. Agoston**

Nielsen, H. J. (IIT Research Institute, Chicago, Illinois) "Equipment Design for Test of Fire Storm Environmental Model," *Final Report under Office of Civil Defense Contract N228(62479)68579* (May 1966)

Equipment was constructed which can be used to perform model experiments of fluid motion phenomena occurring in large-scale fires. The equipment consists of a porous bed six feet in diameter placed in the center of a flat platform 16 feet in width. Heated air or combustible gas is supplied beneath the porous bed to produce either a column of buoyant air or a fire. Adjustable vertical baffles placed around the periphery of the platform are used to control the development of vortex flow in the column.

The purpose of the experiments which can be performed with the facility is to validate previous theoretical studies of mass fires or to define approaches and assumptions made in the studies which need modification.

Subject Headings: *Equipment, for studying fire storms; Fire storm models; Mass Fires, study of; Models, of fire storms, Plumes, study of.*

Old Sec. XII **Author's Abstract**

Rann, C. S. (Australian National University, Canberra, A.C.T., Australia) "Measurements of Gas Velocity in a Flame," *Journal of Scientific Instruments* 44(3), 227–228 (1967)

The author describes a refinement of an old technique to measure velocity in a flame by means of streak photography of incandescent tracer particles (Andrade, 1912). In this new approach, the particle velocity is determined by two photomultiplier detectors; their output signals indicate the elapsed time for particle transit between two viewing slits (0.7 mm wide by 1.0 cm long), 1 cm apart. It is presumed that the particle velocity is equal to the gas velocity (probably valid for all but high-speed flames) and therefore the gas velocity can be measured to better than 1% accuracy by this relatively simple convenient method.

The procedure requires introducing selected carbon particles, between 3 to 10 μm in size, into a vertical flame. Care must be taken to impart virtually no horizontal velocity component to the particles. At the first slit, the particle glow is reflected by a prism mirror onto the first photomultiplier detector. The output signal of this sensor initiates an oscilloscope trace. Similarly, as the incandescent particle moves past the second viewing slit, its glow is reflected onto the second photomultiplier detector and the resulting electrical signal is displayed on the dual-beam oscilloscope. The two photomultiplier pulses are recorded photographically for later analysis leading to flame velocity determination. Timing of the oscilloscope traces is provided by modulation of the electron beam with a high precision audio oscillator.

The author states that a typical pulse duration of 3×10^{-4} sec allows the peak signal to be estimated within one cycle of a 40 Kcps modulation. The main acknowledged limitation is the investigator's ability to locate the pulse peak with precision.

The theoretical basis for the claimed accuracy of the method is not developed in detail in Rann's article; a reference[1] is made to justify the Stokes law assumption. Without more searching inquiry, it appears likely that the method is most valuable for sheathed burners having vertical flames with no significant lateral velocity components.

Reference

1. Fristrom, R. M., and Westenberg, A. A.: *Flame Structure*, McGraw-Hill Book Co., New York (1965).

Subject Headings: ***Flame, velocity measurement in; Velocity, measurements in flames.***

Old Sec. XII **K. M. Foreman**

Williamson, H. V. (Cardox Division, Chemetron Corporation, Chicago, Illinois) "New Protection for Electronic Equipment," *Fire Technology* 2(4), 279–286 (1966)

A carbon dioxide fire extinguishing system is described which appears to offer a practical solution to the problem of protecting computers and similar sensitive electronic equipment without destroying the equipment in the process. Because of its simplicity the system should provide good protection with high reliability and low maintenance.

The system is designed for flooding individual cabinets containing this equipment with carbon dioxide vapor which has been warmed to room temperature. Warming the carbon dioxide eliminates the damaging refrigeration effects of using the gas in its liquid or low temperature vapor form. Flooding of individual cabinets is obviously superior to flooding an entire room because the latter approach would require evacuation of the room.

Most computer component cabinets contain a forced-air ventilation system which draws air in at the bottom of the cabinet and exhausts it at the top. The fire extinguishment system described is designed for this type of ventilation system.

Liquid carbon dioxide is first passed through a vaporizing unit consisting of a set of coils immersed in a stored-heat hot water bath. The warmed vapor is then passed through a special low velocity nozzle into the bottom of the cabinet. If the carbon dioxide can be injected faster than it can leak out the bottom of the cabinet, it will fill the cabinet and overflow from the top generating a completely inert atmosphere in the cabinet. Flow rate tests on both a large and a small system indicate that flow rates can be attained to provide such an atmosphere. Vaporizing flow rates in both tests were found to be at least 400 lbs/min.

Preliminary tests on simulated insulation fires were also made to determine the extinguishment effect of different carbon dioxide concentrations. These tests showed that concentrations of 80% or more applied for a short period of time of two min or so were more effective than concentrations of approximately 50% applied for a period of twenty min. From the system's operational standpoint short periods of high concentration are also more economical than long periods of low concentration. Further testing is needed to determine more accurately the length of high concentration time needed to extinguish fires in electronic equipment.

Subject Headings: *Carbon dioxide extinguishers, for electronic equipment; Electronic equipment, fire protection of; Fire protection, of electronic equipment.*

Old Sec. XIII A. W. McMasters

O. Miscellaneous

Van Dolah, R. W. and Staff (Explosives Research Center, U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Abstracts of Bureau of Mines Publications on Flames and Explosions for Fiscal Year 1966," *U.S. Bureau of Mines Information Circular 8349.*

Subject Headings: *Explosions, coal; Explosions, dust; Explosives research, U. S. Bureau of Mines; Flames research, U. S. Bureau of Mines.*

Old Sec. XIV

MEETINGS

First Meeting of Eastern Section of the Combustion Institute—Carnegie-Mellon University, Pittsburgh, Pennsylvania, November 27–28, 1968

Discussion on Scientific Aspects of Fire Hazards (Emphasizing Solids and Liquids)

Introductory Lecture: *The State of Fire Research*

Howard W. Emmons
Harvard University

Session I. Flame Spread*
Chairman: R. Friedman, Atlantic Research Corporation

Session II. Ignition Mechanisms
Chairman: D. Burgess, U.S. Bureau of Mines

Session III. Flame Retardation, Extinction, and Flammability Limts
Chairman: C. P. Fenimore, General Electric Research and Development Center

Session IV. General
Chairman: R. M. Fristrom, Applied Physics Laboratory, The Johns Hopkins University

ABSTRACTS

Session I

A Survey of Knowledge about Idealized Fire Spread over Surfaces—

R. Friedman, Atlantic Research Corporation*

Recent data on rate of flame spread across the surface of a combustible solid or liquid are reviewed in a comparative fashion. These results were obtained at Atlantic Research Corporation, Naval Research Laboratory, Stevens Institute of Technology, Linde Division of Union Carbide, and the U.S. Forest Service. Effects of roughness, exposed edges, orientation, chemical composition, scale, pressure, oxygen-mole fraction, and nature of inert gas on flame spread are commented upon. A short qualitative commentary on mathematical theories to describe this steady state process is given.

Subject Headings: *Fire Spread, on surfaces; Surfaces, fire spread over.*

Sec. D Old Sec. V

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* See Review Article, p. 1 of this issue.

Flame Spread along Cellulosic Materials—W. J. Parker, U.S. Naval Radiological Defense Laboratory

There is a popular belief that a flame moves along a cellulosic material by propagating into a combustible mixture of air and pyrolysis gases distilled from the surface ahead of the flame front. Usually it is assumed that this surface is heated to the pyrolysis temperature by radiative and convective heat transfer. However, these processes appear inadequate when it is considered that (1) the convective air flow is toward the flame and (2) the radiation level outside a small flame in burning cellulose is extremely low.

Visual observations of the flame spread along wood, paper, cellulose, and cotton cloth suggest that the pyrolysis gases are released entirely behind rather than in front of the flame front. This can be seen most readily by watching the progress of a flame moving down a white card in a darkened room. The pyrolysis region is clearly visible under the flame as a black charring region bordered by a very narrow brownish band. The flame front is indicated by the bottom edge of the luminous blue band just below the charring region.

Measurements of temperature as the flame front passed a point on the surface confirmed that no appreciable pyrolysis occurred in front of the flame. These measurements were taken with a one mil alumel-chromel thermocouple inserted in a slot cut parallel to and midway between the surfaces of a 3 in.×5 in. white index card. Heat transfer calculations indicate that a nearly uniform temperature exists through the thickness of the card for the two inches per minute flame spread rate observed. The card was oriented in the vertical plane so that the flames on both sides would be identical. The downward direction of propagation was chosen to make the process slow enough to follow conveniently. The temperature of the surface directly underneath the flame front was found to be less than 250°C which is too low to produce a significant amount of pyrolysis products in the time period established by the observed flame spread rate.[1] There is a large decrease in the rate of temperature rise as the charring region passes over the thermocouple since a large part of the heat feedback from the flame is consumed in the pyrolysis process. At this time the temperature exceeds 400°C where the measured pyrolysis rate of cellulose is very rapid.[1] The appearance of a pyrolysis plateau in the temperature profile along with the low numerical value of the temperature at the flame front and the visual observation of the location of the char region is convincing evidence that pyrolysis products are generated under the flame instead of ahead of it. The results of visual observations and temperature measurements of horizontal flame spread along upholstered panels consisting of cotton sailcloth over cotton batting one inch thick lead to the same conclusion. Shadowgrams taken of the flame show that the point ahead of the flame where the temperature begins to rise significantly coincides with the limit of the hot conductively heated air adjacent to the flame front. The important heat transfer mechanisms associated with moving flames along cellulosic materials, therefore, are no different than those of stationary flames. For small flames these are mainly gaseous heat conduction from the flame front and the transfer of heat by the diffusion of combustion products back to the surface.

The dimensions of a flame at its base exceed the dimensions of the fuel gas aperture supplying it. This effect is known as overhang and is due to an excess pressure under the flame caused by heating, expansion, and acceleration of gases in the flame front.[2] It is this projection of the flame front beyond the pyrolysis zone in the cellulosic materials that heats the unreacted surface causing the zone to move forward. The velocity of the flame propagation is proportional to the length of this projection divided by the time required to heat the surface to the temperature of rapid pyrolysis.

In order to investigate the overhang, an artificial flame spread surface was constructed. It consists of a tank, connected to the gas supply, with a 2 in. slot in the top whose width can be adjusted to that of the observed pyrolysis zone. The gas flow rate is set to yield approximately the same energy release rate as that of the burning card. Although no detailed measurements have as yet been made, the flame height and overhang are approximately the same as that for the card. With this device it can be readily seen that the overhang increases drastically with wind velocity and with the angle of elevation for flame propagation in the upward direction. In order to determine the rate of flame spread along cellulosic materials as a function of atmospheric composition and pressure, angle, incident radiation, and wind velocity it is necessary to examine the effect of these parameters on the length of overhang and the rate of heat transfer to the surface at the base of the flame.

References

1. Lipska, A. E., and Parker, W. J.: J. Appl. Polymer Sci., *10*, 1439 (1966).
2. Gaydon, A. G., and Wolfhard, H. G.: *Flames, their Structure, Radiation and Temperature*, Chapman and Hall, London (1953) p. 52.

Subject Headings: *Cellulosic materials, flame spread along; Flame spread, on cellulose; Pyrolysis, of cellulose.*

Sec. D Old Sec. V

The Spread of a Diffusion Flame over a Thin Combustible Surface—J. de Ris, National Bureau of Standards

Using the Schvab-Zel'dovitch formulation of diffusion flames, an analytical model is developed for the spread of a diffusion flame against the prevailing wind. The fuel bed is pictured as a thin sheet whose back side is insulated. The fuel's flash point is assumed sufficiently above the ambient temperature, so that vaporization ahead of the flame front is unimportant. The conduction from the flame through the gas phase is considered to be the primary mode of forward heat transfer. This precludes the radiation effects expected in large fires.

The Oseen approximation is used for the convection terms in the governing equations. The "heat blocking" effect caused by the fuel vaporization under the flame is approximated by the mass transfer factor $[\ln(1+B)]/B$. A unit Lewis number is considered together with constant transport properties.

With these simplifications, the governing equations are transformed into two simultaneous integral equations of the Wiener Hope form. These equations are solved by the substitute kernel technique. The solution predicts the flame speed to be approximately

$$\sigma V(T_{\text{vap}}-T_{\infty})\cong\sqrt{2}\lambda(T_f-T_{\infty}),$$

where: σ is the fuel heat capacity per unit surface area
V is the flame speed
$T_{\text{vap}}-T_{\infty}$ is the temperature rise of the fuel flash point above ambient
λ is the gas phase conductivity
T_f-T_{∞} is the temperature rise of the flame above ambient.

Subject Headings: *Combustible surfaces, flame spread over; Diffusion flame, over surfaces; Flame spread, over surfaces; Flame theory, diffusion flame.*

Sec. D Old Sec. V

Flame Propagation of Burning Solid Material with Moisture—S. J. Ying, The Catholic University of America

Flame propagation of burning solid has been studied theoretically. By considering that the heat transferred into the unburned material is balanced by the evaporation rate of the moisture in the material and the increasing rate of enthalpy of the material, the analytical expressions of the temperature distribution in the unburned material and the flame propagating speed are obtained. The temperature decreases exponentially with the distance away from the flame front. The flame propagating speed depends mainly on the rate of heat released from the combustion, the heat dissipated by the evaporation process, and the property of the material. From this study, the way for controlling the fire by liquids becomes more clear.

Subject Headings: *Flame propagation, of solids; Moisture, effect on flame propagation, of solids; Solids, flame propagation on.*

Sec. D Old Sec. V

Flame Spread down Paper Cylinders*—J. P. Stumbar and R. H. Essenhigh, The Pennsylvania State University

The rate of flame spread down vertical paper cylinders has been measured for cylinder diameters ranging from $\frac{1}{8}$ in. to about $2\frac{1}{2}$ in. The rates of spread were in the range 0.05 in/sec to 0.2 in/sec, and were found to be a prime function of diameter. As the diameter increased from $\frac{1}{8}$ in., the rate initially fell, but it soon reached a minimum (at about $\frac{1}{4}$ in. dia) and then started to rise again. After going through a point of inflection it continued to rise but tending to an upper limit. This general behavior, expressible by an equation quoted, was found to be obeyed when the

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cylinder bottom was either open or closed (plugged with a stopper), and also at two different levels of humidity.

This study is part of a program on abatement of smoke and grit emissions from incinerators and is intended to provide information on the rates and mechanisms of flame spread on a material representative of typical wastes, for prediction of transient behavior in a test incinerator. The overall objectives and relation to the associated programs have been described recently.[1] Analyses of typical incinerator wastes have shown them to be mostly cellulosic in origin with a high proportion of paper.[2] When fed into the incinerator they form a porous bed, and fast flame spread through the bed with minimum smoke is desirable. The porous bed has been successively approximated by us, by a roll of newspaper in a steel pipe, and by a bed of wooden dowels. In both cases it was found that downward spread of flame against an uprising air current behaved in such a way that we concluded that a paper cylinder could be used as an isolated, and more controllable "element" of the bed for initial study.

The method of experiment is to form the cylinders around wooden or metal formers and tape the adjacent edges together (with no overlap). The paper used is a bond paper containing 50% cotton fiber. After removal from the formers they are held vertical in a clamp, with the bottom end either open or plugged, and lit at the top with a match. As the flame spreads down, the times at which it crosses successive pencil lines an inch apart on the paper are recorded by a pulse to a pen recorder. This checks the uniformity of flame-spread down the cylinder.

The results thus obtained are based on a total of about 150 measurements of the flame spread speed. In all cases the rate of spread, R, was found to obey the following phenomenological equation

$$R=K^2d[(1+\delta/d)^2-(1-\delta'/d)^2] \qquad (1)$$

where $(1-\delta'/d)=0$ for all $d<\delta'$; d is the cylinder diameter; and δ and δ' are two constants whose values are equal to the diameter at the minimum and point of inflection respectively. K is a constant given by

$$K^2=\rho_0 f_{O_2}\bar{C}_p T_0 v_0/4W[B\rho_0 f_{O_2}+\alpha\bar{C}_p T_0(1+E/100)] \qquad (2)$$

where ρ_0 is the air density (stp); f_{O_2} is the *mass* fraction of oxygen in air; $\bar{C}_p$ is the mean mass specific heat of air at const. press.; T_0 is the surroundings temperature; v_0 is the equivalent cold gas velocity leaving the top of the flame zone; W is the paper weight (mass/unit area); B is the heat of combustion per unit mass; α is the stoichiometric oxygen ratio for the paper used; and E is the excess air entrained.

The effect of change of humidity, or opening or closing the tube bottom, is only to change the three constants, δ, δ', and K; the form of the Eq. (1) is unchanged. The values of δ were about $\frac{1}{4}$ in.; of δ' about $\frac{3}{4}$ in.; and of K^2 about 0.06 per sec. Differentiation of Eq. (1) predicts that the slope of the flame speed curve should rise linearly with $(1/d)$ till the point of inflection (at δ') is reached, and then should fall linearly with $(1/d)$. Graphical differentiation of the best fit to the experimental curve drawn by eye substantiated this prediction. Other methods of substantiating Eq. (1) included plots of $(R/d)^{1/2}$ vs $(1/d)$, and R vs $(1/d)$.

The Eq. (1) was derived by considering a heat and mass balance across a control volume defined on the basis of such considerations as stack theory, boundary layer behavior, etc. The control volume is in essence two concentric cylinders surrounding the flame at the top of the paper cylinder. The outer cylinder is of diameter $(d+\delta)$, and the inner one is $(d-\delta')$. The height of the cylinders can be specified but does not appear in the final equation. The analysis is phenomenological, not mechanistic. The Eq. (1) obtained is therefore independent of fuel (i.e., paper types) used, and implies no mechanisms.

Probable mechanisms of flame spread may, however, be induced. The flame is a diffusion flame supported by volatile products pyrolyzed out of the paper. Heat transfer from the flame to the paper is therefore a prime factor in controlling the flame speed. The initial fall in flame speed with increasing diameter obeys the relation R proportional to $(1/d)$. This is consistent with expectations from oil drop theory according to which the distance of the flame from the surface increases as the radius of curvature increases, thus reducing the heat transfer. However, as diameter increases, calculation from the phenomenological analysis shows that the cold air velocity crossing the cylinder boundary also increases. The effect of this increased convection flow is to offset and finally reverse the effect of increased radius of curvature. When reversed, the distance of the flame from the solid surface starts to decrease again, thus increasing the rate of heat transfer and therefore the flame speed. This effect, in turn, is itself offset by further increase of diameter. When the center cylinder finally opens (at $d>\delta'$) a further surface for supply of air is opened up, and the rate of increase of air velocity across the outer surface is reduced. The rate of increase of flame speed therefore diminishes and the speed tends to a maximum.

The effect of humidity seems to be consistent with a reduction in the net value of the heat of combustion B, due to absorbed moisture, not to the moisture in the air.

Considerations of stack theory indicate that most of the air should be supplied horizontally, so the leading edge of the diffusion flame is advancing through reasonably still air. This conclusion is supported by extinction of the flame when the upward velocity of air supply at the leading edge is increased by fitting a reasonably wide glass chimney over the paper cylinder with its bottom edge just below the level of the leading edge of the flame. There is a sudden flash up the chimney as it is lowered into position, and the flame goes out.

References

1. Essenhigh, R. H., and Gelernter, G.: "Systematic Appraisal of Incinerator Research Requirements," Am. Inst. Chem. Engrs. Sixtieth Annual Meeting, N. Y., November, 1967, Preprint No. 37C.
2. Kaiser, E. R., and Friedman, S. B.: "The Pyrolysis of Refuse Components," Am. Inst. Chem. Engrs. Sixtieth Annual Meeting, N. Y., Preprint 37D.

Subject Headings: *Diffusion flames, on paper cylinders; Flame spread, down paper cylinders; Paper cylinders, flame spread down.*

Sec. D Old Sec. V

Flame Spreading at Elevated Pressures over the Surface of Igniting Solid Propellants and Propellant Ingredients in Oxygen/Inert Environments*—R. F. McAlevy, III, R. S. Magee, and J. A. Wrubel, Stevens Institute of Technology

The velocity at which a flame spreads over the surface of igniting nitrate ester propellants, and two thermoplastics typical of composite propellant binders, has been measured in quiescent environments composed of oxygen-inert gas mixtures at elevated pressures. Preliminary data obtained in O_2/N_2 mixtures at subatmospheric pressures have been published. The proposed paper will present data obtained with mixtures of O_2 and He, O_2 and Ar, as well as O_2 and N_2 at pressures up to 415 psia; also included will be an improved theoretical analysis of the phenomenon that provides an excellent basis for data correlation. The new analysis incorporates recent results obtained by using very fine thermocouples (7.5 μ) to yield detailed measurements of the heat flux distribution ahead of the spreading flame.

The new analytical treatment results in an explicit dependence of V on pressure (P) and oxygen mole fraction (Y_{ox}) of the ambient environment in the form:

$$V \propto (Y_{ox}^{s} P)^{\beta}$$

where s is a function of diluent gas and type of specimen, i.e., either solid propellant or thermoplastic, while β although slightly dependent on the type of specimen is relatively insensitive to the diluent gas. Small test specimens (3 in. $\times \frac{3}{8}$ in. surface) were mounted in a relatively large chamber that was filled with O_2/N_2, O_2/He, and O_2/Ar mixtures for the thermoplastics having various oxygen mole fractions and total pressures. All of the data produced could be correlated by means of the derived equation shown above. Considering that the pressure was varied by a factor of 100 during the program, the success of the analysis is particularly striking. Implications of this new understanding with respect to improvement of motor ignition systems, as well as interpretation of the results of elementary propellant ignition experiments—such as those performed with shock tubes—will be discussed.

Subject Headings: *Flame spread, on solid propellants; Ignition, solid propellants; Solid propellants, flame spread on.*

Sec. D Old Secs. V and I

An Investigation of the Spread of Fire through a Randomly Packed Fuel Bed—J. B. Fang and F. R. Steward, University of New Brunswick (Canada)

Reproducible small-scale fires were obtained by burning randomly packed wood shavings (poplar) under controlled environmental conditions. The rate of linear fire spread over the uniform slab-like fuel bed was measured for each of the perti-

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nent variables over the following ranges:

Relative humidity of ambient air:	24–59%
Fuel bed voidage:	0.838–0.941
Fuel particle length:	1–3 in.
Fuel loading density:	0.153–0.307 lbs/ft^2

A significant increase in the rate of fire spread across the wood shavings was obtained when the relative humidity of the ambient air was decreased, when the fuel particle length was increased, and when the fuel bed voidage was increased. The fuel loading density was found to have no effect on the rate of fire spread over the range investigated.

Radiation flux density data obtained from a wide angle view total radiation pyrometer, indicated that the radiation from the burning fuel embers through the fuel bed is significantly greater than that from the overhead flame. Very fine thermocouples inserted into the fuel bed showed that the radiative heating of the unburned fuel amounts to approximately 40% of the heat required for ignition.

A simplified theoretical model derived by assuming the radiation from the burning zone to be the major mechanism of heat transfer, has been developed to relate the rate of fire spread and the physical properties of the system. The theoretical derivation correlates this work and that of other previous investigators to a certain extent.

Subject Headings: *Fire spread, through fuel beds; Fuel beds, fire spread in.*

Sec. D Old Sec. V

Flame Propagation Zones for Hydrocarbon Fuels at Low Pressure—M. Gerstein and W. R. Yates, Dynamic Science Corporation

Abstract not available.

Sec. D Old Sec. V

Session II

Two Man Space Environment Simulator Accident—B. P. Botteri, Air Force Aero Propulsion Laboratory

During 1967 two fire tragedies involving 100% oxygen atmospheres occurred which have had significant repercussions on the national space program. This technical discussion will be directed toward the analysis of the cause of one of these fires, the Two Man Space Environment Simulator Accident at Brooks Air Force Base, Texas. Specific aspects of the accident which will be discussed include: nature of the experiment being performed in the simulator, history of events immediately prior to the fire, fire pattern, potential sources of ignition, ignition and flammability properties of materials present in the simulator, and the establishment of the most probable cause of the accident. In addition specific protective measures which are being implemented to preclude the recurrence of disastrous fires in chambers involving oxygen-enriched atmospheres will be reviewed.

Subject Headings: *Environment simulator, for space, fire in; Fire, in space simulator; Oxygen atmosphere fire; Space simulator, fire in.*

Sec A Old Sec. XIV

Description of Fires in the Distribution Pipelines of a Gaseous High Purity, High Pressure Oxygen System—F. J. Correy, F. D. Guild, and J. Pearson, The Steel Company of Canada, Limited

This paper describes recent fires in the main oxygen distribution system at Hilton Works of the Steel Company of Canada, Limited, in Hamilton, Ontario, Canada.

The oxygen distribution system is of an unusually large size, which briefly contains 4000 ft of 12 in. diameter pipeline operating at 550 psig, 700 ft of 16 in. diameter pipeline operating at 225 psig, and 2000 ft of 10 in. diameter pipeline operating at 160 psig. In addition, there is a gaseous oxygen storage system containing 15 vessels each 9 ft in diameter and 69 ft in height or a capacity of 69 tons available from storage.

Currently about 550–600 tons/day of oxygen are used. The oxygen is delivered by pipeline from a supplier outside the Works in gaseous form and is maintained at a quality of 99.5% or better of oxygen at a pressure of 550 psig.

During the period 1963–1967, the main oxygen distribution system suffered 8 fires. The case history of each fire will make available all that is known as a result of the individual investigation of each fire complete with photographs taken after each fire. We have outlined the probable cause together with changes in design and/or operation taken to prevent a recurrence.

The oxygen fires we have encountered in recent years at first seem to have little common ground. However, after considerable investigation we can offer some definite comments with respect to certain items which appear to be present in nearly all of our fires.

In 7 out of 8 fires, nonmetallic materials were present. In 6 fires, a change in direction of flow at the point of the fire. In 4 fires, high velocity flow was present with the added possibility of the presence of particulate matter.

We found the amount of fundamental data available on ignition of various materials in high purity, high pressure oxygen and the design data for oxygen systems with respect to pipelines, valves, etc. to be inadequate and far less than is required to build and operate oxygen systems to a standard that will guarantee full control and safe operation of the system.

Modifications to our system and work procedures are discussed to show the adjustments made and those planned for the future in order to provide improved security for the oxygen system.

Subject Headings: *Fires, in oxygen lines; Oxygen line fires; Pipeline fires; Steel mill fires.*

Sec. O Old Sec. XIV

Fire Hazards to Urban Areas from Nuclear Detonation—J. Bracciaventi, S. Feldman, and W. Derksen, U.S. Naval Applied Science Laboratory

The Naval Applied Science Laboratory, under the sponsorship and as part of the damage assessment program of the Office of Civil Defense, has conducted a program for the development of a general statement or model for quantitively expressing the interrelationship among the factors that will determine or predict the number and distribution of fire starts among real world arrays of tinder and kindling fuels in urban areas subject to nuclear detonation. Weapons and environmental parameters that are included as input into the fire-start prediction model are practical range of weapon yields, height-of-burst, atmosphere transmission, and recent weather history.

To serve as other necessary input to the fire-start prediction model, the laboratory has determined radiant exposures for ignition of representative urban tinder material when exposed to thermal radiation from nuclear weapons. The material selected included: paper products; woven fabrics of cotton, rayon, wool, nylon, and dacron; wood and miscellaneous material of interest in possible fire situations. In all, 41 different materials were exposed with variations in exposure conditions which resulted in 69 different exposure situations. The materials exposed have such common usage as reading material, packaging, window hangings, clothing, upholstery, floor coverings, and construction materials. The materials were exposed to simulated nuclear detonation pulses of thermal radiation in yield range covered by times-to-maximum irradiance between 0.5 msec and 10 sec.

An additional input, physical surveys of the residential and nonresidential areas of two cities, Providence, Rhode Island and Detroit, Michigan, have been made to determine types, distribution and orientation of tinder and kindling fuels and major fuels by land use class and building occupancies. Structure and geometric characteristics which affect shielding of the fuel and modification of the thermal radiation falling on the target was obtained, too. The data recorded for each site visited by the survey team were building size, construction details such as type of walls, floors, roof, number of stories, number of windows, and building conditions. Information on adjacent sites which affect shielding or shadowing was obtained. Within the rooms, recorded were room size, orientation, window area, exterior view, window hangings, interior tinder, kindling fuels, and major fuels. Exterior tinder and kindling fuels were recorded together with their proximity to major fuels which can be involved in fire spread.

The fire-start prediction model will be developed in the form of a computer program which accepts the above weapon, environmental, critical radiant exposures, and urban parameters as inputs, and whose output is of the form of density and distribution of ignitions.

Subject Headings: *Fire hazards, in urban areas; Nuclear detonations; Urban fire hazards, in nuclear attack.*

Sec. M Old Sec. VIII

Mechanisms of Fuel Ignition by Lightning Discharges—M. Gerstein and F. Kester, Dynamic Science Corporation

Abstract not available.

Ignition Temperatures and Flame Spread Rates of Materials in Oxygen-Enriched Atmospheres*—J. M. Kuchta, A. L. Furno, G. H. Martindill, and A. C. Imhof, U.S. Bureau of Mines

Hot plate ignition temperatures and flame spread rates were determined in oxygen-enriched atmospheres for 10 combustible solid materials likely to be present in hyperbaric chambers. Air, oxygen, and various oxygen-nitrogen atmospheres were employed at pressures from 0.2 to 6 atm. The combustibles included cotton sheeting, cotton sheeting treated with fire retardant, paper drapes, conductive rubber sheeting, blanket wool, polyvinyl chloride sheet, Plexiglas sheet, cellulose acetate sheet, white pine strips, and a Nomex fabric. The ignition temperatures were determined in a 6 in. diameter cylindrical vessel and the flame spread rates in a 2 ft diameter sphere.

Minimum ignition temperatures for all materials decreased noticeably when the oxygen concentration was increased to 42 volume percent or higher. The values obtained in oxygen at 1 atm were comparable to or less than those found in air at 6 atmospheres. A linear relationship appears to exist between the logarithm of the ignition temperature and the logarithm of the oxygen partial pressure for each of the combustibles; however, the dependence on oxygen partial pressure was not great. Cotton sheeting treated with a certain fire retardant was found to ignite in oxygen-enriched atmospheres at lower temperatures than those required to ignite the untreated material.

Most of the test materials did not propagate flame (45° angle burning) in air at 1 atm and required higher oxygen concentrations or total pressure to achieve propagation beyond the point of ignition. All the materials examined in oxygen at reduced pressures were capable of propagating flame at pressures down to at least 0.2 atm. The greatest flame spread hazard, that is, flash-type propagation, was observed with blanket wool in oxygen atmospheres. Its flame spread rates tended to depend more upon oxygen percentage than upon total pressure; the greatest variation was observed at high oxygen percentages ($\geq 42\%$). Also, the rates obtained in oxygen at reduced and elevated pressures correlated fairly well with the oxygen partial pressure.

Subject Headings: *Flame spread, in oxygen atmospheres; Ignition temperatures, in oxygen atmospheres; Oxygen atmospheres, ignition and flame spread in.*

Sec. B Old Sec. I

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* The work upon which this paper is based was sponsored by the Public Health Service, Department of Health, Education, and Welfare.

The Urban Fire Threat of Nuclear Attack—S. B. Martin and R. W. Ramstad, URS Corporation

Abstract not available.

Flammability of Materials in Unusual Atmospheres—J. E. Johnson and F. J. Woods, Naval Research Laboratory

An investigation is underway to determine the flammability of materials under some unusual atmospheric conditions. Ignition and flame spread of several materials have been measured at pressures from 315 psia down to the limiting pressures for ignition. The atmospheres studied have included helium and nitrogen as diluents, with varying percentages of oxygen. The nature of the combustible material has been found to have a marked influence on the variables such as pressure, oxygen content, and diluent on the rate of flame spread. For example, although materials generally have a faster burning rate in helium mixtures than in nitrogen mixtures, there are some significant exceptions to this finding. Minimum pressure limits were obtained for flammability of filter paper in O_2/N_2 mixtures containing 21% and 41% O_2. Not only was the minimum total pressure limit much lower at 41% O_2, but the partial pressure of O_2 at these limits decreased markedly also.

Subject Headings: *Flammability, in unusual atmospheres; Helium (oxygen) atmospheres, flammability in; High pressure atmospheres, flammability in; Ignition, in unusual atmospheres; Oxygen enriched atmospheres, flammability in.*

Sec. B Old Sec. I

Ignition Energy for Condensed Materials—E. L. Litchfield, U.S. Bureau of Mines

Abstract not available

Preignition Mechanism of the Hydrazine-Nitrogen Tetroxide System*—H. E. Perlee, H. K. James, and Y. Miron, U.S. Bureau of Mines

As a result of an investigation sponsored by the Manned Spacecraft Center and conducted at the Bureau of Mines, it was found that hydrazine, monomethyl hydrazine, and unsymmetrical dimethylhydrazine enter into preflame chemical reactions with nitrogen tetroxide. It was established that at pressures below 4 torr hydrazine and monomethyl hydrazine vapors react with nitrogen tetroxide vapor without a flame to form solid deposits of the respective fuel nitrates. Further, unsymmetrical dimethylhydrazine was found to react under similar conditions with the oxidant to form ammonium nitrate. In the case of hydrazine, the reaction

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* The work upon which this paper is based was sponsored by the Manned Spacecraft Center, National Aeronautics and Space Administration.

appears to be:

$$3N_2H_4 + 2N_2O_4 \rightarrow 2N_2H_4 \cdot HNO_3 + N_2O + H_2O + N_2.$$

An extensive study of the physical and combustion characteristics of these preignition reaction products has shown them to represent a definite fire hazard. Hydrazine nitrate is about 1.5 times more destructive per unit weight than TNT, and molten films as thin as 0.01 in. were capable of supporting stable detonations exhibiting both low and high velocities; the high velocities correspond to about 25,000 ft/sec and the low to about 7000 ft/sec. It was also found that water and hydrazine solutions of hydrazine nitrate containing more than 80 weight percent of the solute are capable of supporting stable detonations in films less than 0.01 in. Thicker films of the hydrazine solution support detonations in mixtures having hydrazine nitrate concentrations as low as 25 weight percent. Similarly, for the water solution, stable detonations were obtained in mixtures having solute concentrations as low as 75 weight percent. Physical property studies of the neat nitrates and their water and hydrazine solutions have also been completed.

Subject Headings: *Hydrazine-nitrogen tetroxide reaction; Nitrogen tetroxide-hydrazine reaction; Preignition reaction, of hydrazine-nitrogen tetroxide.*

Sec. H Old Sec. V

Section III

Current Status of Proposed Fire Legislation—A. F. Robertson, National Bureau of Standards

Abstract not available.

Inhibition of Low Pressure Flames—P. H. Vree and W. J. Miller, AeroChem Research Laboratories, Inc.

The effectiveness of a variety of known flame inhibitors has been tested in low pressure methane flames. Both diffusion flames and premixed flames have been employed and the inhibitors studied were 15 selected compounds previously found to exhibit a wide range of efficiencies. Flames inhibited by CCl_4, $Fe(CO)_5$ and CrO_2Cl_2 were examined in detail to determine their spectral emission characteristics, ion content and temperature profiles. The results have been studied in an attempt to elucidate the inhibition mechanisms involved—especially one involving catalytic radical recombination by small particles formed in *in situ.*

The relative efficiencies of the compounds studied have, with few exceptions, been found to be the same in both premixed and diffusion flames at 10^{-2} atm. The criterion for evaluation in both cases was the amount of material necessary to produce extinction. Large differences do exist, however, in the efficiencies of different compounds; e.g., $Fe(CO)_5$ was found to be about 25 times more effective than CCl_4.

Ion profiles in diffusion flames inhibited with CCl_4 include those of a large number of positively-charged hydrocarbon ions, possibly the precursors of soot particles. These ions increase in mass and concentration with increasing distance from the visible flame front. These findings are in apparent agreement with the evidence described by Weinberg[1] in support of an ionic nucleation mechanism for soot formation.

Analogous ion profiles for positively-charged oxidized metallic species were taken in diffusion flames containing $Fe(CO)_5$ and CrO_2Cl_2. Emission spectra of these systems exhibit atomic Fe or Cr lines, FeO or CrO bands and broad continua in addition to the CH, C_2 and OH emissions of normal flames. No spatial resolution is possible in the spherical diffusion flame, but spatially-resolved emission profiles were taken in flat premixed flames inhibited with $Fe(CO)_5$. Emissions from atomic Fe, FeO and a continuum attributed to hot particles are observed in the region upstream of the CH and C_2 bands and well upstream of the temperature maximum.

The results of these studies have been interpreted as indicative that flame inhibition by volatile metallic compounds proceeds via very small particles formed in the relatively cooler, O_2-rich regions of the flame. The dependences of the various emission characteristics on additive concentration were also examined in an attempt to determine the origins of observed chemiluminescence.

Reference

1. Place, E. R., and Weinberg, F. J.: *Eleventh Symposium (International) on Combustion*, p. 47, The Combustion Institute, Pittsburgh, 1965.

Subject Headings: *Flame, inhibition of; Inhibition, of low pressure flame.*

Secs. H, E Old Sec. VII

Fire Extinguishing Agents for Oxygen Enriched Atmosphere (OEA) Applications—

B. P. Botteri, Air Force Aero Propulsion Laboratory

As a result of the Apollo and Two Man Space Environment Simulator Fires, technical effort has been directed by industry and various government agencies toward the investigation of suitable fire extinguishing agents for closed-environment, OEA fire protection applications. This presentation will summarize status of Air Force technical effort on this problem as it applies to fire protection for hypobaric and hyperbaric chambers. Specific aspects which will be discussed include: general theory of fire extinguishing system selection criteria for Air Force OEA chamber applications, applicability of conventional fire extinguishing agents, candidate fire extinguishing agent's effectiveness as established by laboratory-scale experiments, and the results of full-scale hypobaric and hyperbaric fire extinguishing system evaluation tests.

Subject Headings: *Fire extinguishing agents, for oxygen atmospheres; Hyperbaric chambers, fire extinguishers for; Oxygen enriched atmospheres, extinguishers for.*

Sec. E Old Sec. VII

Some Interfacial Surface Characteristics of Fluorocarbon Surfactants and Their Fire Extinguishment Applications—R. L. Tuve, Naval Research Laboratory

In the search for new fire fighting foams, superior to the protein hydrolysate types, a new interfacial phenomenon was discovered involving air foams and water solutions of fluorocarbon surfactants spreading on the surface of liquid flammable hydrocarbons. Utilizing very dilute water solutions of compounds of the type, $C_8F_{17}SO_2NH(CH_2)_3—N(CH_3)_3^+I^-$, air foams were made by a mechanical process and applied to flammable fuel surfaces. Drainage from the foam resulted in surface spreading of the water solution ("Light Water") extending the efficiency of the foam for fuel vapor retention by a factor of at least four times.

The mechanism has been successfully applied to fire extinguishment operations using existing field practices and equipment and in company with potassium bicarbonate dry chemical agents for special fire extinguishment purposes. Efficiencies of three to twelve times that obtainable with other agents have been demonstrated over a wide spectrum of fire protection problems by domestic and foreign fire authorities.

Subject Headings: *Fire extinguishment, by foams and surfactants; Fluorocarbon surfactants; Foams and surfactants, for fire extinguishment; Interfacial characteristics, fluorocarbon surfactants.*

Sec. E Old Sec. VII

The Mechanism of Fire Retardance of Dripping Thermoplastic Compositions—E. V. Gouinlock, J. F. Porter, and R. R. Hundersinn, Hooker Research Center

Abstract not available.

Inhibition of Polystyrene Ignition by Tris(2,3 Dibromo Propyl)Phosphate and Dicumyl Peroxide—C. P. Fenimore, General Electric Research and Development Center

The first pyrolysis products evolved from polystyrene which contains the bromine additive alone are 3 to 7 times richer in bromine than the original plastic, and this initial burst is thought to inhibit the ignition. The addition of dicumyl peroxide increases the inhibition still more—possibly, it has been suggested, because the peroxide concentrates the evolution of bromine into some particularly crucial period where it can poison the ignition still more. Hindersinn, however, attributed the effect of peroxide to its degradation of the hot polymer; the polymer appearing more flame resistant by most test methods because its melt is more fluid and drips more easily. This paper shows that the peroxide has little effect on the evolution of bromine; it supports Hindersinn's views.

Subject Headings: *Dicumyl peroxide and tris(2,3 dibromo propyl)phosphate, inhibition by; Inhibition, of polystyrene; Polystyrene, inhibition of; Tris(2,3dibromo propyl)phosphate and dicumyl peroxide, inhibition by.*

Sec. H Old Sec. V

The Region of Zero Flame Spread—V. A. Dorr, Union Carbide Corporation, Linde Division Research Laboratory

Paper, cotton cloth, and other flammable materials burn readily in air at atmospheric pressure. However, in mixtures of nitrogen and oxygen in which the percentage of oxygen is less than it is in air (20.95%), there is a concentration of oxygen below which the combustion of a given flammable material at a total pressure of one atmosphere will no longer be supported. If we compress the gas mixture which contains the maximum percent of oxygen that will not support the combustion of paper or cotton, there will be some pressure at which ignition takes place and combustion is again supported. Thus a curve can be drawn for percent oxygen vs total pressure, below which not even waxed paper or cotton terry cloth would ignite. A similar curve can be drawn for helium–oxygen mixtures.

We have carried out combustion tests on vertical sample strips ignited at the lower end in dry gas mixtures to represent the most severe conditions for combustion.

Results will be presented for nitrogen–oxygen mixtures over the pressure range 0.5 to 20 atm abs and for helium–oxygen mixtures from 0.5 to 42 atm abs.

Terry cloth proved to be slightly less flammable than filter paper in both diluents. In both diluents, waxed paper was nonflammable under the same conditions as filter paper.

Subject Headings: *Flame spread, region of zero; Helium-oxygen atmospheres, flame spread in; Oxygen enriched atmospheres, flame spread in; Zero flame spread, region of.*

Sec. D Old Sec. V

Flammability of Woven Fabrics—F. J. Martin, General Electric Research and Development Center

Abstract not available.

Lethal Effects of Mattress Fires—K. Sumi and G. Williams-Leir, National Research Council (Canada)

Fatal fires are often attributed to smoking in bed, and it is sometimes found that in some cases the only material consumed is the victim's mattress. The mode of burning of cotton wadding in mattresses ignited in this way is unusual: there is no flame or glow, but heat and smoke are released.

In a series of experiments with varying degrees of ventilation, the products of combustion were measured and the temperature recorded.

On the basis of published information on toxicity, estimates were made of the duration of human survival in each case; this is found to be of the order of one hour either in a sealed room or with the door two inches open.

Some simple passive defence measures against this class of fire were tested and found effective.

Subject Headings: *Lethal effects, of mattress fires; Mattress fires, lethal effects of.*

Sec. K Old Sec. XV

Section IV

Technical Observations of Recent Fires aboard Aircraft Carriers—R. L. Tuve, Naval Research Laboratory

The massive pyrotechnic fire aboard the USS Oriskany demonstrated the blowtorch effect of uncontrolled burning of large quantities of balanced oxidizer-reducer compositions and the production of gaseous hydrogen by decomposition of insufficient amounts of water to cool the reaction or separate the reactants. The damaging effect of high temperature gas travel in ships' passageways was graphically shown.

An unfortunate large-scale fire and explosion consequence ensued aboard the USS Forrestal when a combat-required area loading of fire and heat vulnerable explosive materials could not be segregated except by heroic measures following ignition of a moderately-sized fuel spill. Difficulties of manual fire fighting operations under imminent blast danger, even when excellent equipment is available, have been adequately noted for future design requirements.

Subject Headings: *Aircraft carriers, fires aboard; Fires, on aircraft carriers; Pyrotechnic fires.*

Sec. E Old Sec. XIII

Scaling of Flames above Free-Burning Structural Models—W. D. Weatherford, Jr., Southwest Research Institute

An experimental and theoretical study of the modeling of free-burning structures is described. An analytical model of buoyancy-controlled *nonturbulent* flames is developed and compared with experimental data obtained by burning compartmented structural models. The analytical model predicts the same type of maximum-flame-height correlations as those previously developed empirically for large cribs, and it successfully correlates such burning characteristics for compartmented structural models, ranging in cubical size from 1 to 12 in. Empirical correlations are also developed for burning rate and burning time.

The results of the study raise questions regarding some previously developed concepts relative to the characterization of turbulent and *nonturbulent* flames over a free-burning structure.

Subject Headings: *Flames, scaling of; Models, burning of; Nonturbulent flames, in fires.*

Sec. M Old Sec. VIII

The Spread of Fire in Corridors—J. H. McGuire, National Research Council (Canada)

For at least twenty years tests have existed whereby materials can be given comparative ratings so far as their spread of flame characteristics are concerned. How the results of such tests should be applied, however, has been in some doubt, largely because the average room, hall, or other compartment of a building almost invariably contains sufficient combustible material to allow a fully developed fire to become established. The time scale of the development will be important but doubt again exists as to the nature of its importance.

The corridor constitutes a special case in that it can be designed so that it will not of itself sustain a fully developed fire. The relation between propagation and the flammability of the lining materials was first investigated on a small scale with a model corridor 2 ft square by 16 ft long. It was found that fire involving the whole cross section of the corridor either decisively propagated to the end of the corridor or else proceeded much more slowly and died out before reaching the end. The results of 22 tests indicated that fire would not propagate indefinitely if the flame spread indices of the floor (F), walls (W) and ceiling (C) met the criterion $C+2W+F/2<75$.

Tests using a large scale corridor (8 ft high by 6 ft wide by 64 ft long) showed that floor coverings play much less part in the propagation of fire than on the small scale while walls, in comparison with ceilings, had a rather greater influence. With noncombustible walls and floor, a ceiling with a rating of 130 failed to propagate fire indefinitely. The combination of a ceiling rated at 90 and a floor rated at 250 (fiber insulation board) gave a less severe fire than the previous one and hence indicated that floor coverings have only a limited effect.

Where ceiling and floor were noncombustible, wall linings with a rating of 35 permitted fire to envelop the whole corridor while linings with a rating of 27 did not.

Subject Headings: *Corridors, fire spread in; Fire spread, in corridors.*

Sec. D Old Sec. V

A Narrow Band Ultraviolet Radiation Detection System with a Millisecond Decision Time for Flame Extinction Devices—R. G. Johnson and R. E. Axmark, Honeywell Corporate Research Center

Rapidly igniting or explosive fuels and combustible materials must be quickly detected if extinguishing devices are to be effective. In such applications the extinguishing action must be automatic and false alarms are quite undesirable. Honeywell UV detectors, sensitive in the 1850 to 2400 Angstrom range, have been evaluated in a prototype solid state circuit with fast SCR output. This spectral bandwidth effectively eliminates false alarms that could occur with optical sensors which may respond to sunlight or normal artificial illumination. Detection times shorter than one millisecond are obtainable at seven feet from a 2800 joule stoichiometric gas–oxygen explosion, and effective detection is obtained out to distances of 25 feet without benefit of optical gain in the system.

An application of interest is the detection and suppression of exploding methane-air mixtures in coal mines. A prototype system has been developed for this purpose. In Honeywell laboratory tests, detection times are found to be in the 20 to 30 msec range for a 500 cubic centimeter gas–air explosion with a 1200 joule heat release when viewed at a distance of 15 feet. The circuit provides for a variable discrimination against background signal if desired. This system is now under evaluation at the U.S. Bureau of Mines Research and Testing Center in Pittsburgh.

Subject Headings: *Detector, ultraviolet, for fires; Millisecond detectors, for fires; Ultraviolet detector, for fires.*

Sec. N Old Sec. XII

Sundance Fire—R. C. Rothermel, Intermountain Forest and Range Experiment Station, U.S. Forest Service

The Sundance fire, which was ignited by lightning on August 23, 1967, in northern Idaho, offers a unique opportunity for researchers to study fire behavior. The major run of almost 20 miles occurred within one afternoon and evening under constant weather conditions. Between the hours of 1400 and 2300 on September 1, the fire traveled approximately 16 miles and grew in area from 4000 to 56,000 acres. During this time, the estimated mean gradient wind at the 5000 ft level increased from 23 mph to a maximum of 46 mph at 2200 hrs. before it began to slacken. Relative humidity at this level rose from a minimum of 20% during the afternoon to 30% at about 2200 hrs and continued to increase during the early morning hours of September 2 to a maximum of 62%. This was the first time in 4 days and nights that the relative humidity had gone above 35%.

The Sundance fire was preceded by one of the hottest and driest summers in the Northwest. Many cities experienced new records of highest average temperatures, lowest average humidities, and most number of days without precipitation. The break in the high pressure ridge over the Northwestern States that usually occurs in late August did not occur that year and the summer conditions persisted into mid-September.

A detailed postfire analysis of the behavior of the Sundance fire was made by a research team from the Northern Forest Fire Laboratory in Missoula, Montana. A fire history has been reconstructed from a review of fire and weather records, observations of the fire area, aerial photos, timber records, and eyewitness interviews.

The Sundance fire persistently resisted suppression efforts. By midmorning on September 1, there was an active fire front about 4 miles long, oriented in a general northwest-southeast direction on timbered slopes with a westerly aspect. The major run began about 1300 hrs on September 1 when southwest winds of 22 mph hit the fire area. The fire built up in intensity and moved northeast through a large creek drainage to the main Selkirk Divide. At this time, the average linear rate of spread was 1.6 mph and the fire was releasing between 72 and 145 million Btu per sec.

The fire hesitated near the top of the Divide but many firebrands carried beyond and resulted in spot fires that subsequently burned back toward the Divide. Two men clearing roads in this area were trapped between the spot fires and the main fire front and were unable to escape. The wind continued to increase from the southwest, and the fire continued its run into the Pack River Valley.

Evidence from tree-fall pattern and damage indicates severe fire whirls occurred in the valley near the mouth of McCormick Creek and the Pack River bridge. This area is referred to as the "fire storm area." The convection column at this time, as witnessed by a jet pilot, reached a height of 31,000 ft.

Leaving the Pack River Valley, the fire ran up a major ridge and into a plateau region that included several minor drainages that lay normal to its advancement. The maximum average spread rate was 6 mph up the ridge, with an estimated energy release of 92 to 174 million Btu per sec. The convection column reached a height of 35,000 ft. The time was then 1930 hrs.

Within the next hour, spot fires occurred up to 10 miles ahead of the front. From 2000 to 2400 hrs the fire spread erratically, with many spot fires throughout the final burnout area. The Roman Nose fire lookout was isolated and forced to remain near his tower as the fire burned past. He reported that the fire burned in several areas simultaneously without maintaining a consistent front such as that observed earlier. Near midnight the winds began to subside, the humidity rose, and the fire stopped at the edge of the Kootenai Valley.

Why did the run stop even though the winds were still strong? No single variable appears to be the dominant contributing factor. It is quite apparent that no single theory can explain all of fire behavior, just as there is no single explanation for cessation of the main fire front. The run terminated in an area that was primarily sloping downhill. Some of this area had been previously logged with good slash disposal, thus reducing the amount of available fuel. Although there was still considerable unburned fuel available for the fire's progress, there was less continuity of fuel than there had been earlier in the run. This condition was intensified by the fire itself, which, through its own spotting, was in effect causing backfires and building its own fireline. As a result, the available fuel apparently could not maintain a sustained fire front throughout the area. Another contributing factor in the cessation of the main fire front is the rise in relative humidity that occurred at this time. This phenomenon is still not well understood. One would not expect that the rise in relative humidity could have an effect sufficient to stop a major fire of this size; however, in other fires there have been indications of a marked reduction in ability to propagate by spotting when relative humidity rose above about 30%.

In any attempt to interpret and explain the behavior of this fire, one of the most interesting problems is the development of spot fires 8 to 10 miles ahead of their probable source. In a discussion of the fire whirls and vortices that form on the downwind side of a convection column, Professors Berlad and Lee of New York State University suggested that perhaps these vortices form and move downstream in a manner similar to that of a Von Karmen vortex street. After further study of the spot-fire pattern downwind of the main fire area, they proposed that these streaming vortices might be the mechanism for carrying firebrands long distances. This is opposed to the hypothesis that firebrands are carried to some sufficiently high altitude in the convection column and then ejected into the freestream, where they fall, and depending upon their burning rate and size, have some potential distance to travel while still burning.

Several pieces of evidence gathered before the establishment of the vortex hypothesis offer previously unrecognized support for it. Among these are the observations of a Forest Service employee driving a pickup truck in the region downstream from the main convection column. When questioned about any unusual fire behavior, he said it was the winds, that they were terrific in this area, and that on several occasions he was forced to stop his truck to wait for large and intense dust devils to move past. The dust devils were estimated to be from 10 to 25 ft in diameter. We interpret the dust devils to be minor swirls shed from large-scale vortices traveling with the gradient wind. The most significant observation was that made by the fire lookout on Black Mountain, who observed the initiation and growth of the large spot fire in the mouth of Snow Creek. He reported that it seemed to start in a single tree and then grew very rapidly, spreading in all directions with a circular motion.

The exact details of how firebrands would be carried in such vortices have not been worked out, but initial study in this area has already been done by Dr. Lee. This subject is discussed further in the paper by Berlad and Lee, "Long-Range Spotting."

Subject Headings: *Firebrands; Forest fire; Mass fire; Sundance fire.*

Sec. J Old Sec. X

Long Range Spotting—A. L. Berlad and Shao-Lin Lee, State University of New York at Stony Brook

An increasing body of evidence confirms that large forest fires can be spread by transport of firebrands over ranges of the order of ten or more miles.

The spotting transport process associated with such long ranges is considered in the light of both current and past observations and it is concluded that successful long range ignition derives from:

(a) Firebrands that support glowing (surface) combustion.
(b) Firebrand structures that stabilize easily within vortices (are not easily centrifuged).
(c) A firebrand trajectory that is prescribed largely by the firebrand containing vortex street. The vortex street is supported by a very large vertical convection column which is in turn sustained by a strong prevailing wind and a high surface burning rate.

Subject Headings: *Firebrands, long range; Spotting of fires, at long range.*

Sec. D Old Sec. V

Fundamental Combustion Research as Related to Airplane Safety—R. Laustsen, The Boeing Company

Airplane safety because of its tremendous importance has always required constant effort in design. Historically this effort has been primarily the use of good engineering sense—to isolate probable fire zones with fireproof barriers, eliminate ignition sources, utilize fireproof materials, starve fire zones of oxygen or fuel, use fire extinguishing systems, use flame arresters, etc. This has resulted in an excellent safety record for commercial aviation.

To fulfill our desire to do more toward safety there must be an extension of knowledge of flame propagation and flame quenching as related to airplanes. We at Boeing feel we are nearing a plateau in what we can accomplish considering the present state-of-the-art. Fire research must be fundamental in nature to allow creation of mathematical models useful to analysis; simulation testing is not good enough because it usually "lumps" the variables and does not provide as good a basis for valued judgment for analysis of different situations.

Dedicated to the analytical rather than empirical approach we are addressing ourselves to fire safety problems. Two typical areas are (1) flame propagation and arrest in vent systems using reticulated polyurethane foam and (2) extinguishment of fire by "Light Water" (a fluorocarbon surfactant foam).

We soon became painfully aware of our own lack of fundamental information. In arresting flames in vents we did not know the mechanism by which our material quenched flames. We knew very little of the nature or speeds of the flames that could be encountered and we were not aware of all the parameters affecting the flames. In the Light Water work we did not know the relative effects of the controlling parameters relative to overall fire-airplane configuration or how the foam was affected by fire.

We now see a need for considerable fundamental knowledge related to airplanes; a list of some areas is as follows:

Flame Propagation

Acoustic effects (vibrating flames)
1. How flame causes acoustic waves.
2. How acoustic waves affect propagation.
3. Geometry effects.

    Flame speed
        Parameters involved (particularly dynamic pressure oscillation)

    Flame fronts
        Characteristics

    Role of mixture composition or fuel surface films

Flame Arrest

Mechanism
Parameters controlling each mechanism
Effect of mixture temperature on flame arrest

Ignition

Autogenous
Heat or spark

Fires (open)

Characteristics (mathematical representation)
Effects

Fire Extinguishment

Mechanisms

We visualize a very large effort required. We also feel that the nature of the needed information is such that all available, and interested, talent in the country should be utilized to the greatest extent possible. The benefits, however, are in the same proportion. The entire aviation industry will benefit, all phases, commercial and military, and we can expect considerable fall-out to benefit non-aviation industry as well.

Subject Headings: *Airplane safety, and combustion research; Combustion research, and airplane safety.*

Sec. O Old Sec. XIV

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Volume 10 Number 2

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FOREWORD

This issue begins with a Review entitled "Fire Research Abroad," by Professor Howard Emmons of Harvard University, chairman of the Committee on Fire Research. During the past year he has visited most of the major fire research establishments in the world. This paper is a condensation of a more extensive report which is also reviewed in this issue. His impressions provide a valuable survey of world fire research. These papers reinforced your editor's opinion that too little fire research is undertaken and that many of the present studies should be more firmly connected with basic science on one side and with real life problems on the other side. These shortcomings are not due to blindness on the part of the investigators; to the contrary, most of these men are acutely aware of the shortcomings of the work. The difficulty lies with the constraints under which most fire problems are investigated. They are usually undertaken with limited funds earmarked for specific objectives. This precludes both extensive study of the fundamentals of the problem and full-scale investigations to connect the tests with real world problems. Achieving a reasonable balance between long- and short-range research seems as pressing a problem as expansion of the over-all effort in the fire field. Too much of the present work is so involved with immediate problems that it contributes very little to the ultimate understanding of fire.

Fire research efforts vary from country to country, but even work in such advanced countries as England and Japan suffers from lack of appreciation by the public and by the fire services who should be their stanchest supporters. There is truly a massive educational problem in the field.

Several meetings of interest to the fire research community have been scheduled. This fall the Western States Section of the Combustion Institute has scheduled a meeting with "Chemical Kinetic Calculations" as a subject. The Central States Section of the Combustion Institute has scheduled a spring meeting with the title "Fire Research—Experimental and Analytical Modeling of Fires" and the Eastern Section of the Combustion Institute has scheduled a fall meeting with the title "Heterogeneous Combustion." The American Chemical Society offers two symposia this fall: "Fundamental Processes in Gas Kinetics" and "Physical Chemistry of Gaseous Fuel Oxidation." In Sweden a symposium is scheduled for next April with the title "Corrosion Risks in Connection with Fires in Plastics." Details will be found in the section on meetings.

R. M. Fristrom, *Editor*

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REVIEWS

Fire Research Abroad

HOWARD W. EMMONS
Harvard University

Abstract

Between September 6, 1966 and January 11, 1967, one-day visits were made to 42 organizations in 11 countries. These organizations are engaged in all phases of the fire problem: fire protection, fire fighting, fire testing, fire equipment manufacturing, fire training, and fire research. This report summarizes the findings and discusses the strengths and weaknesses of the fire effort abroad.

Introduction

The enormous waste occasioned by the unwanted fire falls into two broad classes—urban and forest. Although my study abroad included both types, my report here will be confined to the problems of the city fire. Even this part of the problem is too broad for more than a brief treatment, in view of the wide range of materials and processes in use in a modern society. I will attempt to paint a general picture of the present state of fire research abroad, discuss several specific illustrative examples, and state my general conclusions.

Nature of the Fire Problem

One cannot evaluate research in a vacuum. Its importance can only be judged relative to the problem to which it is addressed. Let me first lay out the fire problem in a way which will disclose its full nature and permit us to see what fire research is and is not doing, can and cannot do. Table 1 looks at an unwanted fire from initiation to clean-up and tries to recognize in separate columns the nature of:

A. The Practical Problem as encountered by the citizen, the fireman, the architect, the business man.
B. The Basic Processes that occur during the course of the fire which by their effects produce the Practical Fire Problem.
C. The Fundamental Phenomena in the sense of classical physics which occur in the Basic Processes and determine their quantitative and qualitative nature.
D. The antics of Electrons, Atoms, Molecules, and Quanta for want of a better name. It is the various atomic events which cause the macroscopic phenomena called "Fundamental" to occur as they do.

Table 1 is not complete. Many more items can be added in each column. I have tried to put in sufficient material to make clear the meaning of the 4 levels of technical problem identification. Each level is subject to research potentially leading to solutions of some part of the practical problem. Each level is a more obvious and practical effect of the level in the column to the right, and through its effects produces the still more obvious and practical effects in the column to the left.

TABLE 1.

A classification of the urban fire problem

Stage of fire development	A Practical problem	B Basic processes	C Fundamental properties and phenomena	D Electrons, atoms, molecules and quanta
		Growth of hot spot		
	Prevention	Decomposition processes		
	Rating appliances	Spontaneous combustion	Decomposition and combustion reactions, reaction kinetics, and products	Atomic and Molecular organization in materials
Initiation	Materials selection	Combustion process		
	Detection	Fire spread process by glowing, by flaming		
Initial growth	Supression by novice	Smoke production	Properties and chemistry of inhibitors	Crystal structure, wood atomic structure
	The fire department	Natural convection		
	Ventilation for safety	Effect of fuel geometry	Thermodynamic properties	
Spread in enclosure	Suppression (automatic)	Radiation heat transfer		Energy levels, atom and electron mobility
	Rate of value	Model laws for fire tests	Transport properties	
Flash over	Destruction	Forced and natural convection in ventilation systems and stair wells	Heat and mass transfer by Conduction Diffusion Convection	
	Suppression by experts	Extinguishment by water		Production and absorption of phonons and photons

Spread to other rooms	Ventilation (fire safety)	Fire spread through walls		
	Fire stops	Natural convection through openings	Emission, transmission absorption and scattering of radiation for both heat transfer and communication	
	Life safety	Toxic effects of gases		Atomic and electronic details of reaction
Spread to other buildings	Prevention by design	Radiation production		
	City planning	Radiation ignition	Thermodynamics of phase changes	
	Ventilation (fire spread)	Thermal and decomposition		Mechanisms with and without O_2, with and without inhibitors
Rapid combustion	Explosion hazard	Distortion of structures	Surface tension effects: drop formation, jet spread, foam formation, agglomeration	
	Strength of structures	Air flow through opening		
	Safety of structures	Heating of structure		Nucleation of phase change
Burnout	Conflagration control	Spalling	Strength of structural materials at high temperature	
	Let it burn?	Model laws for heated structures		
Clean-up	Loss evaluation	Discoloration by smoke	The dynamics of collapse by heating, by explosion	Dislocation formation and movement
	Evidence of cause	Sound transmission in damaged structures		
	Salvage	Distortion by explosion		

The Visits

During the second six months of 1966, 42 laboratories were visited in 11 countries of Asia and Europe. To state even briefly all that they are doing makes a big report.* The Appendix lists the laboratories.** These include a few fire departments, a few equipment manufacturers, a couple of fire colleges, various kinds of testing laboratories, and a few research laboratories. The universities visited were those at which colleagues or my former students now work and were not necessarily doing fire oriented work. The visits included large and small laboratories, and institutions supported by private industry, or government, or both.

Figure 1 shows approximately how current efforts are distributed over the 4 levels A, B, C, D of Table 1. The shaded area shows the distribution of man hours, while the cross-hatched area shows the distribution of laboratories. Each laboratory was listed in each column in which it was working; some laboratories were listed 4 times, others only once.

Figure 2 shows how current efforts (manpower) are directed toward various parts of the fire development. A special category "Extinguishment" is introduced because it is an obvious one to the general public, but receives scant assistance from laboratories.

The Results

One might suppose from Figs. 1 and 2 that the practical problem of the collapse of structures was THE most important fire problem in view of the attention it receives. There is no denying its importance. However, it would seem even more important to discover how fires start and how to design buildings to prevent their growth and spread. Let me mention a few of these ignition and growth problems.

Spontaneous combustion by the oily rag has almost passed into history now that saturated petroleum products have, for many purposes, replaced unsaturated oils. However, it is not commonly known that wood can spontaneously ignite in air. A two-inch diameter sphere of solid wood is covered all around with 2 inches of mineral wool insulation and is put into a furnace at 180°C (355°F). The wood temperature rises rapidly to the furnace temperature, then very slowly for 5–8 days and then goes on up to rapid combustion temperature. This means that wood oxidizes rapidly enough at just a little above the water boiling point to accumulate heat if some insulation is provided. Occasional fires have been traced to this cause. It would seem important to relate these tests to the known data on wood decomposition, but this step has not yet been taken.

Only a small amount of work has been done on the spontaneous ignition of the many new materials coming on the market, and almost nothing is known of the effect of oxygen enriched (space craft) or oxygen deficient (vitiated air extinguishment) atmospheres. More work is needed.

What would appear as an obvious must is the evaluation of the combustibility of building materials. There are some eight different standard "tests" in as many countries. An informal comparison of results showed various disagreements, so an international group, a committee of I.S.O., selected 24 more or less combustible materials and sent them to all the laboratories which were asked to arrange them in order of combustibility; 1—most combustible, 24—least combustible. The

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* See page 144.

** No laboratories in Russia were visited because they did not answer their mail.

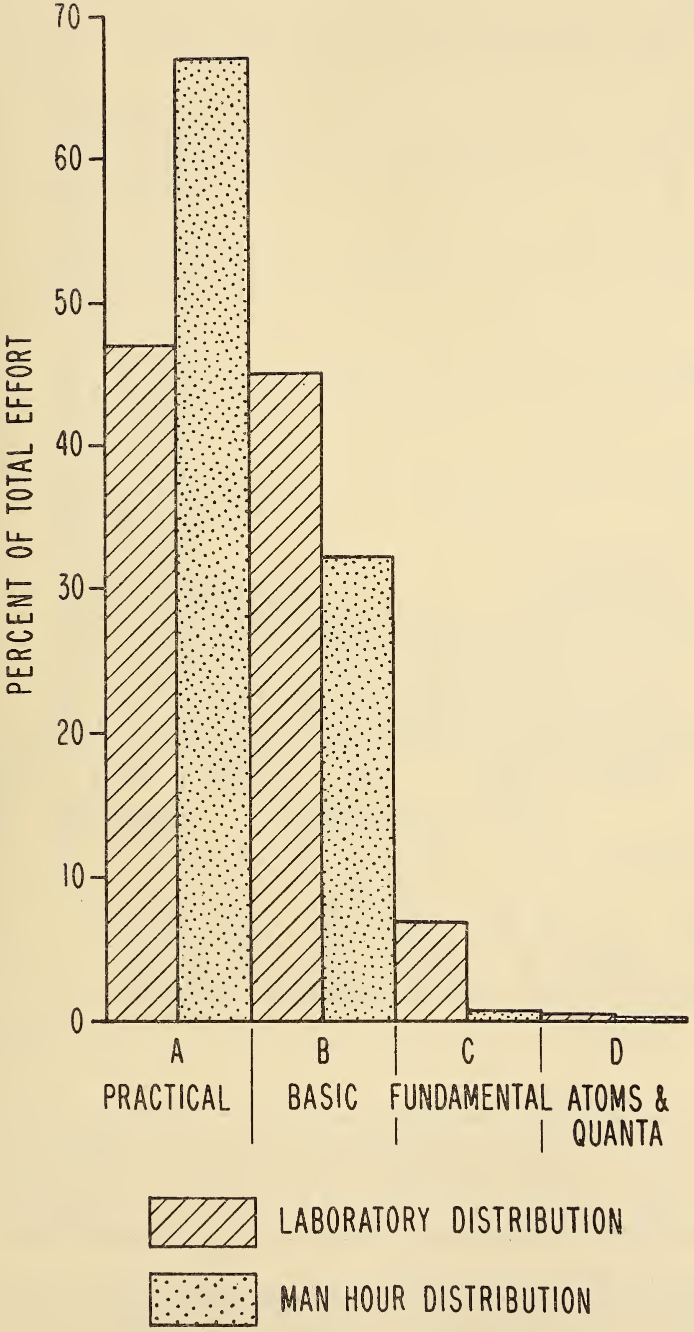

Fig. 1. Distribution of effort in urban fire problems according to classification of effort in Table 1.

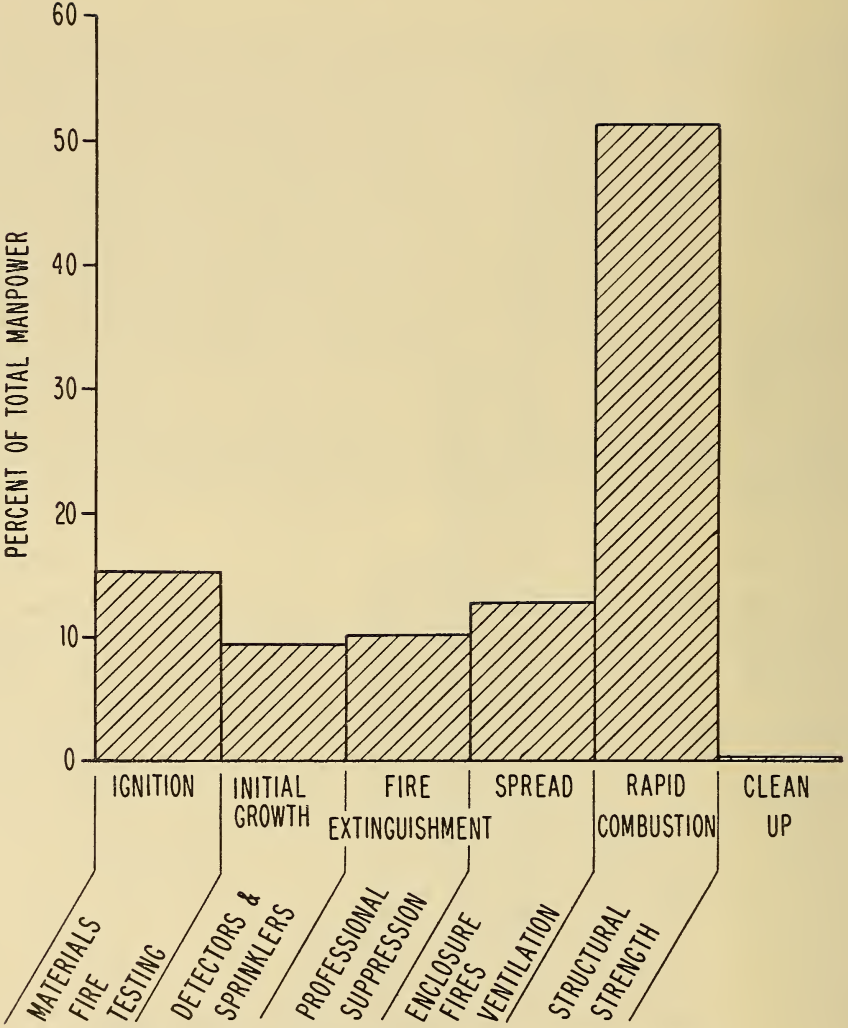

Fig. 2. Distribution of manpower effort toward various parts of fire development.

results are shown in Table 2. Just casual inspection reveals the poor agreement. In fact, the two tests of Denmark and Germany moves #16, phenolic foam an inch thick, from most to least combustible, while the same two tests move material #13, acrylic sheet, from near the bottom to near the top in the *opposite direction.* A statistical analysis of results shows the mean binary correlation coefficient to be only 0.44.

To show graphically just how bad the present agreement is, the test data is plotted in Fig. 3. Here, for each material, an average relative rating was calculated and used for the "combustibility" order of the materials tested i.e. the independent variable. If all tests agreed on the relative fire danger of these materials, all points would lie on the 45° line. Even perfect agreement in this figure would not be im-

TABLE 2.
Relative rating of 24 materials by 6 different national standard fire rating tests

No.	Material	Thickness m.m.	Treatment	Germany	Belgium	Denmark	France	Nether-lands	England	Average position
1	Flexboard	25	No	9	7	9	10	9	10	5
2	Flexboard	25	Yes	20	19	21	20	17	12	20
3	Hard-board	4	Yes	7	13	14	18	15	16	14
4	Hard-board	4	No	16	20.5	8	2	4	13	12
5	Plywood	6	Yes	10	15	19	9	10	17	15
6	Plywood	20	Yes	14	16	17	13	16	18	17
7	Plywood	6	No	5	6	10	3	8	8	4
8	Plywood	20	Yes	8	10	12	11	11	7	9
9	Particle board	20	No	12	12	13	8	5	3	13
10	Expanded polystyrene	20	No	15	1	4	17	21	1	8
11	Expanded polystyrene	20	Yes	23	5	5	16	23	23	19
12	Phenolic paper laminate	1.5	No	6	9	16	5	12	6	6
12a	Phenolic paper laminate	15	Yes	19	22	15	22	22	14	21
13	Acrylic sheet	3		3	2	22	1	7	22	7
14	Particle board	25	Yes	13	14	11	7	6	9	10
15	Wood wool/cement slab	25	Yes	18	23.5	23	24	24	24	24
16	Phenolic foam	25	No	24	23.5	1	21	19	19	18
20	P.V.C. sheet	1.5		21	18	10	19	18	21	22
21	Hard-board	12	Yes	22	20.5	24	23	20	15	23
22	Particle board	3.5	No	4	11	2	4	2	2	1
23	Particle board	5	Yes	17	17	3	15	13	20	16
24	Flexboard	10	No	11	3	6	6	3	4	2
25	Polyester/glass laminate	1.5	No	1	8	7	12	1	5	3
26	Polyester/glass laminate	1.5	Yes	2	4	18	14	14	11	11

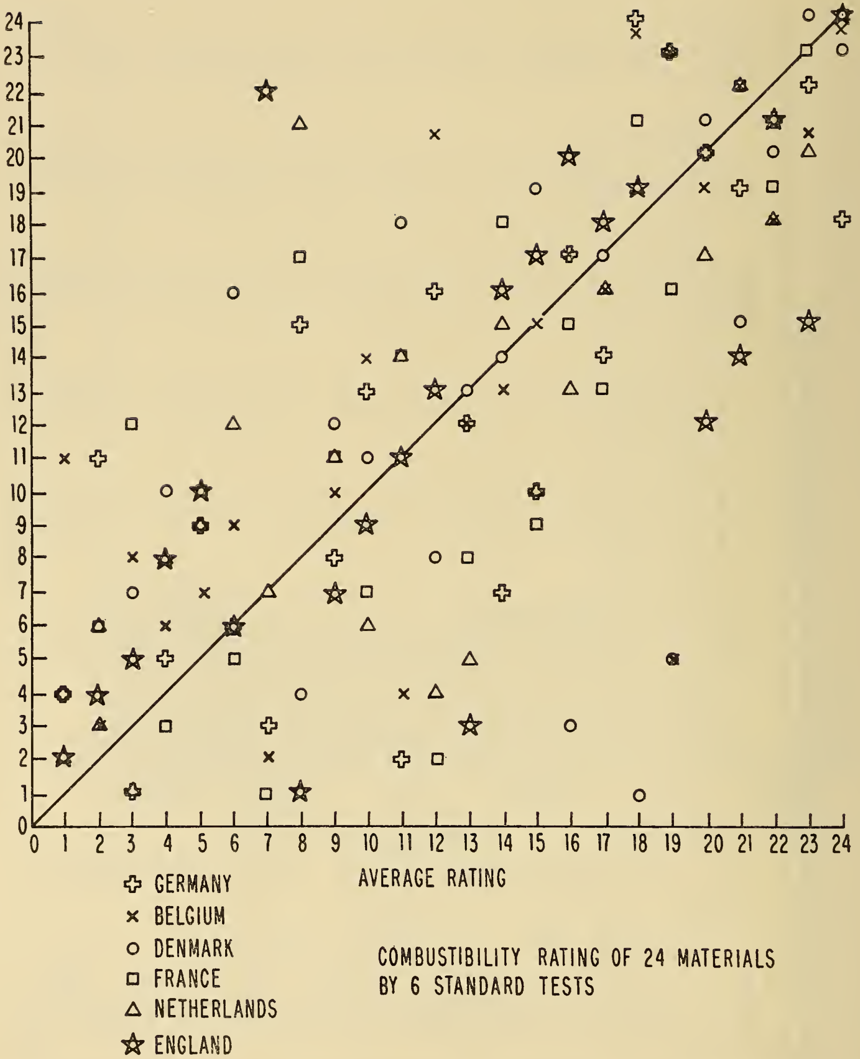

Fig. 3. Relative combustibility ratings of materials by national fire tests in 6 different countries.

pressive, since Fig. 3 considers relative rating only and not any absolute scale. But as you see, the test results fall far from the 45° line. To see just how bad this agreement really is I show Fig. 4 constructed in *exactly the same way* except that the "test data" on relative rating of 24 fictitious materials by six fictitious laboratories was obtained by drawing 24 numbers from a hat. Fig. 4 is pure random data with *no* significance. It is a little worse than the real data of Fig. 3, but not much.

Such profound disagreement between serious attempts to measure combustibility points out better than any argument that we really don't know what we are talking about when we say "this is more combustible than that"; "this is a more safe building material than that." It is not clear that the many factors that may be

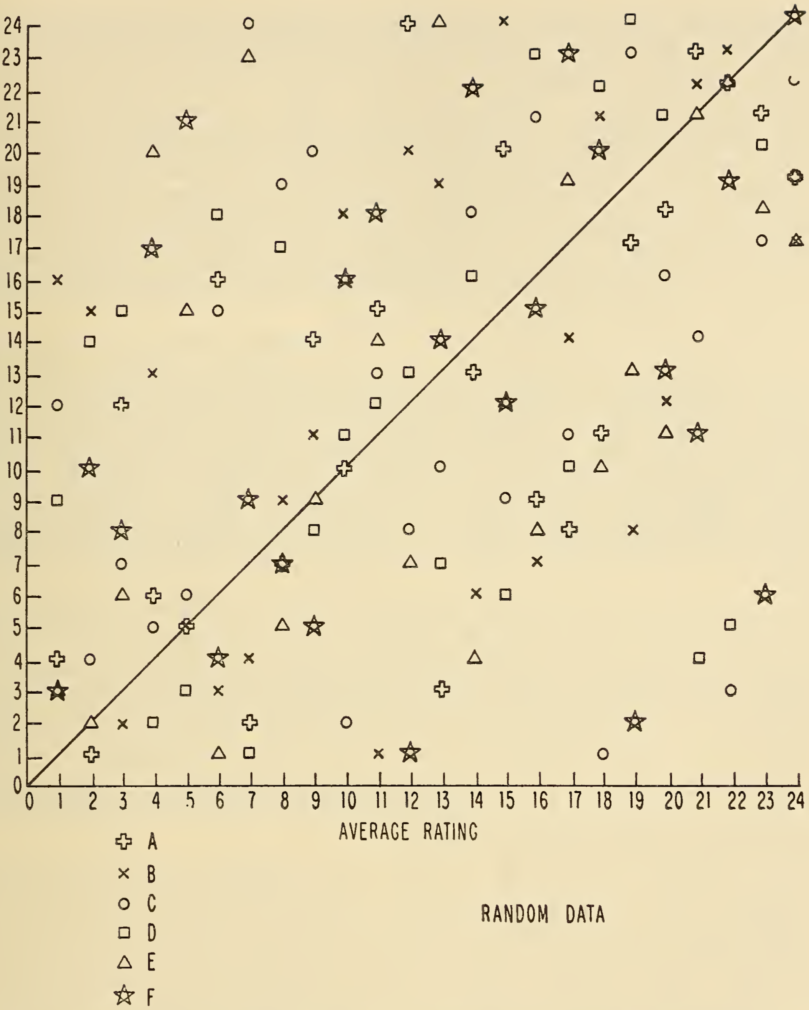

Fig. 4. Random combustibility test data on 24 fictitious materials by 6 fictitious laboratories.

important: ease of ignition, rate of burning, smoke production, transmission of heat, etc., can in any practical way be expressed as a single number, whether we like it or not.

What we need at the present time is a considerable research program at the practical, basic, and fundamental levels, in order to find out what we really do want to know. After this is done it will be easy to devise one (or a series) of internationally agreed upon tests. To devise any test before we know what we want is to risk making, with much test effort, a handbook for material's combustibility which must be thrown away when future studies show the tests to be inadequate or worthless.

It is, of course, clear to all of the test groups producing this data that the different "standard" tests really measure different mixes of different physical properties and phenomena. What is not now clear is just which properties and phenomena are really essential in a building fire.

As another example, let us look at the very active area of fire strength of structures. Reinforced concrete floor panels are tested in some laboratories by being built into a sturdy frame which puts considerable constraint on the edge of the panels when they expand from heating. A certain panel thus tested carried its load four hours before collapsing. In another laboratory an identical panel, built without a frame and tested with simple supports all around, collapsed in one hour. In this second laboratory they say that obviously panels must be tested with simple support if the test duration results are to be valid.

In fact, however, no such conclusion is at all obvious. What we really want to know, and what fire codes should really require, is that the building, *as built*, have a two-hour or four-hour or some other rating. The engineer who computes with fair precision the strength of the structure as needed to support the anticipated use (standard) load, also should be required to compute or otherwise determine that the structure is safe in a fire for a specified time. The fire strength tests with or without restraint are model tests. To be useful they must be corrected, like any model tests, for longer or shorter span, for more or less restraint, as used in the real building.

At the present time no one has any idea of how to make such corrections and *nowhere is there any program of tests designed to find out how to do it.* The British Fire Research Laboratory is considering some test work along these lines. All other laboratories abroad fall into two classes. Either the head of the laboratory sees the inadequacy of the present test procedures and laments that the heavy routine test schedule and budget limitations prevent him from undertaking any effective more fundamental study of the problem, or the laboratory has been so heavily loaded with routine testing for so many years that the head of the laboratory and all of his assistants have stopped thinking.

As a last example, let us look at some of the fireman's needs. The technique and equipment now provided the fireman are largely those which have evolved from antiquity. He no longer uses buckets, nor hand raised ladders for the 5th floor of a building. But he is not provided with the equipment which modern technology makes possible. Why should a fireman have to make hydraulic calculations at a fire? The pumper should have valves to set at the nozzle size used and should then provide the required *flow* (within safe pressure limits). Why should the fireman at the controls of an aerial ladder strain his eyes to see how close the top of the ladder is to the 8th floor window sill? A light at the top of the ladder could fully illuminate the building and an optical periscope (or closed circuit T.V.) could put the image of that window sill within a foot of his eyes. A man in Houston, Texas, can manipulate a space ship photographing the moon but the fireman must climb up to the top of a 100 foot ladder to find out just where it is. Ridiculous! Why should the fireman risk his life entering a smoke filled building to seek out and control a fire? In fact, in some cities the firemen rarely do fight the fire inside unless someone must be rescued. And yet further work with breathing apparatus could make it lighter, with better communications (using electronics not megaphones), and with better seeing in spite of the smoke (using infrared or microwaves).

In spite of all these obvious potential contributions from modern technology, who is working on them! In first approximation *No One.* Actually a little work along these lines is done as always by various firemen. But their business is fighting fires, not the science and engineering of modern technology. We don't ask the pilots to design their new supersonic aircraft and we don't expect the astronauts to design the space ships. The fireman is just as important to our society and deserves the same assistance. A little work is done now and again by equipment manufacturers but here the market is so limited and the competition so keen that more often he resists the expense implied by the urgent demands of firemen for modifications of his new equipment. Finally, I should mention the fact that in both England and Japan the support of fire studies is sufficiently great and sufficiently broad that some work on the fireman's problems is possible and is being done.

Conclusions

Almost everywhere the proper application of modern technology to the fire problem is hampered by grossly inadequate budgets. As a consequence only in very limited areas has enough practical and basic work been done to provide a reasonable foundation for present-day practices and even in these areas many important basic ideas remain unexamined. In most areas, such glaring uncertainties remain, that present practices may be worse than useless, since a routine satisfying of incorrect requirements gives one a false impression of security.

Acknowledgments

This work was supported in part by the National Science Foundation under Grant GK-771, and by the Division of Engineering and Applied Physics, Harvard University.

Subject Headings: ***Fire research; World fire research.***

Fire Research—A Trip Report

H. W. Emmons, Harvard University, Cambridge, Massachusetts 1966–67. Report No. 1. N. S. F. Grant, GK 771. 481 pp.

As indicated by Professor Emmons in the preceding review, he has made an exhaustive study of fire research by devoting a sabbatical year to visiting the major fire research laboratories of the world. His experiences and impressions have been collected in an extensive report to the National Science Foundation.* This document provides one of the most extensive surveys of fire research in recent years, and Professor Emmons' perceptive comments provide a good perspective of the field. It includes a list of laboratories outlining their facilities, personnel, interests, and views. Information on laboratory organization and budget are also included. This report is an invaluable source of information on the fire research effort of the world and anyone interested in understanding the present status of the field should study this document. A major gap in Professor Emmons' coverage is the Soviet Union, where he was unable to obtain permission to visit laboratories. This is unfortunate but the omission is, partially, filled by an earlier report of Mr. D. I. Lawson, Director of Great Britain's Boreham Wood Laboratory (See *Fire Research Abstracts and Reviews* 7, 1, 1965).

A list of laboratories visited by Professor Emmons is given below.

Laboratories Visited by Professor Emmons

Australia

Commonwealth Experiment Building Station
Chatswood, New South Wales

Forest Research Institute
Forestry and Timber Bureau
Canberra, ACT

Commonwealth Science and Industrial Research Organization
Melbourne

Australian Fire Protection Association
Melbourne, C.1 Victoria

Institute of Forest Research and Protection
Perth

Canada

National Research Council of Canada
Ottawa, Ontario

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* Copies of this report can be obtained by addressing Prof. H. W. Emmons, Pierce Hall, Harvard University, Cambridge, Massachusetts 02138.

Denmark

Statsproveanstalten
Copenhagen

Københavns Brandvaesen Laboratorium
Copenhagen SV

Dansk Brandvaerns-Komite
Copenhagen-Valby

England

Joint Fire Research Organization
Boreham Wood, Herts

Fire Service College
Dorking, Surrey

Mather and Platt, Ltd.
Manchester

France

Centre Scientifique et Technique du Batiment
Paris

STELF-Station D'Essais-Laboratorie du Feu
Champs-sur-Marne, Seine-et-Marne

Centre Technique du Bois
Paris

Germany

Institut fur Holzforschung und Holztechnik
Munich

Forschungsstelle fur Brandschutztechnik
Karlsruhe

Institut fur Baustoffkunde und Stahlbetonbau
Braunschweig

Bundesanstalt fur Materialprufung
Berlin

Bundesforschungsanstalt fur Forst-und Holzwirtschaft
Hamburg

Institut fur Elektrische Nachrichtentechnik
Aachen

Technische Prufstelle des Verbandes der Sachverscherer E.V.
Koln

Holland

International Flame Research Foundation
Ijmuiden

Brandveiligheidsinstituut, T.N.O.
Delft

India

National Aeronautical Laboratory
Bangalore

Indian Institute of Science
Bangalore

Defence Science Laboratory
Delhi

Indian Institute of Technology
Kanpur

Italy

University of Naples
Instituto di Scienza delle Construzioni
Naples

Centro Studi ed Esperienze del Servizio Antincendi
Rome

Japan

Building Research Institute
Tokyo

Fire Research Institute
Tokyo

Tokyo Metropolitan Fire Board
Tokyo

International Symposium on Boundary Layers and Turbulence, Including Geophysical Applications
Kyoto

Spain

Instituto Nacional de Technica Aeronautica
Madrid

Sweden

Statens Provningsanstalt
Stockholm

Switzerland

Cerberus, Ltd.
Maennedorf

United States

Factory Mutual Engineering Research Corporation
Norwood, Massachusetts

Sudbury Fire Department
Sudbury, Massachusetts

11th International Symposium on Combustion
Berkeley, California

University of California
Berkeley, California

U. S. Naval Radiological Defense Laboratory
San Francisco, California

Pacific Southwest Forest and Range Experiment Station
Berkeley, California

Pacific Southwest Forest and Range Experiment Station
Riverside, California

University of Maryland
College Park, Maryland

National Bureau of Standards
Washington, D. C. and Gaithersburg, Maryland

U. S. Naval Research Laboratory
Washington, D. C.

Southeastern Forest Experiment Station
Macon, Georgia

Southwest Research Institute
San Antonio, Texas

Flame Dynamics Laboratory
Norman, Oklahoma

Prescribed Fire Research Project
Forestry Sciences Laboratory
Flagstaff, Arizona

Los Angeles Fire Department
Los Angeles, California

National Fire Protection Association
Boston, Massachusetts

Bureau of Mines
Pittsburgh, Pennsylvania

Portland Cement Association
Skokie, Illinois

Underwriters' Laboratories, Inc.
Northbrook, Illinois

Illinois Institute of Technology and IIT Research Institute
Chicago, Illinois

Chicago Fire Academy
Chicago, Illinois

Forest Products Laboratory
Madison, Wisconsin

Northern Forest Fire Laboratory
Missoula, Montana

Equipment Development Center
Missoula, Montana

Pacific Northwest Forest and Range Experiment Station
Seattle, Washington

R. M. Fristrom, *Editor of FRAR*

ABSTRACTS

A. Prevention of Fires and Fire Safety Measures

"Electrical Apparatus in Flammable Atmospheres," *Electr. Rev. 181*(8), 280 (1967)*

Abridged from the Annual Report of H.M. Chief Inspector of Factories 1966. The report discusses the safe use of electrical apparatus in places where the atmosphere may contain petroleum or other explosive vapours. Safe methods mentioned are the use of non-sparking construction, flameproof enclosure and intrinsic safety systems.

Subject Headings: *Electrical apparatus, in flammable atmospheres; Flammable atmospheres, electrical apparatus in.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(1), 29. By permission.

Brown, F. (Shell International Petroleum Company) and **Haxby, L. P.** (Shell Oil Company) "Added Safety in Aircraft Fueling," *Fire Technology* 3(3), 232–240 (1967)

In spite of the fact that most authorities recognize the potential hazard of electrostatic ignition during aircraft fueling, the adoption of the antistatic additive approach to safety may seem to have been somewhat slow. This has been partly due to the need to convince all concerned that the additive is effective and does not introduce any new hazards or economic penalties and also to some extent, due to the scarcity of dramatic incidents involving static electricity. However, a number of accidents—some 50 involving JP-4 and one associated with kerosene—have been reported, and these have helped to remove the earlier complacency.

There is no doubt that a potential hazard does exist and that the higher fueling speeds required for the next generation of civil aircraft, such as the Jumbo Jet and the SST, will tend to aggravate the hazard.

An inexpensive and effective means exists for eliminating the risk. In practice, it has been demonstrated that there are no undesirable side effects, and it is suggested that we can no longer afford not to take this simple precaution to eliminate a potential hazard.

Subject Headings: *Aircraft, fueling safety; Safety, aircraft fueling, antistatic additives.*

Authors' Conclusion

Burgoyne, J. H. "Designing for Protection against Dust Explosions," *Chemy Ind.*, 854–858 (27 May 1967)*

The Ministry of Labour classifies dusts into three Classes: (I) those which ignite and propagate flame readily, the source of heat required for ignition being small; (II) those which ignite readily but require a larger source of ignition; and (III) those which do not ignite in the tests described by K. C. Brown in SMRE Research Report No. 21. To illustrate the problems and suggest solutions the author takes the case of a new large powder-handling plant being built in which all possible steps are taken to minimize the effect of a dust explosion. In conclusion, measures are indicated for the elimination of sources of ignition.

Subject Headings: ***Dust explosion; Explosion, of dust.***

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(4), 17. By permission.

Craven, A. D. and Foster, M. G. (ICI Fibres Limited, Harrogate, Yorkshire, England) "Dust Explosion Prevention—Determination of Critical Oxygen Concentration by Vertical Tube Method," *Combustion and Flame* **11**(5), 408–414 (1967)

The primary purpose of this paper is to shed light on flame propagation in organic dusts or powders. In the plastics and synthetic fibers industries, storage of large quantities of polymers and their intermediates in the form of finely divided powders has become common practice. Since most of these powders are flammable, the potential dust explosion hazard is constantly present. Usually vents are provided at strategic points to relieve an explosion if one should occur. Ignition sources are not ordinarily present, but certain powders have very low minimum ignition energy. Therefore, ignition could occur by static sparks generated internally by dust movement. An alternative to the provision of relief vents is to reduce the oxygen concentration in the powder-handling system to a level that will not support the propagation of flame. There seems to be a great deal of uncertainty about the maximum oxygen concentration which can be tolerated in such a system. From the information that is available, it appears that a safe oxygen concentration would be far below 4% to avoid ignition by either sparks or hot surfaces. Such low oxygen concentrations are impractical in complex storage and conveyer systems. Generally, explosions are the result of extensive propagation of flame in a dust cloud from a local ignition source. It follows that preventing propagation of flame in the powder system will make it safe even in the event of local ignition. Accordingly, the authors launched a study of the effect of oxygen concentration on flame propagation limits of terephthalic acid.

The terephthalic acid was 98% pure, and particle size analysis showed that the powder consisted of material which was less than 200 microns with 80% below 75 microns. Air and nitrogen were used for atmospheres into which the powder was dispersed. The apparatus consisted of a flame tube 6 in. i.d. and 5 ft long placed in a vertical position. It was possible to ignite the powder from a closed or open bottom. When ignition was from an open end, a plate was placed over the top to avoid a very pronounced chimney effect. Ignition sources used were flames from a Meker burner or burning gun cotton.

Powder was fed to the top of the tube through a variable speed screw feeder and distributed by agitating a 30-mesh sieve. Dust clouds of varying density could be produced by varying the speed of the screw feeder. A test run involved filling the tube with the required gas mixture, introducing the powder at the predetermined rate, and igniting with the powder feed still in operation but the gas feed cut off.

In open-end ignition, it was found that ordinary automobile sparks did not ignite dust clouds with 14% oxygen. However, Meker burner flames or burning gun cotton resulted in propagation in only 13.2% O_2. A graph showing powder concentration vs % oxygen in an atmosphere diluted with nitrogen summarizes the open-end ignition experiments. It appears that the results describe quite well flammability limits, regardless of ignition source employed. In closed end ignition experiments burning gun cotton was used exclusively to ignite the powder. Use of a wide range of dust concentrations shows conclusively an upper flammability limit in atmospheres containing 13 to 15% oxygen.

The authors believe the observation of an upper flammability limit is the important discovery in this paper. Because of this, a true critical oxygen concentration can be defined below which flame propagation is not possible regardless of the dust concentration. This fact makes the flammability characteristics of powders very much the same as those of gases and vapors. Critical oxygen values can be changed easily by increasing the test temperature. A so-called "standard test method" published by the National Bureau of Standards supplies critical oxygen values for many dusts and/or powders at an arbitrary temperature of 850°C. When the test temperature is increased, it is clearly demonstrated that the critical oxygen value is decreased.

The writers are convinced that their limited experiments definitely indicate the uncertainties in applying the standard furnace test to critical oxygen determinations. They believe that a complete reappraisal of the standard method is warranted. More meaningful critical oxygen values can be of practical use. Extension of inert gas blanketing to powder-handling systems is much easier, especially when the organic dusts are related characteristically to terephthalic acid.

Subject Headings: *Dust, explosion prevention; Explosion, of dust, prevention of; Oxygen, critical concentration, for dust explosion.*

C. O'Neal, Jr.

Genkin, S. R. and Saraev, S. P. "The Flame-Quenching Properties of Flame Traps," *Trudy VostNII 7 Voprosy Bezopasnosti v Ugol'nykh Shakhtakh,* 246–252 (1966) Moscow, Nedra. (S.M.R.E. translation No. 5482)*

Tests were made on flame traps of the following types; granular packing, spiral and single- and multi-layer wire mesh. The negative results obtained in the testing of specified flametraps with mesh or wire packing are sufficient reason for considering them to be unsuitable for containing fire outbreaks and explosions in the chemical industry. Gravel-packed flame-traps are efficient with respect to the quenching of the flame from mixtures of the vapours of benzene and alcohol products with air, provided that they are packed with 6–8 mm gravel to a height not less than 150–200 mm.

Subject Headings: ***Flame traps; Quenching, by flame traps.***

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(4), 18. By permission.

Glock, G. *Explosion Hazards and Protection against Explosions in Industrial Establishments.* Weinheim/Bergstr., Verlag Chemie (1966) (In German)*

Second revised edition of an explanation of the characteristic coefficients for inflammable liquids, gases and dusts, used as the basis for measures prescribed in various rules and regulations for the advance detection or the combating of explosion hazards. The seven sections of the booklet, each subdivided, deal with general fire and explosion hazards of inflammable liquids, define the concepts "group" and "danger category" used in the VbF Regulations for Inflammable Liquids, define the concepts and characteristic coefficients used in the field of "explosion hazards in industrial establishments" and those in "protection against explosions in industrial establishments" deal with primary protection against explosions (prevention of the occurrence or accumulation of explosive mixtures) and secondary protection against explosions (prevention of various ignition sources), with explosionproof electrical equipment (protected by increased safety, pressureproof enclosures, extraneous ventilation, intrinsic safety), with ignition groups and explosion groups, and with explosion hazards and protection in laboratories and experimental stations. Some practical examples are given. Nineteen references to tables, rules and regulations, directives, and other literature are included.

Subject Headings: ***Explosions, hazards and protection; Industrial explosions.***

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(5), 22. By permission.

Osipov, S. N. "Increasing the Effectiveness of Anti-Pyrogens Used to Prevent Endogenous Fires," *Ugol'Ukr.* **10**(9), 39–41 (1966) (In Russian)*

The possible effect of anti-pyrogens is examined in the light of the "chain" theory of oxidation (N. N. Semenov). Proceeding from this theoretical examination, experiments are suggested with various substances in order to find the most suitable one for use as an anti-pyrogen.

Subject Headings: *Anti-pyrogens; Endogenous fires; Fire prevention.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(3), 70. By permission.

Moiseev, V. A. "Determining the Degree of Fire Hazard," *Soviet Mining Science* (translation of Fiziko-Tekhnicheskie Problemy Razrabotki Poleznykh Iskopaemykh) (2), 222–225 (1966)*

The present relative assessment of fire hazard, in which the absolute number of fires occurring is related to a million tons of coal mined, the number of worked-out locations, or to 1000 m of take mined out to the rise of the seam, only gives an approximate idea of the effect of different factors on the fire hazard. An attempt has been made here to put forward a theoretical basis for solving the problem and for linking all the factors into a unified whole, which would make it possible to assess the degree of fire hazard and calculate the fire safety characteristics.

Subject Headings: *Fire hazards; Hazards, of fire.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(3), 69. By permission.

Palmer, K. N. "Explosion Suppression and Relief Venting," *Chemy Ind.* (23) 936–942 (1967)*

After describing the physical factors which determine the generation of an explosion, the elimination of sources of explosions is discussed. The main body of the article is then concerned with two methods to be adopted for the case when preventive measures have failed, so as to minimise the effect of the explosion. These methods are the provision of explosion relief venting and the installation of flame arresters. Finally, automatic suppression of explosions is briefly discussed.

Subject Headings: *Explosion, suppression by venting; Venting, for explosion prevention.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(4), 19. By permission.

Seki, K. et al. "On the Protection for Incendive Sparking of a High Inductive Circuit," *Mining and Safety* (Japan) 12(4), 1–6 (1966) (In Japanese)*

An investigation has been carried out on the simple protective methods for incendive sparking. It represents a continuation of a previous study on the ignition phenomena in methane-air mixtures by weak electric sparks of a high inductive circuit. Shunting the high inductor by resistors or capacitors reduces the incendive power of the inductor and the mechanism of this reduction is observed.

Subject Headings: *Incendive sparking; Inductive sparks.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(5), 84. By permission.

Smid, M. and Suchan, L. "Conference on the Origin, Prevention, and Control of Mine Fires," *Uhli* 9(2), 81–86 (1966) (In Czech)*

This Conference, organised by the (Czechoslovak) Scientific Coal Research Institute and the Main Mine Rescue Station, was held on 18–20 October, 1966, at Roznov p/Radhostem, and was attended by scientists and technologists from many European and Asian countries. The Conference was divided into the following sections: (1) Endogenous fires; (2) Exogenous fires; (3) Methods for the control of fires; (4) Training of, and equipment for, mine rescue teams, and (5) Signalling equipment and installations for warning and rescuing the miners. Brief summaries are given of the papers read, and the directions which further research should take are indicated.

Subject Headings: *Control, of mine fires; Mine fires, control of; Prevention, of mine fires'*

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Williams, C. G. "The Development of a Fire Retardant for the Impregnation of Mining Timber," *Mining & Minerals Engng.* 2(11), 427–434 (1966)*

Describes the work leading up to the production of the N.C.B. proprietary mixture of fire retardant and preservative chemicals, known as Fyreprufe. The author first deals with methods of imparting fire resistance to timber, with the economic aspects of the problem, and with the theory of the fire retardant action of chemicals. He then discusses the formulation and proving of a fire retardant mixture and refers to laboratory tests for fire resistance, optimum salt loading, determination of salt loading, permanence of salt retention, corrosion effects of fire retardants, protection of equipment, and health and safety aspects.

Subject Headings: *Fire retardant, for mine timber; Mine timber, fire retardant for; Timber, fire retardant for.*

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B. Ignition of Fires

Clancey, V. J. and Sayce, H. C. "The Explosive and Fire Hazard Characteristics of Ammonium Nitrate Fertilizers. Part 2. Assessment of the Fire Hazard," *R.A.R.D.E. (Royal Armament Research Development Establishment) Report 1/66* (May 1966)*

Experiments have been carried out to investigate the possible fire hazards involved in the storage and transport of ammonium nitrate and fertilizers based on ammonium nitrate. The flammability characteristics of ammonium nitrate in admixture with sawdust, and the effect of various diluents, have been studied under open and partially confined conditions.

Subject Headings: *Ammonium nitrate, explosion of; Explosion hazards, of ammonium nitrate; Fertilizers, fire and explosions in; Fire hazard, of ammonium nitrate.*

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(4), 23. By permission.

Fells, I. and Lowes, T. (University of Newcastle upon Tyne, England) "Spark Ignition of Cyclopropane-Oxygen Mixtures," *Combustion and Flame* **11**(5), 430–434 (1967) Letter to the Editor.

For a long time, the explosive risks associated with the use of anaesthetic gas–oxygen mixtures in operating rooms have been well known. Unfortunately, the oxygen concentrations necessary to maintain life fall within the limits of flammability, and the minimum ignition energies and quenching distances are both so small that all sources of ignition must be avoided.

Ignition sources might include electrically heated wires for cauterizing, or accidental static sparks generated by walking across the floor, or by clothes rubbing together.

The authors of the present paper present an improvement on the classical theory of thermal ignition, in the presence of heat sinks. Agreement with published values of quenching distances for various hydrocarbon–air–oxygen mixtures is quite good, but not quite so with respect to minimum ignition energies, perhaps because the latter are not so well-defined.

To set up the model, it was necessary to make certain assumptions, which included that for minimum ignition conditions immediately after discharge (1 millisecond), the temperature at the center of the system is at the spontaneous ignition temperature, and the temperature of the outer edge of the system is ambient. The temperature profile is unknown and diffusion of radicals is not considered. It is not made clear how a minimum ignition energy can be associated with electrically heated cauterizing wires.

The quenching distance calculated for cyclopropane oxygen mixtures is 0.015 cm, and the minimum ignition energy is 0.03×10^{-6} calories—both being in the same range as for other hydrocarbon–oxygen mixtures. Both quantities vary inversely as the pressure.

Subject Headings: ***Ignition, of anaesthetic explosions; Ignition, of cyclopropane-oxygen; Spark ignition, of cyclopropane.***

J. K. Richmond

Goodall, D. G. and Ingle, R. (Rolls-Royce Ltd.) "The Ignition of Flammable Liquids by Hot Surfaces," *Fire Technology* **3**(2) 115–128 (1967).

Results of this work have shown quite clearly that the risk of spontaneous ignition in any given application is determined by the temperature of a critical volume of mixture rather than by a hot surface temperature and that the surface temperature is a controlling factor only in so far as it affects the temperature of any flammable mixture. It is possible, therefore, to justify current aircraft practice in which it is considered safe to operate with local surfaces much hotter than closed-vessel ignition tests would indicate. Of course, where all the surfaces of the enclosure are at high temperature, as in supersonic aircraft spaces or where the temperature of ventilating air is high, spontaneous ignition will be possible at temperatures approaching those of closed vessels of similar size. However, it may be possible to raise the ignition limit by considering transit time in these cases, but any stagnant regions will constitute an ignition hazard at temperatures near those for closed vessels.

Calculations of mixture temperature gradients adjacent to hot surfaces may yet prove too complicated to be practicable, particularly where incidental or deliberate airflows are passing over irregularly shaped surfaces, such as that formed by a flanged pipe joint.

Subject Headings: ***Ignition, by surfaces; Surface ignition, of liquids; Liquids, ignition by surfaces.***

Authors' Conclusions

Hodges, D. J. and Acherjee, B. "A Microcalorimetric Study of the Influence of Moisture on the Spontaneous Heating of Coal," *Min. Engr.* **74,** 121–131 (1966) (T.I.M.E. 126)*

Describes a laboratory investigation into the influence of moisture on the spontaneous heating of coal on a quantitative basis. The results of the investigation are presented and discussed.

Subject Headings: ***Coal, spontaneous heating of; Moisture in coal, spontaneous heating; Microcalorimetry, of moist coal; Spontaneous heating, of coal.***

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(6), 15. By permission.

Komarov, V. S. "The Energy of an Electric Spark—the Criterion for the Incendivity of an Explosive Gas Mixture," *Trudy VostNII 6 Voprosy Bezapasnosti v Ugol'nykh Shakhtakh,* 168–170 (1965) Moscow, Nedra. S.M.R.E. translation No. 5384.*

The energy of a spark is the sole condition for ignition provided that the volume within which it is disseminated and the duration of the discharge do not exceed certain critical limits.

Subject Headings: *Electric sparks, ignition by; Energy, of ignition of gases; Gases, ignition of; Ignition energy; Incendivity of gases.*

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(3), 11. By permission.

Komarov, V. S. and Belikova, T. V. "The Minimum Ignition Energy of Explosive Gas Mixtures," *Trudy VostNII 6 Voprosy Bezapasnosti v Ugol'nykh Shakhtakh* 170–176 (1965) Moscow, Nedra. S.M.R.E. translation No. 5385.*

A procedure for measuring the minimal ignition energy has been found to be satisfactory and the apparatus for its measurement has been arranged so that the discharge energy can be varied over a large interval. The measured ignition energy of certain explosive mixtures makes possible a more correct assessment of the spark hazard in low-voltage electrical circuits, discharges of static electricity, etc.

Subject Headings: *Gases, ignition of; Ignition, of gases; Minimum ignition energy.*

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Münzner, H. and Peters, W. "The Spontaneous Ignition Characteristics of Coal," *Erdöl und Kohle-Erdgas-Petrochemie* **19**(6), 417–421 (1966) S.M.R.E. translation No. 5458.*

The self-ignition of coal: An objective determination of the tendency of coal to self-ignition is of practical importance for planning the mining of coal and safety precautions. When coal comes into contact with air, exothermic processes of autoxidation cause a self-heating of the coal, the extent of which is determined, on the one hand, by the conditions for oxygen intake and heat accumulation, on the other hand, by the rate of autoxidation. Oxygen and heat transport depend in each case on the local conditions; however, the rate of reaction with oxygen and of formation of heat is a property of the coal. By measuring the rate of oxidation (transport in-

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fluences excluded), it is possible to characterise different coals as to their self-ignition tendency if measuring techniques for temperature, pressure, O_2 concentration and moisture of the coal are adapted to the conditions prevailing in the seam.

Subject Headings: *Coal, spontaneous ignition of; Ignition, spontaneous, of coal; Spontaneous ignition, of coal.*

Mitchell, E. W., Murphy, E. M., and Holtz, J. C. (U. S. Bureau of Mines) "Flammability of Rigid Urethane Foam," Paper at Conference on Flammability Characteristics of Polymeric Materials, Wayne State University, Detroit, Michigan (June 13, 1966)*

Paper presented at Conference on Flammability Characteristics of Polymeric Materials, 1966 Polymer Conference Series, to be sponsored by the College of Engineering at Wayne State University, Detroit, Michigan, week of June 13, 1966. The flammability of rigid urethane foam was investigated by the Federal Bureau of Mines in tests simulating conditions in operating mines. Foam-covered barriers, walls and roof were subjected to fires liberating 9,000 to 640,000 Btu per minute. Results of these full-scale tests were compared with those from small-scale tests used by industrial laboratories to evaluate the relative flammability of building materials. All urethane foams ignite easily and, while burning, produce black acrid smoke. Some of these foams exhibit intumescence when exposed to fire, a swelling and surface-pyrolysis change that forms an insulative skin resistant to further degradation by flame. Foam flammability can be predicted to some extent by the combined results of small-scale tests for flame spread and fire endurance. However, the full-scale tests proved these predicted characteristics are meaningless should chemicals be inadequately mixed or should foam be applied on roof and adjacent walls. Flame propagation on foam can be arrested by water sprays. Coatings on foam are of doubtful effectiveness. Although coatings inhibit ignition, they enhance thermal decomposition of the underlying foam.

Subject Headings: *Flammability, of foam; Foam, flammability of; Urethane foams, flammability of.*

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Pursall, B. R. and Narain, C. "Spontaneous Heating of Coal," *Colliery Guard* **213** (5506), 553–558 (1966)*

Reviews the kind of research done over the past few years and the present position with regard to the CO/O_2 deficiency ratio, the association of hydrocarbons with

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spontaneous heating, evidence from laboratory experiments, the theory of partial distillation of coal, and the association of pressure changes with spontaneous heating.

Subject Headings: *Coal, spontaneous heating; Spontaneous heating, of coal.*

Rudenko, K. P. "Metamorphism and Spontaneous Ignition of Bituminous Coals in the Donbass," *Ugol'Ukr.* **10**(12), 46–47 (1967) (In Russian)*

The article reviews cases of spontaneous ignition of coals at various states of metamorphism in the central region of the Donetsk basin from 1955–62. The author concludes that although the stage of metamorphism influences the tendency to spontaneous ignition, geological and mining-technological factors are of considerable importance in this respect.

Subject Headings: *Coal, spontaneous ignition of; Bituminous coal; Donbass; Metamorphism, and spontaneous ignition; Spontaneous ignition, of coal.*

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Sinha, K. N. P. and Weigel, K. "Spontaneous Ignition Tendency of Lignite Briquettes as a Function of Their Porosity and Gas Permeability," *Freiberger Forsch Hft A***406**, 5–39 (1967) (In German)*

The authors consider the factors which create the risk of spontaneous ignition: the geological conditions, coal-winning methods, rock pressure, climatic conditions, and the chemical and physical properties of coal. They describe methods of calculating the permeability of coal, the average pore diameter and the specific surface of porous bodies. They conclude that there is a definite relationship between the gas permeability and the spontaneous ignition tendencies of lignite briquettes but point out that the experimental conditions exert a strong influence on the results. The gas flow speed within the pores determines the time required for spontaneous ignition.

Subject Headings: *Briquettes of lignite, porosity of; Lignite, spontaneous ignition of; Spontaneous ignition, of lignite; Porosity, of lignite.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(2), 11. By permission.

Tanaka, R. "The Ignition of Methane-Air Mixtures by Sparks with Snapping (Breaking) Wire Apparatus," *Reports of the Research Institute of Industrial Safety, Japan* **14**(3), 1–6 (1966) (In Japanese)*

Measurements have been made of minimum igniting currents for low voltage d.c. inductive and non-inductive circuits, in methane-air mixtures, with a snapping copper wire apparatus. It is shown that more incendive sparks are achieved for inductive circuits than with the British break-flash No. 3 apparatus, hinting at the need for a larger safety factor in cases of live wire break incidents. The incendivity of the apparatus is almost equal to that of the German Schnellunterbrecher. With non-inductive circuits obvious differences of the minimum igniting currents are not indicated throughout the range of voltages investigated. As for the effect of the wire diameter, the minimum igniting currents are nearly constant over a limited range of diameter of 0.1–0.4 mm, other conditions being equal.

Subject Headings: *Ignition, by sparks; Methane–air, ignition by sparks; Snapping wire ignition; Spark ignition.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(5), 84. By permission.

Tsurumi, H. and Matsuda, T. "Study of the Safe Gaps with Hydrogen-Air Mixtures," *Reports of the Research Institute of Industrial Safety, Japan* **15**(1), 11–18 (1967) (In Japanese)*

Experimental safe gaps with hydrogen-air mixtures have been measured with an 8 litre spherical stainless steel vessel with 1 inch flanges at atmospheric pressure and 0.5 kg/cm^2 gauge pressure. From the experiments, the following facts became evident: (1) the maximum experimental safe gap (m.s.e.g.) is 0.22 mm at atmosphereic pressure; (2) the experimental safe gap is influenced by concentration and pressure; (3) hydrogen concentration from 18 to 51% belongs to explosion grade No. 3; (4) the experimental safe gap is correlative to the quenching distance.

Subject Headings: *Gaps, safe for hydrogen-air; Hydrogen-air, quenching distance in; Quenching distance, in hydrogen-air; Safe gaps, for hydrogen-air.*

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Wahl, H. "Temperature and Incendivity of Grinding Sparks in Various Gas Mixtures," *Zeitschrift für angewandte Physik.* 12(2), 60–62 (1960) S.M.R.E. translation No. 5419.*

The author examines the temperature of grinding sparks in various gas and vapour atmospheres, determining the ratio of the intensities of the spark luminosity at two different wave lengths.

Subject Headings: ***Gas mixtures, ignition by grinding sparks; Grinding sparks, temperature and ignition by; Ignition, by grinding sparks; Incendivity, of grinding sparks; Temperature, of grinding sparks.***

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Yantovskii, S. A. and Chernyak, M. V. "Concentration Range in Which Hydrogen-Oxygen Mixtures are Explosive at Superatmospheric Pressures," *Russ. Jnl. Phys. Chem.* (11), 1557–1558 (1966)*

Explosions were produced of rich and lean hydrogen-oxygen mixtures in a vertical stainless steel reaction vessel, giving pressures up to 20 atmospheres. The limiting compositions where incomplete combustion takes place were 4.5–11% of hydrogen for lean mixtures and 95.5–93% of hydrogen for rich mixtures.

Subject Headings: ***Explosive range, of hydrogen–oxygen; Hydrogen–oxygen explosion, limits of; Oxygen–hydrogen explosion, limits of.***

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Salooja, K. A. (Esso Research Centre, Abington, Berks., England) "Studies of Oxidation Processes Leading to Ignition of Butanes, Butenes and Cyclobutane," *Combustion and Flame* 11(4), 320–328 (1967).

The pre-ignition characteristics of a number of saturated and unsaturated C_4 hydrocarbons have been investigated under identical experimental conditions. The ignition lag and the extent of reaction in terms of percentage of CO in product gases are reported as a function of temperature from 300° to 650°C for twice-stoichiometric fuel to air mixtures at one atmosphere pressure. The intermediate combustion products are reported in terms of major and minor constituents in the low temperature region (below 420°C) and the high temperature region (above 480°C).

The saturated compounds (butane and cyclobutane) were found to oxidize significantly in the low temperature region but the numerous unsaturated compounds did not react to an appreciable extent below 480°C. The relative ease of oxidation of the compounds tested in the high temperature range going from more to less reactive is 1-butene, 2-cis-butene, 2-trans-butene, cyclobutane, butane, isobutane, and isobutene. This trend is generally consistent with data from a test engine on the knocking tendencies of the identical compounds in that the more reactive C_4 hydrocarbons knock at lower compression ratios.

A number of oxidation mechanisms for the various compounds are proposed in order to explain the intermediate product distributions obtained.

Subject Headings: *Butanes, oxidation and ignition of; Ignition, of butanes; Oxidation, leading to ignition.*

F. R. Steward

Schetz, J. A. and Jannone, J. (General Applied Science Laboratories, Inc., Westbury, New York) "The Ignition of Flowing Hydrocarbon/Air Mixtures by a Hydrogen Pilot Flame," *Pyrodynamics* 2(1), 1–14 (1965)

This analytic study sponsored by Air Force Office of Scientific Research deals with a mechanism for igniting a flowing hydrocarbon/air mixture in fully turbulent flow with a pilot hydrogen flame. The study undertakes to examine analytically the specific problem of ignition of an elevated temperature main stream under conditions precluding spontaneous thermal ignition, as for example, in a ramjet employing supersonic combustion but in which the compression of the ambient air does not elevate the temperature to the thermal autoignition point.

The authors undertake to delineate the flow field of a pilot flame which burns hydrogen and air using either a fuel-rich or a fuel-lean mixture. The flow field behind the jet issuing from the pilot is treated as turbulent flow, and for the fuel-rich condition, the excess hydrogen diffuses into the main hydrocarbon–air mixture, whereas for the fuel-lean pilot, the hot gas exhaust species are considered to be inert. The criterion for propagating the reaction into the main stream depends upon the presence of a flow regime in which the static temperature and the oxidizer/fuel ratio in the immediate vicinity of the hot spot permit a combustion reaction to occur. This reaction is governed by the transfer of mass and heat from the burned to the unburned region and the kinetics of the combustion reaction. If, however, a strong velocity gradient is present, the propagating flame front is distorted by a "stretch factor"—a function of the velocity gradient and the ratio of the preheat zone width to the stream velocity. The limiting case, when the stretch factor is zero, corresponds to a normal combustion wave front.

The authors have chosen a "stretch factor" of 2 at the inflammability limit as the maximum allowable without inducing quenching. The problem has been somewhat simplified by the use of uniform initial conditions, the authors having rejected the necessity for considering initial boundary layers. The hydrocarbon/air and the hydrogen/air reactions are treated as distinct and separate kinetic problems. The authors derive the general equations for describing the flow field.

The conclusion reached is that a fuel-oxidizer concentration vs time trace along a flow field together with a superimposed plot of the limits of inflammability is most instructive in understanding the details of the ignition mechanism. Such analytic treatment permits study of the piloting mechanism in depth and with some unexpected results. For example, in applying their equations to a particular problem, namely a comparison between a pilot of hydrogen air at stoichiometric to produce a total temperature of 2000°K and one of a pilot using a fuel-rich mixture at a temperature of 1000°K, (static isotherms being shown for both cases) the authors showed that the latter condition produces a more efficient ignition source. Therefore a fuel-rich pilot jet at lower temperature is a more effective ignition source than a jet of inert gas at a considerably higher initial static temperature.

Subject Headings: *Flammability limits; Hydrocarbons, ignition in air; Ignition, by hydrogen pilot flame; Pilot flame, ignition.*

D. Dembrow

Varga, E. "A Hitherto Unknown Factor in the Spontaneous Ignition of Coal," *Publications Hungarian Research Institute of Mining* (8–9), 137–147 (1965–1966) (In German)*

Heating occasionally occurs even where no ventilation current passes, e.g., in the centre of a heap of small coal from a fall of coal. The question arises what produces the pressure drop necessary to cause sufficient oxygen to be drawn into the coal mass. From tests made under field conditions to identify the cause of this pressure drop it is concluded that sorption of O_2 by the coal takes place more rapidly than desorption of CO_2 and CO from the coal, thus producing a vacuum which in a closed space amounted within 48 hours to several 100 mm w.g. A method has been developed for the measurement of this pressure drop by means of which it is possible to calculate all the pressure parameters that affect both spontaneous combustion and ventilation in general. The specific surface of coal in the seam is not large enough for the sorption processes mentioned to take place. The theory proposed throws doubt on the accepted opinion that the rise in temperature of the mine air is due to slow oxidation. A separate investigation will be needed to determine the source of the CO_2.

Subject Headings: *Coal, spontaneous ignition of; Ignition, spontaneous of coal; Spontaneous ignition, of coal; Sorption, on coal and spontaneous ignition.*

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C. Detection of Fires

Kokorin, P. I., Moiseev, V. I., and Lyurai, L. L. "Remarks on Conditions Leading to the Determination of Initial Signs of Spontaneous Combustion of Coal," *Bezop. Truda v Promyshl* 10(10), 809 (1966) (In Russian)*

Discusses observations carried out in Kuzbass mines and gives a critical assessment of current practice in determining the first signs of spontaneous ignition. Proposals are made for improved methods of detection.

Subject Headings: *Coal, detection of spontaneous combustion; Detection, of spontaneous combustion; Spontaneous combustion, detection in coal.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(6), 15. By permission.

Narain, C. "Early Detection of Spontaneous Combustion. Part I. Field Investigations. Part II. Results," *Colliery Guard* 214 Part I. 609–615; Part II. 637–641 (1967)*

In Part I, which is based on a project at the University of Sheffield, some field investigations are described and conclusions drawn to show that ethylene in the atmosphere of a mine can be used as an indicator of spontaneous heating underground.

In Part II, results are compared with some past work to test the validity of the interpretations given in Part I. The paper ends with general conclusions and a brief discussion of scope for future work.

Subject Headings: *Detection, of spontaneous combustion; Spontaneous combustion, detection of.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications* Part I *16*(4) 74; Part II *16*(4) 15. By permission.

D. Propagation of Fires

Kimzey, J. H. (Manned Spacecraft Center, Houston, Texas) "Flammability during Weightlessness," Presented to the Twelfth Annual Technical Meeting of the Institute of Environmental Sciences, San Diego, California, April 13, 1966. *NASA Technical Memorandum NASA TM X*-58001 (May 1966)

Paraffin and other combustibles were burned in a zero-gravity environment. Zero-gravity intervals of 12 seconds, maximum duration, were obtained in the cabin of an aircraft flying Keplerian parabolas. Experiments were photographed with infrared sensitive film at 100 frames per second and 16 mm color film (ER-B) at 200 frames per second. Test results indicate that ignition is essentially unchanged compared to a one-gravity environment but that combustion is suppressed, in some instances, to the extent that the fire appeared to be extinguished. In all cases, the flame was brightest during periods of acceleration, such as at impact of the test chamber with the aircraft and when returning to level flight. Flame conditions at zero gravity were typical of those expected of a pure diffusion flame in which steady-state conditions were not achieved.

Subject Headings: *Flammability, at zero gravity; Gravity, effects on ignition and combustion; Paraffins, flammability at zero gravity; Zero gravity flammability.*

Author's Abstract

Monaghan, M. T.,* Siddall, R. G., and Thring, M. W.† (University of Sheffield, Sheffield, England) "The Influence of Initial Diameter on the Combustion of Single Drops of Liquid Fuel," *Combustion and Flame* 12(1), 45–54 (1968)

Experimental studies of the combustion of single drops of liquid fuels have concentrated almost exclusively on drops whose initial diameter has been an order-of-magnitude larger than the size of drops associated with fuel sprays (1000 μ compared with 100 μ drops in a fuel spray). In this investigation, single drops of initial diameter 150 μ to 2000 μ have been studied, using *n*-heptane and kerosene as being representative of distillate fuels, and benzene, ethyl benzene, and tertiary butyl benzene, which have been studied by earlier investigators. The drops, produced by a micro-pipette, were suspended from a fine silica fiber. By careful positioning of the drop in an optical system, the combustion process could be recorded by a modified drum camera and also by cine photography.

From theoretical considerations, it has been shown that the burning time (t_B) of a single drop is proportional to the square of the initial drop diameter (D_0), i.e.,

$$(D_0)^2 = Kt_B$$

where K is a constant, sometimes referred to as the "Burning Constant."

The experimental results showed that the burning rate of a drop is a function of its instantaneous diameter as well as its initial diameter, and that the experimental results obtained from large drops would require up to a 30% reduction to predict the burning rate for drops in sprays.

In order to explain the deviation from the idealized model, the effect of heat transfer by radiation, conduction, and natural convection to the drop has been examined. Radiation was considered to exert only a small effect, because the change in radiation with initial diameter could only be due to alterations in the temperature and emissivity of the droplet flame and this would not be significant.

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Conduction has been discounted (although the initial stages of burning are modified by conduction of heat from the flame envelope) because the influence of initial diameter on flame shape could not be explained by this mechanism.

Natural convection enhances the burning rate of 1000 μ drops by up to 40%, but the smaller the initial diameter of the drop, the smaller is the convection current created. It is argued that the initial natural convection effect is sustained throughout the burning time of a drop and that a small drop will never establish a sufficiently large convection current. By relating the burning rate to the initial Grashof number, the calculated reduction of between 8% and 10% compares reasonably well with the 14% change in burning rate measured experimentally for drops of 1370 μ and 300 μ initial diameter. Further confirmation of the argument was obtained by analyzing the change in the ratio of flame to drop radius with initial diameter.

The experimental results were used to derive a single law for all the fuels used in the experiments. Although it could be shown that

$$t_B = \Omega D_0^{1.83}$$

there was insufficient information to relate Ω to the thermodynamic properties of the fuels.

As the oxygen concentration of the atmosphere surrounding the drop was increased, the burning rate for small drops followed the theoretically predicted rate more closely, and therefore the idealized theories of burning drops under these conditions might be more nearly correct than hitherto has been thought. It was demonstrated that the ratio flame radius to drop radius increased with time during combustion in air and that a decrease in initial diameter produced an increase in this ratio. Increasing the oxygen concentration decreased the ratio. These results were explained by considering the flow of oxidant to be independent of the instantaneous diameter, and it was shown that initial drop diameter was also important. The reduction in the ratio flame radius to drop radius was shown to be proportional to $D_0^{1/4}$.

Principally, this work has shown that previous experimental results on large single drops require corrections of up to 30% to predict the burning rate of spray sized drops.

Subject Headings: *Combustion, of drops; Drop diameter, effect on combustion.*

P. L. Start

Rasbash, D. J. and Langford, B. (Joint Fire Research Organization, Boreham Wood, England) "Burning of Wood in Atmospheres of Reduced Oxygen Concentration," *Combustion and Flame* **12**(1), 33–40 (1968)

Arrangements of wooden dowels were burned in atmospheres of reduced oxygen concentration using nitrogen and carbon dioxide as diluents. The dowels (0.32 and 0.48 cm diameter) were supported in a combustion vessel 182 cm long by 30.4 cm square through which the diluted oxidant gas flowed at 2.7 cm/sec. Time lapse movies (at 30 sec intervals) gave data of flame spread rate, flame height, and flame width at the base of the dowel cribs. In the upward flame propagation experiments, single and triple dowel specimens of 91.5 cm length were used; in horizontal flame propagation the dowel cribs were 61 cm long in either three or seven layers.

Rate of flame spread

Experimental results of flame spread agreed with the expected effect of thermal load of the diluents in reducing the flame temperature and heat transfer rate (taking the thermal load to be the thermal capacity of total diluent gases associated with a unit quantity of oxygen). The difference in flame spread rates in horizontal and upward propagation was attributed to differences in heat transfer modes (convective heat transfer from the flame for upward burning and radiative heat transfer from the fuel bed for horizontal propagation). Data indicated that the flame spread rate was reduced in proportion to the inverse fourth power of the increase in thermal load in horizontal propagation and to the inverse first power of the increase in thermal load in upward burning.

Equations of Thomas *et al.*[1] were used to compare experimental and theoretical temperatures of horizontal flame spread in the seven layer cribs (heat transfer by radiation):

$$R\rho_b\Delta H = I - aQ \tag{1}$$

$$\epsilon = 1 - \rho^{-bD} \tag{2}$$

$$b = \rho_b/2\rho_f d \tag{3}$$

where R is the rate of fire spread, ρ_b is bulk density of crib, ΔH is the enthalpy rise of uniformly heated wood at the ignition temperature of a pilot flame (taken as 750 Joules/g for moisture content of 10%), a is a coefficient for nonuniform direction of radiative heat transfer, Q is the rate of heat loss of fuel close to the ignition point, I is the forward heat flux assured to be $\epsilon\sigma T^4$, ϵ is the emissivity of the solids in the flame zone, σ is the Stephan-Boltzman constant, T is the absolute temperature of the fuel surface in the burning crib, b is an attenuation coefficient, D is the flame thickness, and ρ_f is the density of the sticks. Flame radiation from the burning zone was insufficient to account for the measured flame spread.

Rate of burning

There was no consistent variation of burning rate for upward or horizontal propagation with respect to oxygen concentration, or with respect to differences between different cribs in horizontal propagation. Burning times of the dowels were inversely proportional to the 1.9 power of the stick diameter. This relationship was shown to be in accordance with a convective heat transfer mechanism.

Extinction of fire

Flames were extinguished with reduced oxygen concentrations of 13.2 to 18%. If one assumes an empirical formula of CH_2O for wood volatiles and a heat of combustion of 4000 cal/g, the limit of oxygen concentration when diluted with nitrogen is estimated to be 11.3%. Some factors (and predictions) that relate to flame extinction are noted:

1. In horizontal flame propagation, limits may occur because the flame does not spread at a sufficiently fast rate to cover fluctuations of volatile production due to variation in wood. In upward flame propagation the limits are due to flame extinction instead of insufficient rate of flame spread as indicated by the substantial flame size at extinction.

2. Diffusion flames from cellulosic fuels should be extinguished at higher oxygen concentrations than premixed gaseous flames because of additional opportunity for heat loss by radiation and conduction to the fuel surface.

3. The following results are predicted based on radiant heat loss considerations:

a. Radiant emissivity is less than proportional to the flame diameter, Eq. (2)

b. Emissive flames of a given dimension are more easily extinguished than nonemissive flames, and

c. The presence of a large number of small radiative bodies in a flame aids extinction.

Authors suggest that the conclusions reached in the small-scale study can be applied to practical large-scale burning. For example if burning or flame spread rates depend on flame radiation, then substantial reductions can be expected with reduction of oxygen concentration. The effect would be less marked if the burning process were controlled by convective heat transfer.

Reference

1. Thomas, P. H., Simms, D. L., and Wraight, H. G. H.: "Fire Spread in Wooden Cribs. Part 2. Heat Transfer Experiments in Still Air," *Joint Fire Research Organization Fire Research Note No. 599* (1965)

Subject Headings: *Burning of wood, in oxygen-poor atmosphere; Oxygen-poor atmosphere, combustion of wood; Wood, burning in oxygen-poor atmosphere.*

J. M. Singer

Roberts, A. F. and Clough, G. (Safety in Mines Research Establishment, Sheffield, England) "The Propagation of Fires in Passages Lined with Flammable Material," *Combustion and Flame* **11**(5), 365–376 (1967)

Fires in confined spaces lined with wood begin in an oxygen-rich atmosphere in which spreading occurs as heat radiated and conveyed from the flames releases volatile fuel by pyrolysis of neighboring wood. As the fire becomes larger, the temperature of the air may rise enough to pyrolyze more distant wood and add more volatile fuel for further combustion and increase in temperature. Combustion becomes self-accelerating. A limiting situation can develop in which all oxygen in the air supply is consumed. The rate of supply of air then controls the progress of the fire in a fuel-rich atmosphere.

Ventilated passages lend themselves better than rooms for study because the passages provide an organized route for the ventilation and gaseous products that result in distinct zones along the axis of passage, x. As the fire progresses from its point of ignition at the air inlet ($x=0$), a charcoal zone soon develops in which flaming has ceased from exhaustion of volatile fuel at $x=L_a$. With good ventilation, glowing charcoal alters the oxygen content and temperature of the air stream only negligibly. Next comes a zone of wood pyrolysis (L_a to L_c) in which volatile fuel is evolved and burns in flames. Temperature rises steeply and oxygen content of the air drops sharply along the axis. If at a point $x=L_b$ the oxygen level falls to zero, the gas temperature attains a maximum, T_g, and flaming ceases, ending the combustion section of the pyrolysis zone; evolution of volatile fuel continues in the excess fuel section of the pyrolysis zone until at point $x=L_c$ the gas temperature falls to T_g', where active pyrolysis ceases. Beyond L_c, the preheating zone, the products of the fire gradually cool and the wood walls are warmed. If the conditions are such that the oxygen content of the air stream remains above 15% no excess fuel section develops in the pyrolysis zone and the fire either dies out or continues in the oxygen rich condition until all wood is consumed.

All fires in large tunnels for which data are available in the literature remained oxygen rich whether they spread through considerable lengths of roadway or died with fuel still available. All fires in the 30 cm duct described further on rapidly became fuel rich when the igniting source was large (a crib) and remained so until most of the fuel was consumed. With small-scale local ignition the fires either went fuel rich or died with fuel still available. No small-scale fire spread continuously in an oxygen-rich condition. Although fuel-rich fires have been demonstrated only on a small scale, the possibility of such a fire occurring on a large scale when started by a large igniting source must not be overlooked, especially since the rate of heat release and rate of propagation can be more than ten times as great in fuel-rich as in oxygen-rich condition.

The 30 cm duct for the experiments consisted of 33 cylindrical steel sections 90 cm long, sealed end to end with asbestos, lined with vermiculite/concrete to 5 cm minimum thickness, with a 30 cm square passage along the axis. Wood strips of desired thickness were fastened to desired portion of walls and roof by steel framework. The duct was ventilated by a centrifugal fan at controlled velocities up to 5 m/sec. To study the growth of fires a gas burner gave a stabilized line of flame around the perimeter of the flow passage with the ventilation set at the required value. To study well-established fires a crib of sticks was ignited with the ventilation set very low until fire was well under way, then ventilation was raised to the required level. By suitable sampling for gas analysis practically continuous record was kept of carbon monoxide and carbon dioxide content at 5 points along the duct and of hydrogen, oxygen, water, and unburnt fuel in the exit gases. Further samples were taken at one selected time at 20 points for subsequent analysis to determine a reaction profile at a known stage of the fire. Twenty photocells responsive to diffusion flame but not to glowing charcoal were mounted at 90 cm intervals to record progress of flames. Thermocouples recorded temperatures in the gases along and across a section of the duct as well as temperatures at the wood surface and at various depths in the refractory lining and wood linings. Rate of pyrolysis was determined by continuous weighing on a load cell of a section of the lining. The total rate of fuel addition to the gas was estimated by use of a venturi meter for the mass flow of gases leaving the duct and subtracting the known rate of mass flow of air supplied by the fan.

A simplified mathematical model of this type of fire was developed that related the propagation rate and temperature distributions to the heat transfer coefficients, fuel emission rates, and other features of the system. The mechanism of propagation in the fuel-rich condition is completely different from that in the oxygen-rich condition. An over-all feature is the normalized propagation velocity, R', which is both the propagation velocity at L_c, the end of the wood pyrolysis zone, and a fuel-air ratio of the combustion products, $R'=4.6\ M_F/M_A$, where M_F is the total rate of evolution of volatiles from the wood and M_A is the mass flow of air entering the fire. In oxygen-rich fires R' is less than 0.3, which corresponds to 15% oxygen remaining in the combustion products. An unstable condition arises if R' exceeds 0.3 because the fire then accelerates spontaneously until it is limited by its ability to preheat the wood fast enough. At this point R' significantly exceeds 1 and may be as much as 3.

The experimental data agreed with the mathematical analysis when the Reynolds number for gas flow exceeded 10^4. Discrepancies for lower Reynolds numbers suggest that the assumption of perfect mixing of fuel and air in the combustion section is no longer valid.

$\bar{T}_g$ increased and T_g' decreased with increased air speed. The trend toward convergence of $\bar{T}_g$ and T_g' at low air speeds suggested approach to insufficient heating to release fuel in the excess fuel section of the pyrolysis zone. No systematic effect of wood moisture content on $\bar{T}_g$ could be observed.

R' determined either from flame spread or from analysis of exit gases agreed with a linear increase in air speed for $R'=3.0$.

The heat transfer coefficient (both convective and radiative) differed for the combustion section and the excess fuel section but each increased linearly with air speed.

The rate of volatile emission from the wood in the combustion section increased linearly with air speed; that in the excess fuel section was nearly constant at low air speeds but increased and at high air speeds became nearly the same as that from the combustion section.

Subject Headings: *Fire, propagation in passages; Passages, fire propagation in.*

F. L. Browne

E. Suppression of Fires

Barker, R. K. and Sprado, C. G. (Minnesota Mining and Manufacturing Company, St. Paul, Minnesota) "Carbon Dioxide System Design Analysis by Computer," *Fire Technology* 3(4), 306–313 (1967)

A method for the design analysis of carbon dioxide systems by computer is discussed. The program is limited to any high pressure system requiring not more than 400 sections of pipe and 50 nozzles. Both local application and total flooding protection, as well as a combination of the two, are provided for in the program.

The procedure begins with much the same pattern normally used in manual system calculations. Firstly, the necessary protection is decided upon; secondly, the nozzle locations, piping arrangements, and cylinder storage location are prepared in the form of a schematic diagram; thirdly, the information is transferred to coding sheets. A keypunch operator produces the computer input data cards from the coding sheets; the cards are fed into the programmed computer and processed. The printout can then be reviewed; if any revisions are necessary, the input cards are changed and the process repeated until a final set of calculations is obtained. Improved accuracy, cost reduction, and saved time are claimed for these design procedures, the results of which are said to conform to the Standard on Carbon Dioxide Extinguishing Systems (NFPA No. 12).

Subject Headings: *Carbon dioxide, extinguishing systems design; Computer design, of extinguishment systems; Extinguishment, by computer design, carbon dioxide systems.*

W. G. Labes

Belpol, A. N. "The Extinction of Burning Methane in Mines by Means of Halogenated Hydrocarbons," *Ugol'* 42(2), 58–60 (1967) (In Russian)*

Describes the use of a mixture of mono-bromo-ethane and tetrafluoro-dibromoethane in OGS-7 and OGS-5 fire extinguishers. It is claimed that dangerous methane fires have been extinguished with a concentration by volume of 1.7% of the vapour from the mixture. Further investigation of the fire extinguishing properties of halogenated hydrocarbons is recommended.

Subject Headings: *Extinction, of mine fires, by halogenated hydrocarbons; Halogenated hydrocarbons, in mine fires; Methane fires, in mines; Mine fires, halogenated hydrocarbons for methane fires in mines.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(2), 78. By permission.

Eickner, H. W. and Schaffer, E. L. (Forest Products Laboratory, U. S. Forest Service, Madison, Wisconsin) "Fire-Retardant Effects of Individual Chemicals on Douglas Fir Plywood," *Fire Technology* 3(2) 90–104 (1967)

The authors studied the effects of individual chemicals on flame spread, smoke density, and the heat index of Douglas fir plywood. Three types of tests were performed in an effort to establish a correlation relationship between test methods.

Of the chemicals investigated, monoammonium phosphate was the most effective in reducing flammability. Zinc chloride was next in effectiveness, although at low retention levels both ammonium sulfate and zinc chloride had nearly equivalent performance. The more effective fire retardant chemicals, monoammonium phosphate and zinc chloride, increased the smoke-index values (8-ft tunnel) at retentions above 2.0 lbs per cu ft. The other chemicals reduced the smoke-index values, unless extremely high retentions were involved. Chemicals such as sodium borate, sodium dichromate, and ammonium sulfate, which do not retard afterglow, showed low smoke development. All of the fire retardant chemicals investigated reduced the heat-index values with increasing retention. The interaction between several chemicals in combination was not studied.

Correlation curves were established for the treated plywood which relate the flame-spread index values derived from the 8-ft tunnel furnace test to results obtained by fire-tube methods. The type of chemical used in the treatment of the plywood strongly influenced the correlation relationship between the 8-ft tunnel and the Schlyter panel methods. The 8-ft tunnel method generally had greater sensitivity in differentiating between treatments at the lower flammability ranges than did the Schlyter panel or fire-tube methods.

Subject Headings: *Douglas fir (See Fir); Fir, fire retardants effects on; Fire retardants, effect on Douglas fir.*

Authors' Summary and Conclusions

Guise, A. B. (Consulting Engineer) "Extinguishment of Natural Gas Pressure Fires," *Fire Technology* 3(3) 175–193 (1967)

Analyses of data provided by testing programs have led to the following conclusions:

Potassium bicarbonate-base dry chemical is superior to sodium bicarbonate-base dry chemical as an extinguishing agent for fires in natural gas.

The degree of superiority of potassium bicarbonate-base dry chemical varies with the type of pressure fire. Based upon comparative dry chemical flow rates for identical fire sizes, it has a minimum superiority of 2 to 1 for vertical jet fires and 7 to 1 for impingement fires. Based upon comparative fire sizes for identical dry chemical flow rates, it has a minimum superiority of 6 to 1 for vertical jet fires and 3 to 1 for impingement fires.

The rate of dry chemical application is critical.

Concentrated, high velocity dry chemical streams are superior to "soft" or fan streams for the extinguishment of natural gas pressure fires.

Fires in impinging jets are much more difficult to extinguish than fires in non-impinging jets, especially after burning long enough to heat to redness the metal or earth upon which they impinge.

Subject Headings: *Extinguishment, of natural gas fires; Fires, natural gas, extinguishment of.*

Author's Conclusions

Fire Research

, v. 10, n. 2 (1968)

Kravchenko, V. I. and Mukhin, V. R. "Methods and Procedure for Extinguishing Complex Underground Fires," Moscow, *Nedra* (NLL shelf mark: R. 40851) (1965) (In Russian)*

The book deals with new types of complicated underground fires, which occur as a result of mining at greater depth, increased gassiness of coal seams, longer mine workings, concentrations of electrical machinery and equipment, more complicated ventilation systems, etc. It is pointed out that so far research into these fires (e.g. burning of methane in the waste, endogenous fires in contiguous seams above active workings, endogenous fires in the worked-out area of the face with the additional complication of methane and coal-dust explosions, etc.) has been inadequate. The authors make a number of recommendations for extinguishing such fires.

Subject Headings: *Extinction, of underground fires; Fires, underground, extinction of; Underground fires, extinction of.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(4), 71. By permission.

McGuire, J. H. (Division of Building Research, National Research Council, Canada) "The Flammability of Exterior Claddings," *Fire Technology* **3**(2) 137–141 (1967)

Flame-spread tests, according to the Tentative Method of Test for Surface Flammability of Materials Using a Radiant Heat Energy Source (ASTM E162-66T), were carried out on samples of all test specimens. Mean results are given in the sixth column of Table 1. The result of the test on imitation brick siding (Test No. 6), which involved a thermally thick assembly, suggests that a cladding with a rating exceeding 200 is likely to propagate fire vertically. As the behavior of the unpainted drop siding in Test No. 8 might also be considered undesirable, critical rating might well be taken as 150 rather than 200.

Since the assemblies in Tests No. 1 and 10 were not thermally thick in relation to the time scale of the test, burning could take place on both the front and rear surfaces of the specimen. This feature influenced performance. The results suggest that, in assemblies that are not thermally thick, a cladding with a rating exceeding 100 will probably propagate fire vertically. Vertical siding used in Test No. 5 had a rating of 109. The assembly included a cavity in which flaming could occur, but the specimen did not propagate fire indefinitely. The siding, roofing felt, and plywood sheathing made the assembly thermally thick.

Subject Headings: *Cladding, flammabilities of; Exterior claddings, flammability of; Flammability, of exterior claddings.*

Author's Conclusions

Peterson, H. B., Tuve, R. L., Jablonski, E. J., Neill, R. R., Bertschy, A. W., and Gipe, R. L. "Fire Equipment Tests aboard the CVA-62 Related to Improved Aircraft Carrier Safety," *NRL Memorandum Report 1851* (January 30, 1968)

A series of tests were conducted at sea aboard the USS INDEPENDENCE (CVA-62) for the purpose of evaluating the application of the twinned agents, "Light Water"—Purple-K-Powder, from the Twin Ball Fire Fighting Unit, application of "Light Water" from a helicopter, and P-K-P from portable extinguishers. Also studied were the characteristics of the NBC "washdown" nozzles as possible basis for the introduction of a "Light Water" based installed fire protection system for the flight deck. Wind speeds and patterns were measured at various heights above the deck to establish their role in fire fighting operations. The major portion of the work was done under 30 knot winds characteristic of the wind speed during aircraft launch and recovery and representing the most severe conditions for extinguishing fires.

The air flow over the deck below the 6 ft level was found to be laminar in character with marked diminishment in speed at levels near the deck. Thus, the detrimental effects of wind on the discharge patterns of fire extinguishing agents was not serious in the down-wind direction but did severely limit the cross-wind agent reach.

The water distribution pattern from the "washdown" nozzles offers good potential as a base for a fire fighting system which with "Light Water" will offer both fire extinguishing and ordnance cooling capabilities. Average water application rate from this system is 0.03 gpm/ft^2 deck area, although the tests proved the wind-blown patterns were very uneven. Previous shore-based fire tests have shown JP-5 fires can be readily extinguished at this application rate of "Light Water" spray. Simulated ordnance made of sponges demonstrated that water spray concentrations of 0.015 gpm were reaching each square foot of exposed munitions surface area. This is equivalent to absorbing about 150 BTU/min/ft^2.

The discharge of water nozzles mounted along the edge of the flight deck and directed inboard was found to be highly deflected by the wind and will present a problem in properly designing a system for those carriers not already fitted with flush-deck nozzles. Additional testing on the pattern, flow, and angle of discharge will be required in order to obtain satisfactory results.

Extreme wind deflection of "Light Water" applied from the boom of the UH-2B helicopter dispersed the stream and made aiming to the site of the fire difficult. These and other helicopter operational problems lead to the recommendation that this method not be considered further for carriers.

Operation of two of the High Capacity Fog Foam System stations revealed problems in getting them into action within the desired time period of 30 sec. Their foam proportioning was found to be erratic but usually on the rich side. Foam concentrate replenishment rates were inadequate.

Subject Headings: *Aircraft carrier safety, USS INDEPENDENCE (CVA-62); Purple-K-Powder, from portable extinguishers; Fire extinguishing agents; Helicopter application of "Light Water"; High capacity fog foam system, evaluating tests of; NBC "washdown" nozzles; "Light Water", in shipboard fires.*

Authors' Summary

Ratushkov, M. R., *et al.* "The Practice of Extinguishing Underground Fires in Coalmines by the Use of Inert Gases," *Ugol'nysh* 40(6), 63–64 (1965) RTS translation No. 3684*

The difficulty of the discontinuous supply of inert gas from cylinders to the fire is overcome by obtaining inert gas mixtures (i.e., gas mixtures with an oxygen content of less than 1–2 per cent) from burning liquid, solid, or gaseous fuels. A movable apparatus has been developed for burning diesel oil for this purpose, giving an output of 500 m³/hour. A description is given of this apparatus, and of the method used for extinguishing an underground fire caused by spontaneous combustion.

Subject Headings: *Coal mine, fire suppression in; Inert gases, for coal mine fires; Mine fires; Underground fires, suppression by inert gas.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(3), 70. By permission.

Schulze, G. "New Methods and Equipment for Fire Control in Mines," *Atemschutz-Informationen* 3(2), 41–45 (1964) (In German)*

After surveying the statistics of causes of fires in East German mines the author discusses the characteristics of open and concealed fires, extinguishing agents and their effect on mine climate, the use of CO_2 as an extinguishing agent, the possibilities of hand fire extinguishers and the compressed air foam method.

Subject Headings: *Climate, in mines; Extinguishing agents, for mine fires; Fire control, in mines; Mines, fire control in.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(6). By permission.

Schulze, G. "Compressed Air Foam for Mine Fires," *Paper No. 24—International Conference on Mine Fires, Rožnov p/R,* October 1966. Scientific Coal Research Institute in Ostrava-Radvanice, Chief Mine Rescue Station in Ostrava-Radvanice. (S.M.R.E. translation No. 5408)*

The difficulties involved in controlling open mine fires and the advantages and disadvantages of the various extinguishing agents and processes are described. The compressed air foam methods and the appliances used are explained.

Subject Headings: *Compressed air foam, for mine fires; Foam, for mine fires; Mine fires, foam for.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(6). By permission.

Slokan, K. "The Use of the CO_2 Occurring in Mine Cavities as a Means of Controlling Mine Fires," *Paper No. 40, International Conference on Mine Fires, Rožnov p/R,* October 1966. Scientific Coal Research Institute in Ostrava-Radvanice, Chief Mine Rescue Station in Ostrava Radvanice. (S.M.R.E. translation No. 5411).*

The author gives the outlines of a method by which the CO_2 developing in the goaf can be used to reduce the risk of firedamp to hinder the rapid oxidation of coal and wood and to extinguish fires in inaccessible parts of the goaf.

Subject Headings: ***Carbon dioxyde, in mine fires; Mine fires, carbon dioxyde for.***

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(6). 62. By permission.

Sovkov, E. P. and Vasilevo, N. "The Highly Expanded Foam—An Effective Means of Putting Out Fires," *NLL translation No. RTS 3755 of Russian Mono* (1965)*

The present work described methods of producing highly expanded foams, the construction of existing foam-producing units and methods of using it for extinguishing fires.

Subject Headings: ***Extinguishment, by foams; Foam, expanded; Mine fires, suppression by foam.***

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(3), 17. By permission.

G. Combustion Engineering

Friedman, M. H. (Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland) "A Generalized Thermal Explosion Criterion—Exposition and Illustrative Applications," *Combustion and Flame* 11(3), 239–246 (1967)*

This paper is concerned with ignition of a heat-conducting material that supports a one-step, zero-order, exothermic, Arrhenius reaction. Results are given for both critical conditions for ignition and ignition time.

First, an exposition is given of a general but approximate theory for critical ignition conditions. It is postulated that ignition will occur if there is a position within the material at which the calculated amount of time spent at temperatures in excess of a particular temperature exceeds the ignition time (or "adiabatic explosion time") ascribed to that particular temperature. The calculation of the time spent

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above a prescribed temperature is to be performed by solving an initial-value problem (with proper boundary conditions) in which the chemical heat source term is neglected. The "adiabatic explosion time" at a prescribed temperature is to be obtained from a particular approximate formula that is given in the paper and was derived from a report by Muller and Bernstein.[1] It is stated that ignition will occur if there exists *any* temperature for which the approximate ignition criterion is satisfied, but it is also acknowledged that in practice the trial temperature must be chosen sufficiently above ambient temperature or else the criterion will always predict ignition but with exceedingly long ignition times.

It is suggested that, within the context of this theory, a useful approximation for the "time to explosion" (the actual duration of the ignition process) under specified initial and boundary conditions, is the minimum, taken over all spatial positions and trial temperatures, of the sum of the calculated time to reach the trial temperature and the "abiabatic explosion time" at that temperature.

The general theory is applied to two particular ignition problems—ignition in an infinite one-dimensional system by means of an initially isothermal hot slab and ignition of a one-dimensional semi-infinite material by means of convective surface heating. Attention is focused on critical conditions for ignition in the first problem and ignition times in the second. In both cases, application of the general theory produces transcendental algebraic equations that are solved iteratively or by trial and error in obtaining the desired results. In both cases, approximate closed-form solutions are derived by introducing further approximations into the transcendental equations. In both cases, predictions of the iterative solutions and of the closed-form equations are compared with results computed from finite-difference solutions to the original partial differential equations; the numerical integrations had been carried out earlier by the author for the first problem and by Hicks[2] for the second. The comparisons are favorable.

There is also some discussion given of the ranges of validity of various approximations for each of the two illustrative problems.

The relationship between the results of this work and results of some earlier work on ignition is discussed. The discussion serves to clarify conditions under which the various theoretical formulas can be used. I believe that, although the discussion of the relationship to other work is rather extensive, it is not complete. Let me take the hot slab problem as an example. Work of Zinn,[3], Boddington,[4] and Muller and Bernstein[1] is considered. However, no reference is made to work of Spalding [Aircraft Engineering **25**, 264 (1953), Proc. Roy. Soc. **A245**, 352 (1958)], Rosen [J. Chem. Phys. **30**, 298 (1959), **31**, 253 (1959)], Bolkhovitinov [Dokl. Akad. Nauk. S.S.S.R. **125**, 570 (1959), Izv. Akad. Nauk S.S.S.R. 754 (1960)], Thomas [Trans. Faraday Soc. **56**, 833 (1960), Proc. Roy. Soc. **A262**, 192 (1961), Combustion and Flame **9**, 369 (1966)], or Merzhanov [Dokl. Akad. Nauk S.S.S.R. **148**, 380 (1963), **169**, 158 (1966), Combustion and Flame **10**, 341 (1966)]. Some of the work that I have cited here treats problems slightly different from the one treated by the author, in that the geometry is sometimes cylindrically symmetrical or spherically symmetrical, or reactant consumption is taken into account. However, these differences are minor ones, and in a number of cases precisely the same problem is considered. In one case (the Combustion and Flame paper of Merzhanov), an approximate formula for the critical hot-slab thickness is developed which superficially appears to be of the same functional form as the approximate formula developed by the author.

In view of the large amount of theoretical research on this specific subject that has appeared and continues to appear in the literature, I propose that reference lists be required to contain more than 30 citations as a condition for publication of a paper on the theory of ignition. The state of development of this subject appears to have reached a point comparable to that attained in 1960 by steady-state, one-dimensional, adiabatic laminar flame theory for one-step reactions.

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2. Hicks, B. L.: *J. Chem. Phys. 22,* 414 (1954).
3. Zinn, J.: *J. Chem. Phys. 36,* 1949 (1962).
4. Boddington, T.: *Ninth Symposium (International) on Combustion,* p. 287, Academic Press, (1963).

Subject Headings: ***Explosion theory, Thermal explosion, theory of.***

F. A. Williams

Cato, R. J., Gilbert, W. H., and Kuchta, J. M. (U. S. Bureau of Mines, Pittsburgh, Pennsylvania) "Effect of Temperature on Upper Flammability Limits of Hydrocarbon Fuel Vapors in Air," *Fire Technology 3*(1) 14–19 (1967)

The effect of temperature on the upper limits of flammability of the hydrocarbons examined here is greater than that which may be predicted by a modified Burgess-Wheeler law for "hot" flame propagation (approximately 7.5 volume per cent per 100°C). The observed values for the low molecular weight paraffins are particularly higher at temperatures greater than 100°C to 120°C; the criterion of flame propagation may explain the higher values. It is also evident from the present data that the above empirical law is not suitable for predicting the upper limits of the high molecular weight paraffins which have low autoignition temperatures and can propagate "cool" flames at low initial mixture temperatures. The low molecular weight hydrocarbons can also be expected to form "cool" flames and display autoignition behavior at temperatures higher than were employed in this work. Where autoignition is a possibility in practice, limits of flammability of the combustible-oxidant system should be known at temperatures as high as those near critical for ignition to insure maximum safety.

Subject Headings: ***Flammability limit, of hydrocarbon; Hydrocarbon, flammability limit of.***

Authors' Conclusions

Eggleston, L. A. and Pryor, A. J. (Southwest Research Institute, San Antonio, Texas) "The Limits of Dust Explosibility," *Fire Technology* **3**(2) 77–89 (1967)

Over the past half century, the dust explosion hazard has been attacked from many angles. This paper examines the problem, briefly reviews past efforts, and discusses recent modifications and techniques for measuring explosibility limits.

Subject Headings: *Dust explosion limits; Explosion limits, for dusts; Limits of explosion of dusts.*

Authors' Summary

Harris, G. F. P. and Briscoe, P. G. (I.C.I. Ltd, Manchester, England) "The Venting of Pentane Vapour-Air Explosions in a Large Vessel," *Combustion and Flame* **11**(4), 329–338 (1967)

The results of the second phase of an experimental program on the design of explosion vents for plant vessels is presented in this paper. The object of the program was to generate vent design criteria from explosion pressure data obtained in a small closed vessel containing explosive mixtures of gaseous pentane and air. The need for this design information arises from the industrial use of explosion vents on pressurized vessels in which some kind of vent closure is employed to prevent leakage of the reaction mixture during normal operation. The bursting pressure of the closure as well as the vent area will affect the maximum pressure developed in an explosion in the vessel. In the first phase of the program, reported elsewhere, it was shown that the turbulence of the explosive mixture has a profound effect on the average and maximum rates of pressure rise in closed vessel explosions.

The experiments were carried out in a 60 ft^3 vessel consisting of a cylinder with dished ends (4 ft, 6 in. in diameter; 4 ft, 9 in. in over-all length). A fan, mounted in the vessel slightly above the center, generated turbulence in the gas-air mixture. At one end of the vessel was a 24 in. diameter neck, which could be fitted with a range of flanges so that vents with diameters of 6.2, 12, 18, and 24 in. could be used on the vessel. Flammable pentane-air mixtures were produced by spraying a measured volume of pentane into the vessel with the fan operating. Analytical checks of the actual concentration in the vessel were carried out. The mixture was ignited at the vessel center and the pressure behavior recorded.

Measurements of the maximum explosion pressure were made as a function of bursting disc operating pressure for three mixtures: 1.7 mol % pentane in air (weakly explosive), 2.5 mol % (average explosibility), and 3.0% (most explosive) using vents of 6.2, 12, and 24 in. diameters. The results showed that the maximum explosion pressure is highest when the vent size is the smallest, but that minima occur in some of the curves when plotted against bursting pressure. These minimum points are followed by a merging of all the explosion pressures curves into nearly the same linear behavior at higher bursting pressures. This behavior occurred with the 2.5 and 3.0 mol % mixtures but not with the 1.7% mixture. In these tests the gas-air mixture was stationary (fan not operative). In order to determine the influence of turbulence on the maximum explosion pressure, tests were also conducted driving the fan up to 2000 rev/min. Unfortunately no measure of the turbulence intensity or scale was performed. Hence fan speed, an indirect measure at best, was used as an indicator of turbulence. The experiments, performed with 1.7 and 3.0 mol % mixtures and a fan speed of 2000 rev/min, showed higher pressures than those obtained with stationary mixtures for a given vent size and disc bursting pressure. This higher pressure is attributable to more rapid burning leading to higher pressures before the gas is expelled through the vent. No minima were observed in the explosion pressure versus bursting pressure curves for the turbulent mixtures, nor were there vibratory explosions of the type observed for stationary gas mixtures in both the closed vessel and vented vessel experiments. With only one exception, namely, the 24 in. diameter vent and a 3.0% mixture, the highest maximum explosion pressure was obtained with the smallest vent size. The explosion trace for the exceptional case consisted of a number of transient peaks and differed considerably from the traces for the same explosive mixture with the smaller vent sizes (12 and 18 in.).

Further measurements were made at various fan speeds. For the two explosive mixtures used, 1.7 and 3.0%, the explosion pressure rose to a maximum with increasing fan speed for the smallest vent (6.2 in.) but for the larger vents the explosion pressure did not reach a maximum at the highest attainable speed (2000 rev/min).

The data obtained for stationary mixtures were compared to that of other investigators using a K factor which was obtained from the cross-sectional area of the vessel divided by the vent area. The results refer to the most explosive mixture in each case. Moderately good agreement was obtained with Burgoyne and Wilson's[1] results, but Cousins and Cotton's[2] pressures are much lower for a given value of K. This discrepancy is attributed to either an L/D effect or to the fact that Cousins used wall ignition rather than center ignition. It was not possible to compare the venting of turbulent gas explosions owing to the afore-mentioned difficulty in not specifying the degree of turbulence.

The results obtained are far from adequate to provide a general method for the design of explosion vents for all types of plant vessels. Within certain limits, however, the data are useful. The maximum explosion pressure is given as a function of the K ratio for both stationary and turbulent gas mixtures of pentane and air. These data are based on a 1.7 and 3.0% mixture in a 60 ft^3 vessel. The full effect of vessel size on explosion pressure is unknown and caution is required in applying these data to vessels larger than 60 ft^3. In addition, although it was originally intended to obtain explosion pressure data at maximum turbulence, where there was no further increase in explosion pressure with increase in turbulence (fan speed), this condition was not reached for the larger vents. No reliable method of relating turbulence intensity in the 60 ft^3 vessel with that in other vessels is available. The possibility of using gas flow rate in the vessel is suggested as a correlating method; however, its usefulness is questionable. Accurate turbulence measurements appear to be a necessity for further progress.

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Subject Headings: ***Explosions, venting of; Pentane-air explosion venting; Venting, of pentane–air explosions.***

L. A. Povinelli

Kennedy, M. and Taylor, G. "Temperature Distributions Downwind of Stationary Mine Fires," *British Journal of Applied Physics* **18**(3), 349–356 (1967)*

This paper describes an experimental and mathematical approach to the evaluation of the variation of temperatures with distance and time downwind of a fire in a ventilated passage through a medium of low thermal conductivity. The experimental results obtained in a 30 ft long, 2½ in. square passage enabled a useful simplification to be made in the analysis. The method of analysis was applied to the similar problem of the air-cooling of a circular passage through a medium of low thermal conductivity and the results of this application agreed quite well with a previous analysis by Van Heerden.

Subject Headings: *Mine fires, temperature distribution in; Temperature distribution, in mine fires.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(2), 9. By permission.

Mason, W. E. and Wilson, M. J. G. (Imperial College, London, England) "Laminar Flames of Lycopodium Dust in Air," *Combustion and Flame* **11**(3), 195–200 (1967)

Burning velocities of laminar lycopodium dust flames were determined for several compositions. The dust suspensions were produced by passing metered quantities of humidified air through a fluidized bed of lycopodium powder. The dust concentration was varied by varying the air flow through the fluid bed. A portion of the suspension passed through a burner tube, symmetrically placed in the apparatus, and the remainder flowed to an exhaust system. The flow velocity in the burner tube could be regulated independently of the dust concentration. Average kinetic concentrations (C_t) were measured by filtering the entire burner stream for a fixed time and weighing the filter.

Flow patterns in the burner tube in the absence of a flame were determined by particle track photography. A fairly wide particle-free region was noted near the burner tube walls (e.g., with flows of 1.25–1.61/min. in a tube 10.9 mm diameter, the particle-free region adjacent to the wall was 1.7 mm in width). The concentration of dust in the part of the stream containing it was thus greater than C_t, on the average about 50% greater than C_t.

Particle track photography showed that flames of lycopodium dust in this burner were stabilized in the diverging flow above the burner lip in a manner similar to flat flames on an Egerton–Powling burner. Flame fronts could be made either flat or saucer-shaped by adjusting the flow. The range of dust concentrations over which flames could be stabilized was $125 \text{ mg/l} \leq C_t \leq 190 \text{ mg/l}$. At the upper end of this range ($C_t > 170$ mg/l), flames could be maintained flat for about 30 sec, following which the flame would gradually attach to the burner lip, and the flame front would take the shape of a shallow cone.

Flame velocities (S_u) for four flames were measured by the particle track method. These ranged from ~14 cm/sec for a flame for which $C_t = 129$ mg/l to ~25 cm/sec in the central region of a flame for which $C_t = 156$ mg/l. The flames of the more concentrated mixtures showed a pronounced radial variation in S_u, e.g., $S_u = \sim 25$

cm/sec at the center and $S_u = \sim 10$ cm/sec near the edge for the mixture for which $C_t = 156$ mg/l.

The preheating zone was estimated to be about 2 mm thick, based on thermocouple measurements. It was concluded that radiation contributes little to heat transfer in the preheating zone. Uncorrected thermocouple measurements of temperature above the flame front afforded a value of 1550°C for $C_t = 140$ mg/l.

Lycopodium dust flames would not propagate more than ~4 cm down a 10.9 mm diameter tube, but would propagate the full 14 cm length of a 13.5 mm diameter burner tube.

Subject Headings: *Dust flames; Lycopodium dust flames; Flames, of lycopodium dust.*

P. R. Ryason

Merzhanov, A. G. (Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Moscow, Russia) "Thermal Explosion and Ignition as a Method for Formal Kinetic Studies of Exothermic Reactions in the Condensed Phase," *Combustion and Flame* **11**(3), 201–211 (1967)

From a "classical" point of view, the kinetics of rapid, exothermic decomposition reactions in the solid or liquid phase are difficult to study because isothermal conditions cannot be maintained and because physical phenomena (e.g., heat transfer) play an important role in determining the observed behavior (which includes non-uniform self-heating and explosion phenomena). However, rather than curse these "complications," one can *exploit* them to betray the kinetics of pre-explosion reactions by measuring, under well-defined conditions of geometry and heat exchange:

(i) the time elapsed before thermal explosion occurs (i.e., the "induction time," t_{ind}) and/or
(ii) the environmental parameters delineating the regime of thermal explosion (from the regime in which thermal explosion does not occur, regardless of how long one waits).

This macrokinetic approach, now known as the "ignition" or "thermal explosion" method,* has indeed been fruitful, especially as a result of ostensive theoretical and experimental investigations in Russia. In the paper under review, Dr. Merzhanov provides a useful summary of results obtained over the last 10 years at the Institute of Chemical Physics of the Academy of Sciences, U.S.S.R., together with a frank appraisal of the possible pit-falls and areas in need of further development. Of special interest are comparisons of inferred kinetic parameters using both ignition/thermal explosion methods and isothermal methods.

The class of problems for which useful theoretical results are now available (to interpret data) is generally characterized by simplicity in:

(i) geometry (i.e., symmetrical or one-dimensional regions);
(ii) thermal boundary conditions (i.e., constant surface temperature or a well-defined convective/radiative boundary condition);
(iii) heat generation law (i.e., of the form $Qf(\eta, T) \cdot A \exp(-E/RT)$ in which the

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* To be distinguished from macrokinetic inferences based on quasi-steady combustion phenomena (e.g., burning rates).

constants Q, A, and E are, respectively, the heat of reaction, the pre-exponential kinetic constant and activation energy; the function $f(\eta, T)$ describes the dependence of instantaneous reaction rate on the fraction reacted† η; and

(iv) transport mechanisms (i.e., heat transport in the condensed phase by conduction only; negligible molecular interdiffusion).

Accordingly, it is necessary to ensure that the experimental system chosen is free of complexities not included in available theoretical treatments (e.g., internal phase transitions, vaporization/sublimation followed by exothermic gas phase reactions, exothermic *surface* reactions, bodily motion in the reaction zone, stepwise kinetics not describable by an over-all Arrhenius expression, changing heat exchange mechanism at boundary, etc.). Included in the present paper are results obtained using four distinct experimental methods, viz.,

1. cylindrical specimen/thermostatically-controlled vessel shell (nearly isothermal, adiabatic at all times),
2. fine spherical particles/hot gas,
3. smooth flat surface sample/heated (aluminum) block (i.e., the "contact" method) and
4. circular cylinder/transverse flowing hot gas,

where, in each case, one monitors either the surface temperature or luminosity to detect the onset of thermal "runaway" or explosion. Using one or more of these techniques and available theoretical formulae for t_{ind} and the explosion "boundary" (necessarily cited but not derived in the present paper), kinetic parameters have been inferred for the thermal decomposition of each of the following solids: dinitroxydiethylnitramine, tetryl, cellulose nitrate, barium azide, polyvinyl nitrate, ammonium bichromate and nitrostarch. These include the values of Q, A,* E and, in some complex cases (autocatalytic reactions), the function $f(\eta, T)$. A typical set of results on the material cellulose nitrate† is collected in Table 1 (reproduced in altered form below), which includes parameters inferred over somewhat different temperature ranges using the methods outlined above.

Dr. Merzhanov concludes that, when comparisons have been possible, agreement has been sufficiently encouraging to warrant continued exploitation and extension of these techniques. For some substances (e.g., barium azide) for which disagreement exists among the available methods, it is believed that this disagreement is real and reflects altered kinetic mechanisms at different temperature levels, thereby providing information on the validity of kinetic law extrapolations commonly used in predicting explosion behavior in engineering applications. For chemical process of duration ≥ 50 msec, Dr. Merzanhov suggests that additional methods (similar in spirit to those already exploited) should be developed to further extend the range of conditions and materials for which kinetic data are available. However, for describing faster processes (e.g., those accompanying very high heating rates) present theory is in an unsatisfactory state and it is not yet clear how one should approach the problem of determining kinetic parameters.

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† A reaction is said to be zero order if $f(\eta)=1$ and first order if $f(\eta)=1-\eta$.

* Frequently, only the product of QA can be inferred from available data.

† In this case it is known that the true kinetics are autocatalytic [i.e., $f(\eta, T) \approx (1-\eta) + k_2'(T) \cdot \eta(1-\eta)$]; however, the rate constant ratio $k_2'(T)$ is such that above 493°K the reaction becomes indistinguishable from a first-order reaction.

TABLE 1.

Kinetic parameters for the thermal decomposition of cellulose nitrate

Method	Temperature interval (°K)	$10^{-22}QA$ cal(gm)$^{-1}$(sec)$^{-1}$	E Kcal(mole)$^{-1}$
Thermal explosion of particles	496–528[a]	0.425	48.5
	593–693[b]	10.0	50
Contact ignition	485–515	2.4	47.7
Ignition by gas flow	573–623	—	48
Isothermal experiments	413–438	0.74	47

[a] based on environmental conditions at explosion "boundary".
[b] based on induction time.

Subject Headings: *Explosion, thermal; Ignition, of condensed materials; Kinetics, of condensed phase reactions.*

D. E. Rosner

Shadrin, P. N., Ivanov, V. A., Gudkov, V. I., and Chekhovskii, A. M., "Shock Waves during Explosions of Methane-Air Mixture in Mine Workings," *Bezop. Truda v Promyshl.* 10(11), 39–40 (1966) (In Russian)*

Describes experiments carried out with the aim of establishing the actual pressures and speeds that occur during explosions of large volumes of methane-air in mine workings, and also the factors that influence the propagation of shock waves. A system was developed by means of which it is possible to record the basic parameters of an artificially induced explosion of large quantities of methane-air over considerable distances. The experiments showed that the centre of the explosion is characterized by a prolonged effect of high temperature and the fact that there is no displacement of various objects on the floor of the working. It is pointed out that these observations may be employed for determining the point of an explosion during investigations of incidents in seams. The pressure and speed of the shock wave increases with the distance from the ignition source. Junctions in workings sharply reduce the pressure in the shock wave.

Subject Headings: *Explosions, mine, shock waves in; Methane-air explosions, in mines; Mine explosion, shock waves in; Shock waves, in mine explosions.*

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(6), 10. By permission.

Takeno, Tadao (Institute of Space and Aeronautical Science, University of Tokyo, Tokyo, Japan) "Experimental Studies on Driving Mechanism of the High Frequency Combustion Oscillation in a Premixed Gas Rocket," *Institute of Space and Aeronautical Science, University of Tokyo Report No.* **420** (January 1968)

Experimental studies were conducted to clarify the initiating and driving mechanisms of longitudinal combustion oscillation with high frequency in a rocket motor in which a premixed gas was burnt as the propellant. The effects of several factors upon the critical oscillation period, which was found in the previous studies to be closely connected with the occurrence of oscillation, were studied first. Then the distribution of gas temperatures in the reaction zone during the oscillation was measured in detail. Finally, the photographic investigation of the reaction zone during the oscillation as well as during steady combustion was made by high speed schlieren motion pictures.

It was made clear that the shock wave theory in which the driving mechanism is considered to depend on chemical factors is invalid for describing the occurrence of oscillation. The interaction between the pressure wave and the combustion process which provides the driving force of oscillation was found to be of rather complicated fluid-mechanical nature. The shock wave plays no important role in this interaction. The characteristic time which is a decisive factor for the occurrence of oscillation was identified with the ignition delay time of the unburnt propellant in the stream of hot combustion gas. The latter was found to depend mostly upon the propellant equivalence ratio, although the pressure in the combustion chamber and the injection Mach number of the propellant were found effective to some extent.

Subject Headings: *Combustion, oscillations in rockets; Oscillatory combustion, in rockets; Rocket combustion, oscillations in.*

Tosiro Kinbara

Yumlu, V. S. ("Shell" Research Ltd., Thornton Research Centre, Chester, England) "Prediction of Burning Velocities of Carbon Monoxide-Hydrogen-Air Flames," *Combustion and Flame* **11**(3), 190–194 (1967) and "Prediction of Burning Velocities of Saturated Carbon Monoxide-Air Flames by Application of Mixing Rules," *Combustion and Flame* **11**(5), 389–396 (1967)

Ability to predict the flame speed of mixtures containing a number of combustible components or combustible mixtures with diluents is desirable mainly because considerable experimental effort can thereby be avoided.

Two "mixing rules" are available in the literature which seek to make it possible to determine the burning velocity of a mixture of fuels from the burning velocity of its components. One is by Payman and Wheeler[1]; the other is by Spalding.[2] The two rules are:

(1) Payman and Wheeler.

$$S_{u,m}=\Sigma a_i S_{u,i}$$

where S_u is the adiabatic flame speed; the subscripts m and i refer to the mixture and a component fuel, while a_i represents the volume fraction of a mixture of a component fuel and oxidant with respect to the whole mixture. In applying this rule it is necessary to decide arbitrarily how the oxidant is to be divided between the fuels if more than one is present and it is usual to suppose that the equivalence ratio for the whole mixture is the same as the equivalence ratio for each component.

(2) Spalding.

$$S_{u,m}{}^2 = \alpha S_u{}^2,\ A,\ T + \beta S_u{}^2,\ B,\ T$$

where S_u, A, T and S_u, B, T are the burning velocities of the component fuel oxidant mixtures when the flame temperature is that of the whole mixture, and α and β are the masses of A and B plus the corresponding amount of oxidant per unit mass of mixture. In applying this rule it is also necessary to decide how the oxidant is divided between fuels in cases where more than one is present. The same assumption is made as in applying the Payman–Wheeler rule.

These two rules are obviously very different in their predictions and character, but whereas the former is based on no conceivable physical system, the latter has its roots at least in flame theory, and might be expected to be more reliable. This is mainly because it takes account of the effect of changes in flame temperature with changes of concentration. With the exception of some work by the present writer[3] which was generally favorable to the Spalding equation, little has been done to check the two equations against experiment. To some extent this has now been remedied by the work under review, which is particularly critical in that it concentrates on mixtures of air and carbon monoxide with either hydrogen or water vapor (small concentrations of which produce considerable effects).

Carbon monoxide-air-hydrogen mixtures.

In order to test the Payman and Wheeler rule it is merely necessary to know the adiabatic flame speeds of the mixture and of the components at the same equivalence ratio. To test the Spalding rule requires in addition knowledge of the dependence of the flame speed on flame temperature for both components and knowledge of the flame temperature for the whole mixture. All this information was determined by the author using the Botha and Spalding method[4] for measuring flame speed, flame temperatures being measured directly by means of a thermocouple and also indirectly by means of a heat balance on the burner. (In the Botha and Spalding method the adiabatic flame speed and adiabatic flame temperature are obtained by extrapolation to zero heat loss from data obtained with nonadiabatic flames with measured heat losses.)

It is found that the Spalding mixing rule gave good agreement with experiment and that the predictions were everywhere within 6% of the measured value—this in circumstances in which the flame speed varied in a nonlinear manner from 10 cm/sec up to 60 cm/sec as the hydrogen in the fuel increased. The Payman-Wheeler rule on the other hand predicted a nearly linear variation of flame speed with increasing hydrogen concentration and was considerably in error, numerically. These conclusions are based on experiments with lean mixtures only, since rich flames proved difficult to observe. With CO–air–H_2 mixtures then, the Spalding rule appears to work, while the Payman–Wheeler rule does not.

CO–air–H_2O mixtures.

Neither rule works when applied to CO–air–H_2O mixtures if the water is treated simply as a diluent. Yumlu, in the second of the two papers under review, shows how the Spalding rule can be adapted to overcome this difficulty provided that the following assumptions are made:

(1) The water added to the mixture of carbon monoxide and air is treated as though it were the equivalent amounts of molecular hydrogen and oxygen.
(2) The oxygen is considered to be shared between the two fuels, carbon monoxide and hydrogen, according to their volumetric proportions.
(3) The final flame temperature is that of the saturated carbon monoxide flame.

The author advances several arguments in support of the credibility of these assumptions. These are:

(a) The presence of the OH emission band in both CO–air–H_2 flames and CO–air–H_2O flames.
(b) The suggestion by Bone and Townend[5] that the water vapor acts as a catalyst by means of the over-all reactions

$$CO+H_2O \rightleftharpoons CO_2+H_2$$

$$2H_2+O_2 \rightleftharpoons 2H_2O$$

in which the first reaction is highly reversible.
(c) Temperature traverses (reported in the paper) normal to a laminar flat flame of a CO–air–H_2 (2% by volume) flame are almost identical to temperature traverses through a CO–air–H_2O (2% by volume) flame.
(d) The curve of heat release rate versus reactedness for an adiabatic stirred reactor, calculated with the aid of rate constants given by Jenkins, Spalding and Yumlu[6] is virtually identical for a CO–air-2% H_2 mixture and for a CO–air–2% H_2O mixture of the same equivalence ratio. These calculations are given in the paper under review.

Given these assumptions, which in view of the evidence seem quite reasonable, the author demonstrates with the aid of further flat flame burner measurements that there is good agreement between experiment and the predictions of the Spalding mixing rule, but that the Payman–Wheeler rule is still not satisfactory.

In a sense the fact that these additional rules are needed to make the Spalding rule work detracts from its value, since it implies that other special cases may exist, each of which requires special treatment. Furthermore, one does not know, in advance of experiment, which these are. Of the two mixing rules available to us, however, there appears to be no doubt but that Spalding's is to be preferred.

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Subject Headings: *Carbon monoxide-air flames, burning velocity prediction; Burning velocity, prediction of.*

D. G. Martin

H. Chemical Aspects of Fire

Bulewicz, E. M. (University College of Swansea, University of Wales, Wales, United Kingdom) "Some Observations on Chemiluminescence and Chemi-Ionization in Flames," *Combustion and Flame* **11**(4), 297–308 (1967)

Previous observations of an apparent parallelism between ion formation and emission from excited CH in flames[1, 2] or shock tube oxidation studies[3] had given rise to speculation that excited CH was a participant in a primary chemi-ionization reaction. This contention has since been discounted[4, 5] on the basis of more recent findings and this paper affords further evidence that the similarities in those observations which originally gave rise to the above theory were fortuitous. It is now quite certain that no causal relationship exists between the presence of electronically excited CH and ion formation; furthermore, the results reported in this paper extend that conclusion to excited states of C_2 and OH.

The variations in electron concentrations in flames of several fuels over a wide range of pressures and stoichiometries have already been studied by the author[6] and others.[7] Analogous variations in the emission features of many of the same flames are reported in this paper and the results are compared with the available information on chemi-ionization. For example, the intensities of CH, C_2 and OH emissions were found to be proportional to pressure to the 2 to 2.5 power in the range from 3 to 30 torr for stoichiometric CH_4, C_2H_2, C_3H_8 and C_4H_{10} flames; electron concentrations have been found to be directly proportional to pressure in these flames.[6]

The reactions through which it had been suggested that excited CH(CH^*) might give rise to chemi-ionization are

$$CH^*+O\rightarrow CHO^++e^- \qquad (1)$$

and

$$CH^*+C_2H_2\rightarrow C_3H_3^++e^- \qquad (2)$$

Now over most of the pressure range covered in this work the dominant ion loss mechanism is H_3O^+/e^- recombination. Thus, since the over-all negative ion concentration is low $[H_3O^+]\approx[e^-]$; at the ion concentration maximum in any flame (where the formation rate equals the decay rate), it can be demonstrated through steady-state considerations that

$$[e^-]=\{k_{1,2}[\mathrm{CH}^*][\mathrm{X}]/\alpha\}^{1/2}$$

where X may be O or C_2H_2 in Reactions 1 or 2 respectively and α is the ion-electron recombination coefficient. For either Reaction 1 or 2 to be consistent with the observations, then, [X] must be independent of pressure—very unlikely behavior for either O or C_2H_2. Since OH* and C_2* exhibit essentially the same pressure dependence, the argument applies equally well to all of the chemi-ionization reactions which have been set forth[8] involving these species.

Plots of [e] and [CH*] as functions of flame stoichiometry in C_2H_2 flames at constant pressure are almost superimposable. The steady-state argument above, when applied to these observations, necessitates that [X] be proportional to [CH*] (or [OH*] or [C_2*], as the case may be). The discrepancy in the requirements imposed by these data and those above is additional evidence invalidating the proposed participation of these excited states in the ionization process. However the similarities in the observations which gave rise to the hypothesis in the first place still remain to be explained.

A correlation is attempted in this paper between the heat of oxidation of carbon in a fuel molecule and the emission intensity or ion formation rate; i.e., plots of ΔH for the reaction

$$C_xH_yO_z+(x-\tfrac{1}{2}z)O_2\rightarrow xCO_2+\tfrac{1}{2}yH_2$$

versus ion formation rates or emission intensities are supposed to give straight lines of equal slope. The ionization plot does indeed fall nicely onto a straight line including points taken from homologous series of paraffins, alcohols, ketones, ethers, esters, acids, aldehydes, and glycols. Similar observations have been reported previously[9] and, in fact, these observations constitute the basis upon which quantitative gas analyses are performed using gas chromatographic flame ionization detectors. The emission intensity plots are much less satisfying than the ionization data and large deviations from linearity can be seen in the data, together with widely varying slopes for the linear plots which do exist. Even if such a quantitative correlation could conclusively be shown to exist, it is not evident from this work what the mechanistic implications of that relationship would be.

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Subject Headings: *Chemi-ionization and chemiluminescence; Chemiluminescence and chemi-ionization.*

W. J. Miller

Miller, W. J. and Vree, P. H. (AeroChem Research Laboratories, Inc., Princeton, New Jersey) "Flame Ionization and Combustion Reactions," *Final Report under Contract CST-102 with National Bureau of Standards* (December 1967)

The purpose of this research program was to examine changes in flame ion content induced by the addition of flame inhibitors in an attempt to elucidate certain flame inhibition mechanisms and the inter-relationships existing between inhibition and ionic phenomena. The study was conducted in low pressure flames in which greatly expanded reaction zones facilitate detailed flame structure determinations.

The effectiveness of a variety of known flame inhibitors has been tested in low pressure methane flames. Both diffusion flames and premixed flames have been employed and the inhibitors studied were 15 selected compounds previously found to exhibit a wide range of efficiencies. Flames inhibited by CCl_4, $Fe(CO)_5$ and CrO_2Cl_2 were examined in detail to determine their spectral emission characteristics, ion content, and temperature profiles. The results have been studied in an attempt to elucidate the inhibition mechanisms involved—especially one involving catalytic radical recombination by small particles formed *in situ.*

The relative efficiencies of the compounds studied have, with few exceptions, been found to be the same in both premixed and diffusion flames at 10^{-2} atm. The criterion for evaluation in both cases was the amount of material necessary to produce extinction. Large differences exist in the efficiencies of different compounds; e.g., $Fe(CO)_5$ was found to be about 25 times more effective than CCl_4.

Ion profiles in diffusion flames inhibited with CCl_4 reveal a large number of positively-charged hydrocarbon ions, possibly the precursors of soot particles. These ions increase in mass and concentration with increasing distance from the visible flame front. The findings are in apparent agreement with other evidence supporting an ionic nucleation mechanism for soot formation.

Analogous ion profiles for positively-charged oxidized metallic species were taken in diffusion flames containing $Fe(CO)_5$ and CrO_2Cl_2. Emission spectra of these systems exhibit atomic Fe or Cr lines, FeO or CrO bands and broad continua in addition to the CH, C_2 and OH emissions of normal hydrocarbon flames. No spatially-resolved emission profiles were taken in flat premixed flames inhibited with $Fe(CO)_5$. Emissions from atomic Fe, FeO and a continuum attributed to hot particles are observed in the region upstream of the CH and C_2 bands and well upstream of the temperature maximum.

The results of these studies have been interpreted as indicative that flame inhibition by volatile metallic compounds proceeds via very small particles formed in the relatively cooler, O_2-rich regions of the flame. The dependences of the various emission characteristics on additive concentration were also examined in an attempt to determine the origins of observed chemiluminescence.

Future work on heterogeneous inhibition by particles formed *in situ* should include microprobe scavenging of the particles themselves and detailed mass spectrometric and stable species studies of the particle formation process (i.e., nucleation and agglomeration at high temperatures).

Subject Headings: ***Ions, in flames; Flame ionization; Combustion, ionization.***

Authors' Summary

Miller, W. J. (AeroChem Research Laboratories, Inc., Princeton, New Jersey) "Flame Ionization and Combustion Inhibition," *Technical Report No. 1 under Contract CST-102 with National Bureau of Standards* (January 1967)

The inhibition of spherically symmetrical low-pressure CH_4 or C_2H_2/O_2 diffusion flames by a variety of additives has been studied. The relative efficiencies of the compounds studied have been found to be very nearly the same as in 1-atm flames. A detailed examination of the effects of CCl_4, $Fe(CO)_5$, and CrO_2Cl_2 upon ion content and emission spectra has been made and the results interpreted in terms of previously postulated correlations between the ability of a given compound to reduce electron concentrations and its effectiveness as a flame inhibitor. No such correlation was found to exist between the two phenomena. The relatively large inhibition efficiencies of $Fe(CO)_5$ and CrO_2Cl_2 are attributed to *in situ* ultrafine particle formation downstream of the flame front and their subsequent diffusion into the reaction zone. The formation of these particles is indicated by ion profiles of nucleating species; the presence of the particles in the reaction zones of inhibited flames is further evidenced by the emission of continuum radiation. The dominance of diffusional over convection mass transport is the characteristic of the system which accounts for its susceptibility to inhibition by these compounds.

Subject Headings: ***Flame ionization; Ionization, in flames.***

Author's Summary

I. Physical Aspects of Fires

Gaskill, J. R. (Lawrence Radiation Laboratory, University of California, Livermore, California) "Hydraulics of Fire Hose Nozzles," *Fire Technology* **3**(1) 20–28 (1967)

The data obtained indicate that impact Pitot tubes can be used to determine flow rates through solid stream fire hose nozzles if proper coefficients, 0.95 in our case, are applied to the standard equation. More significantly, the pressure at the nozzle base can be used to determine over-all coefficient of any size of solid stream nozzle or of a fog nozzle adjusted to a particular setting. Such coefficients provide the means for comparing nozzle efficiency. The higher the coefficient, the more water will be delivered at a given nozzle pressure; therefore, the better the nozzle. Knowing such coefficients, one can then also determine flow rates through various sizes and arrangements of hose lays by measuring the pressure at the nozzle base.

Subject Headings: *Hose nozzle hydraulics; Hydraulics, of fire hoze nozzling; Nozzle hydraulics.*

Author's Conclusions

Reifsnyder, W. E., Herrington, L. P., and Spalt, K. W. (School of Forestry, Yale University, New Haven, Connecticut) "Thermophysical Properties of Bark of Shortleaf, Longleaf, and Red Pine," *Yale University School of Forestry Bulletin No. 70* (1967)

The bark of trees is their protective covering, corresponding in function in many respects to the skin of animals. It varies widely by species and with age in both appearance and physical properties. These variations are sufficiently marked to serve the dendrologist and the botanist well in species identification. The research reported in the above publication is addressed to the question of just how significant the variations are in giving a tree resistance to damage by fire.

To determine this, the physical properties of thermal conductivity, moisture content, density of bark, specific heat including the heat of wetting, and thermal diffusivity were each carefully measured in the bark of three species of pine chosen for the purpose. These were shortleaf (*P. echinata*), longleaf (*P. palustris*) and red pine (*P. resinosa*), respectively.

It was found that thermal conductivity is positively correlated with both bark density and with moisture content. This is what one might expect. The denser the bark and the wetter it is, the more readily will it transmit heat. Thermal diffusivity is related to specific heat. Specific heat values averaging 0.336 were obtained. These closely correspond to determinations by Dunlap in 1912 and to data obtained in an independent but current study by Martin. The formula accepted for this purpose where T is in °C is:

$$c=0.266+0.00116T$$

(To the above must be added the specific heat of the contained water.)

Thermal diffusivity is of course an expression of the end result sought. It varies in a predictable way with moisture content and so with season.

These studies involve difficult techniques in measuring internal temperatures and in developing procedures. Fortunately a parallel study by Robert Martin, carried out as a Ph.D. project, greatly strengthened the information available in this field.

From both studies several deductions may be drawn.

Thermal diffusivity for conditions likely to be found in nature was found to range to a twofold difference. It was associated with species in part.

Moisture content did not fluctuate very much and was only $\frac{1}{4}$ to $\frac{1}{8}$ that of wood.

Density of bark varies greatly by trees and by age; so though it differs by species, it does not carry a very strong species identity.

The specific heat of bark is sufficiently close to that of wood that distinctions are not significant.

The thermal conductivity of the barks tested was somewhat less than that for wood, yet not markedly so.

The net conclusion is that though the physical properties of bark are important in protecting tree stems from fire, and can be measured or computed in various ways, their relationships are far less complex than has been supposed. The thickness of the bark is more important than any other physical parameter.

Subject Headings: ***Bark, thermo-properties of; Pine bark, thermo-properties of; Thermophysical properties, of pine bark.***

A. A. Brown

Rios, J.,* Welker, J. R., and Sliepcevich, C. M. (University of Oklahoma, Norman, Oklahoma) "Interaction Effects of Wind-Blown Flames from Wood Crib Fires," *Fire Technology* **3**(2) 129–136 (1967)

As would be expected, the rate of flame propagation and the depth of the burning zone increase with increasing wind velocity. Although the total burning rate increases at higher wind velocities, the burning rate per unit area decreases, a typical behavior noted by other investigators in burning tests made under calm conditions. The rate of decrease of the burning rate is smaller in the tests made on single fires under windy conditions, probably because of increased ventilation of the burning crib.

If two fires are burning near one another, one upwind of the other, the upwind fire has a greater depth of burning zone than a single fire under wind velocities less than approximately 2 fps because of increased preheating of the fuel. The downwind fire is largely shielded from the wind effects by the upwind fire, and its burning characteristics under calm or low wind velocity conditions are approximately those of a single fire. As the wind velocity increases, the depth of burning zone and flame propagation rate increase more rapidly for a single fire than for the upwind proximate fire, until, at velocities greater than 2 fps, they become greater. This behavior is caused by differences in the air flow into and around the proximate fires as compared to the single fire.

Subject Headings: **Windblown flames; Crib fires.**

Authors' Conclusion

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J. Meteorological Aspects of Fire

Morton, B. R. (National Center for Atmospheric Research, Boulder, Colorado)* "Entrainment Models for Laminar Jets, Plumes, and Wakes," *The Physics of Fluids* **10**(10), 2120–2127 (1967)

The paper is a theoretical study regarding laminar axisymmetric flow in viscous jets, plumes, and wakes. In general, the physical feature of an entrainment model may be briefly stated as follows. In a narrow axially symmetric flow, there are two regions: an inner region near the axis of symmetry within an arbitrarily selected bounding surface, where the velocity change is relatively large; and an outer region where the flow is uniform and approximately irrotational. The ambient fluid, far away from the axis of symmetry, is uniform. The flow in the inner region is subjected to forces, such as buoyancy, pressure gradient, and viscous force. The entrainment of ambient fluid into the inner region creates a weak external pressure field which drives a slow inward replenishing flow towards the bounding surface. This model provides a useful means of obtaining approximate solutions for the behavior of jets, plumes, and other narrow flows under conditions in which more accurate treatments are unduly laborious or unobtainable.

The flow is assumed to be steady laminar axisymmetric and incompressible. The cylindrical axes (r, z) are taken for the coordinates with origin at a virtual source and z axis along the axis of flow; the corresponding velocity components are (u, w). The motion for the case of plume flow is governed by the continuity equation, radial and vertical momentum equations, and energy equation. The buoyancy is in the z direction. For the flow in jets and wakes, the buoyancy term in the momentum equation and the energy equation are dropped. Based on the entrainment model and the equations of motion, and by using order-of-magnitude argument, the entrainment flux scale and the axial velocity, etc. are obtained for each case.

Laminar Jets

The entrainment flux scale is found in proportion to the kinematic viscosity and the axial velocity is obtained as

$$w(r, z) = (m_0/4\pi\rho\nu z) \exp(-m_0 r^2/32\pi\rho\nu^2 z^2)$$

where

$$m_0 = 2\pi\rho\int_0^\infty rw^2 dr,$$

and ρ is the density of fluid.

Laminar Plumes in a Uniform Environment

Laminar plumes in a uniform environment are studied in two asymptotic regimes by considering the Prandtl number $\mathrm{Pr} = \nu/k$ as a major parameter, where k is the thermal conductivity.

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$\mathrm{Pr} > 1$

In addition to $\mathrm{Pr} > 1$, the results found here are also subjected to the condition defined by the inequality.

$$1 \ll (\beta g Q_0 \mathrm{Pr}/\nu^3)^{1/2} z < \mathrm{Re}^2(\mathrm{crit})$$

where β is the coefficient of expansion, g is the gravitational acceleration,

$$Q_0 = \int_0^\infty r w \theta dr, \quad \theta = T - T_a$$

is the local temperature excess, T_a is the ambient temperature and Re(crit) is the critical Reynolds number, approximately 3x10^4 for the plumes in air. The entrainment flux scale is found in proportion to the kinematic viscosity ν. The axial velocity and temperature profile are obtained as

$$w(r, z) = [2(1+\mathrm{Pr}/\mathrm{Pr})(3gQ_0/E\nu)]^{1/2} \exp\{-[(1+\mathrm{Pr}/2\mathrm{Pr})(\beta g Q_0/\nu E^3)]^{1/2}(r^2/\nu z)\}$$

$$\theta(r, z) = (1+\mathrm{Pr}/\mathrm{Pr})(Q_0/kEz) \exp\{-[(1+\mathrm{Pr}/2\mathrm{Pr})(\beta g Q_0/\nu E^3)]^{1/2}(r^2/kz)\}$$

where E is the viscous entrainment constant.

$\mathrm{Pr} < 1$

Under the conditions of $\mathrm{Pr} < 1$ and

$$1 \ll (\beta g Q_0/k^3)^{1/2} z < \mathrm{Pe}^2\mathrm{crit})$$

the entrainment flux scale is found in proportion to the thermal conductivity k, where Pe(crit) is the critical Péclet number, likely to be about 2×10^4. The axial velocity and temperature profile are obtained as

$$w(r, z) = 2(\beta g Q_0/Ek)^{1/2} \exp[-(\beta g Q_0/kE^3)^{1/2}(r^2/kz)]$$

$$\theta(r, z) = z(Q_0/kEz) \exp[-(\beta g Q_0/kE^3)^{1/2}(r^2/kz)]$$

Plumes in a Uniformly Stratified Environment

In this case, the ambient temperature is assumed to be linear in z and the Prandtl number considered is greater than or equal to one. The axial velocity and temperature profile are obtained as

$$w(r, z) = w_0(z) \exp(-r^2/\nu b^2)$$

$$\theta(r, z) = \theta_0(z) \exp(-r^2/kb^2)$$

where

$$w_0^2(z) = [(1+\mathrm{Pr})/\mathrm{Pr}](1/\nu E)(2\beta g Q_0 - \tfrac{1}{2}\nu E \beta T_0 N^2 z^2)$$

$$\nu b^2 = 2(\mathrm{Pr}/1+\mathrm{Pr})^{1/2}(\nu E)^{3/2}(2\beta g Q_0 - \tfrac{1}{2}\nu E \beta T_0 N^2 z^2)^{-1/2} z$$

$$\theta_0(z) = [(1+\mathrm{Pr})/\mathrm{Pr}](1/kE\beta g z)(\beta g Q_0 - \tfrac{1}{2}\nu \beta T_0 N^2 z^2)$$

$$T_0 N^2/g = dTa/dz$$

$$Q_0 = \int_0^\infty r w \theta dr + (\nu E T_0 N^2/2g) z^2$$

Axisymmetric Laminar Wakes

In this case, the kinematic viscosity again serves as the entrainment scale. The axial velocity assumed in the top-hat profile is in the form

$$\begin{aligned} W_0 - w &= w_0(z) & 0 \leq r \leq b(z) \\ &= 0 & b(z) < r \end{aligned}$$

it is found that

$$b = (2E\nu z/W_0)^{1/2}, \qquad w_0 = D/2\pi\rho E\nu z.$$

where W_0 is the velocity in the main stream and D is the total vertical momentum change defined as

$$D = 2\pi\rho \int_0^\infty r W_0 (W_0 - w) dr$$

Subject Headings: *Flow, axisymmetric viscous with lateral entrainment; Laminar axisymmetric viscous flow; Jets, laminar; Plume theory, for viscous fluids.*

S. J. Ying

K. Physiological and Psychological Problems from Fires

Davies, C. N. and Muir, D. C. "Deposition of Inhaled Particles in Human Lungs," *Nature* 211(5044), 90–91 (July 1966) Letter to the Editor.*

The authors refer to measurements of the decrease in concentration of particles in exhaled air during steady breathing and the relationship between particle size and lung deposition. They draw attention to a possible error due to sampling during the period of inhalation and express the opinion that, in the past, there may have been a substantial overestimate of lung deposition.

Subject Headings: *Lungs, particles in; Particles, in lungs.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(4), 31. By permission.

Slater, K. "The Detection and Measurement of Dangerous Quantities of Carbon Monoxide Gas," *Jnl. Scient. Instrum.* **44**(8), 642 (1967)*

A simple and inexpensive method for giving warning of the presence of dangerous concentrations of carbon monoxide gas in enclosed spaces is presented. The chemical

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(4), 34. By permission.

and electrical principles involved are readily applicable to a variety of situations; as an example, adaptation of the apparatus inside a motor vehicle is described in outline. Quantitative operating conditions are left to the discretion of users of the method, although a more exact calibration of the detecting equipment in a form suitable for fitting inside an automobile is at present in progress.

Subject Headings: *Carbon monoxide, detection of; Detection, of carbon monoxide.*

Wise, M. K. "Denver Draws Blood to Check Carbon Monoxide." *Fire Engineering* 119 (7), 28–31 (1966)*

Describes how a cardiologist and a chemist took smoke samples at a fire, and blood samples from the fire fighters, to determine the amount of carbon monoxide inhaled by firemen and to draw attention to the necessity of accelerating the clearing of the hemoglobin after such exposure.

Subject Headings: *Blood; Carbon monoxide; Toxic Gases.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(4), 20. By permission.

L. Operations Research, Mathematical Methods, and Statistics

Joint Fire Research Organization, Boreham Wood, England "United Kingdom Fire Statistics, 1965" *London: Her Majesty's Stationery Office*

Statistical analysis of reports of fires attended by fire brigades in the United Kingdom during 1965.

Subject Headings: *Fire statistics, United Kingdom; United Kingdom, fire statistics.*

Joint Fire Research Organization, Boreham Wood, England "United Kingdom Fire Statistics, 1966" *London: Her Majesty's Stationery Office*

Summary of United Kingdom fire statistics with a statistical analysis of reports of fires attended by fire brigades in the United Kingdom during 1966.

Subject Headings: *Fire statistics, United Kingdom; United Kingdom, fire statistics.*

Vargo, L. G. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service, Berkeley, California) "Optimum Suppression Tactics—A Model and Some Theorems," *Fire Technology* **3**(1) 47–51 (1967)

The author presents an analytic model of tactical decision making for wildland fire suppression, which emphasizes the control line concept. Solutions are determined for several representations of practical constraint conditions. The analysis coupled with additional work performed at the Riverside Forest Fire Laboratory supports the contention that a working quantitative rationale for suppression tactics can be established. This can be achieved short of an automated system by adopting the available analytic tools as an aid to subjective decision making. As Shelley and Bryan have pointed out, the language of problem solution is generally different from the language of decision making. Progress is achieved by translating one to the other. Apparently the former has been too esoteric; the latter not sufficiently precise for effective translation.

Within the scope of the present discussion, several areas need investigation:

Development of probabilistic models as well as those based on deterministic criteria. (Some work has been done in this area and will be reported in a future paper).

Determination of force parameter values from planned tests and/or fire records.

Classification of constraint conditions as to type, and determination of correspondences with field situations.

Generation of computer solutions to the nonlinear equations.

Subject Headings: *Fire suppression; Operations research; Tactics, of fire; Suppression; model for.*

Author's Conclusions

M. Model Studies and Scaling Laws

Bukharov, I. I. and Medvedev, I. I. "Similarity Criteria in Modelling Dust Flows," *Izv. Vyssh. Uchebn. Zaved. Gornyi Zh.* **9**(7), 49–53 (1966) (In Russian)*

An attempt is made to establish a basis for similarity criteria during the modelling of processes that take place in moving dust-laden airflows and are dependent on the dust concentration in the air, the air velocity and relative humidity.

Subject Headings: *Dust flows, modeling of; Modeling, of dust flows.*

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15*(5), 61. By permission.

Roberts, A. F. and Clough, G. "Model Studies of Heat Transfer in Mine Fires," *S.M.R.E. Res. Rep. No. 247* (1967)*

The propagation of fires along the wood lining of ventilated tunnels (which is a hazard encountered in coal mines) is being studied by means of experiments in a ventilated refractory-lined steel duct, with a flow passage of 0.3 m square and 30 m long. The walls and roof of the passage were lined with wood which was ignited at the upwind end. Rates of burning, wall and gas temperature distributions and heat-transfer rates were measured. The data were correlated in a form which was used to calculate the temperature distribution in the walls from heat-conduction theory, and hence the gas temperature distributions. Heat-transfer coefficients were derived from the experimental data by this means. Analysis confirms an experimental observation that the temperature distributions relative to the fire approach a quasi-steady state. The steady-state solutions, which involve only independent variables, are applied to two important processes namely the significance of preheating of the wood lining as a rate-controlling process and the design of firebreaks.

Subject Headings: *Heat transfer, in mine fires; Mine fires, heat transfer in.*

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(4), 75. By permission.

N. Instrumentation and Fire Equipment

"Ultra-Lightweight Cylinder for Breathing Apparatus," *Colliery Engng.* **44**(520), 248 (1967)*

Describes a new alloy steel cylinder for storing compressed air at 3,000 lb/in^2.

Subject Heading: *Breathing apparatus.*

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(4), 21. By permission.

Burton, D. R. "The Thermal Assessment of Personal Conditioning Garments," *Curr. Pap. Aeronaut. Res. Coun.* No. 953 (1967)*

A general equation, which is developed for the case of the convective air ventilated suit supplied with cool air, is modified for the cases of the water conditioned suit, and the air ventilated suit with warm dry air supplies. Results of past experiments at the Institute of Aviation Medicine and the Royal Aircraft Establishment are

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 16*(4), 21. By permission.

reviewed with the aid of this theoretical approach. It is concluded that there is a need for more systematic experimental data on personal conditioning, especially on convective air cooling. The broad outline of a possible experimental programme is discussed, including certain aspects which require new techniques to be developed.

Subject Headings: *Clothing, thermal; Garments (See Clothing); Thermal performance, of clothing.*

McCarter, R. J. and Broido, A. (Pacific Southwest Forest and Range Experiment Station, U.S. Forest Service, Berkeley, California) "A Radiant Energy Dosimeter for Field Use," *Fire Technology* **3**(3) 213–224 (1967)

It was necessary to measure the thermal radiation dose over areas in a large fire. To solve this problem an inexpensive emergency instrument was constructed. The principle used was water volitilization over a measured time period as measured by weight loss. The apparatus consisted of an insulated beer can with one end perforated to allow the water vapor to escape while the other end was blackened for heat absorption. Construction details and performance of the instrument are given. The instrument was useful in the range between 25,000 and 185,000 cal/sq cm. Possible improvements in the instrument are discussed.

Subject Headings: *Dosimeter, thermal; Thermal dosimeter.*

R. Fristrom

Nichols, J. R. and Lipska, A. E. (U. S. Naval Radiological Defense Laboratory, San Francisco, California) "An Analytical Gas Chromatograph for Products of Isothermally Degraded Polymers," *Report under Contract with Office of Civil Defense, USNRDL-TR-68-41* (May 29, 1968)

A Backman Instruments Company Model GC-4 Gas Chromatograph was modified to simultaneously analyze parallel inputs of organic compounds and fixed gases originating as the degradation products of isothermally pyrolyzed α-cellulose. The pyrolysis chamber and a complex gas-handling system for separating and concentrating the pyrolyzates were attached directly to the GC-4 cabinet, and a complete system of temperature control zones was established. A detailed description of the arrangement and operation of (1) an isothermal pyrolysis chamber for sample generation, (2) a temperature control and valving system for sample separation and concentration, and (3) a parallel liquid partition and solid adsorption gas chromatography system for sample analysis is presented. The technique is applied to trial analysis of the degradation products of white α-cellulose pyrolyzed isothermally for 10 minutes in a nitrogen-fluidized sand bath at 360°C.

Subject Headings: *Gas chromatography, isothermal; Degradation, of polymers; Polymers, cellulose, degradation of.*

Authors' Abstract

Milne, T. A. and Greene, F. T. (Midwest Research Institute, Kansas City, Missouri) "Mass Spectrometer Study of Metal-Containing Flames," *Office of Naval Research Contract NONr-3599(00)* (January 1968)

The results of slightly over six years of research on the direct, mass spectrometric sampling of one atmosphere flames and related high pressure systems are summarized. The empirical development of the sampling system and related problems in detection and data interpretation are outlined. The major phenomena accompanying direct, molecular-beam sampling were found to be: (1) orifice-system interaction, (2) mass separation, (3) nucleation, and (4) influence of internal energy state on fragmentation pattern. Each of these problems has been explored qualitatively and quantitatively. A number of areas of immediate application of direct sampling to practical and scientific problems are listed together with suggestions for future research.

Subject Headings: *Flames, metal-containing, sampling of, by mass spectrometry; Sampling, of flames, by mass spectrometry.*

Authors' Summary

Rudkin, R. L. and Laughridge, F. I. (U. S. Naval Radiological Defense Laboratory, San Francisco, California) "Portable Calorimeter Station," *Report under Contract with Defense Atomic Support Agency, USNRDL-TR-68-2* (February 16, 1968)

This report is a general description of the development of the vacuum calorimeter. By eliminating the conduction heat losses in the button calorimeter, these devices can be made both more sensitive and more easily used in a field situation. Information is also presented concerning a portable measuring station and the updating of a thermal source for calibrations of thermal measuring instruments.

Subject Headings: *Calorimeter, thermal radiation; Thermal source, radiation calibration.*

Authors' Abstract

O. Miscellaneous

Joint Fire Research Organization (Boreham Wood, England) "Fire Research 1966," London: *Her Majesty's Stationery Office*

As in previous years, the Annual Report describing the work of the Fire Research Station (Boreham Woods, England) is a model of lucidity and a mine of information. In its more than 20 years of operation this Station has set an example of how effectively good research and useful development can be carried out in one establishment. Consistent emphasis has been placed on advancing the understanding of the nature of fires and their extinguishment, and on translating these insights into solutions of actual problems.

It is particularly pleasing to note that, from a cost-effectiveness standpoint, the work of the Station is "paying off." Quoting from the Director's preface:

> "The number of hours work necessary per capita per annum to make good the direct fire losses in this country is 2.6, the United Kingdom being second only to Switzerland (amongst highly industrial countries excluding the U.S.S.R.), where the figure is 1.7. This is an indication of the effectiveness of not only our fire services, but also indirectly, of the effectiveness of research into fire prevention. But although in this respect we are, as a country, so near the top of the league there is no room for complacency. . . ."
>
> "When money values are standardized, the average loss now is £450 per fire and this may be compared with £505 in 1947. While the size of fires, has, on average, decreased there are considerably more of them, the rate of increase being about 8 per cent per annum. If the 1947 pattern of spread were current today, the total loss would be some £8 million per annum more. A reduction in the size of fires is brought about by the application of the traditional sciences and the improvement in general fire protection methods. A reduction in the number of fires, however, can only be brought about with human co-operation and this is a field which will receive increasing attention in the next few years. . . ."
>
> "Statistics can sometimes be used to measure the value of an investigation. Sufficient time has now elapsed since the investigation of fires due to faulty oil heaters in 1960 for it to be clear that the rising number of fires due to them has been halted. There are between 800 and 2000 fewer fires and between 10 and 25 fewer deaths each year (depending upon whether minimal or maximal figures are taken) than there would have been if the work on oil heaters had not been carried out. . . ."

The Report is too full of good ideas, useful suggestions and summaries of research work in progress to permit itemization or detailed discussion. No practitioner in Fire Research or Fire Technology can afford *not* to leaf through its pages and pick out those matters that strike his fancy.

The following items have particularly impressed this reviewer:

(1) The statistics on fires (given in great detail from 1961 onwards, as to location, source, method of extinction, casualties) show clearly a reversal in total number of fire starts, a significant lowering in specific areas, i.e., causes from solid fuel and oil appliances, and a gratifying slow-down in others. They also expose with great clarity the large contribution made by children who are the largest cause of fire starts in and outside of buildings.

(2) The Bristol Fire Brigade is carrying out a cooperative program with the Fire Research Establishment to optimize the selection of fire stations, so that fires will be attended in minimum arrival time. The effects of changing the location or number of fire stations were also analyzed. The importance of proper choice of location was clear. It is a field evaluation of great potential.

(3) An interesting analysis of automobile fires was carried out on an 80 mile stretch of the M1 high-speed highway. In one year, 96 fires occurred, one-third of which were due to tire problems (mostly on trucks) on downhill stretches where the vehicle speeds were highest.

(4) Work continues on modeling of merging flames from multiple ignition sources (with the intent of evaluating factors giving rise to "fire storms"); studying the early stages of fire growth in compartments and, in particular, the influences of combustible ceilings in enhancing the radiation to the floor; establishing the relationships between fuel loading and window area for fully developed fires in enclosures; and evaluating the potential use of water curtains in buildings as a supplement to roof-venting.

(5) An economic study, discussing the cost of fire prevention in buildings has been completed, evaluating such items as (a) provisions for escape (b) structural fire precaution (c) sprinklers, alarms, detection, and (d) facilities for the fire brigade. It is estimated that from 2% to 5% of the building cost can be assigned to fire prevention measures.

Many other projects (the generation of toxic gases during combustion of plastics, use of liquid nitrogen as a non-damaging extinguishant, water distribution from sprinklers, development of reliable heat- and smoke-detectors) indicate the breadth of the program. The Director also mentions in his introductory preface that "the prototype inert gas generator, using the exhaust gases from a jet engine, is now in course of development and should be effective on about 200 large or difficult fires each year in the United Kingdom."

Members of the staff gave 53 lectures, wrote 27 Fire Research Notes, and published 26 technical papers, all for a total expenditure of £303,000. It appears to be money well spent.

Subject Headings: *Fire research, in United Kingdom; United Kingdom, fire research.*

W. G. Berl

"A List of Cities and Towns in Texas with Fire Protection and Fire Record Data,"
State Board of Insurance of Texas, Austin, Texas (March 1, 1968)

This pamphlet gives the fire record data for the cities and towns of Texas where there is an average annual net fire insurance premium volume of at least $1,500 over the fire record period, with the exception that a city or town with a key rate of eighty cents or less shall qualify regardless of the amount of premiums. Incorporated towns and villages which do not pay at least the average of $1,500 are not included here. The premiums and losses paid on suburban, farm, and country property are not shown in this booklet.

Subject Headings: *Fires, in Texas; Texas, city and town fire records.*

DASA Information and Analysis Center, (816 State Street, Santa Barbara, California) "Proceedings of the Tripartite Technical Cooperation Program, Panel N-3 (Thermal Radiation) Mass Fire Research Symposium," *DASTAC Special Report 59* (May 1967) 421 pages. DASA Document No. 1949.

These Proceedings cover the papers presented at the Tripartite Technical Cooperation Program, Panel N-3, Mass Fire Research Symposium, which was held on 6–9 February 1967 at the Defense Atomic Support Agency Headquarters in Washington, D. C. Subjects covered are: Research Requirements of the Office of Civil Defense, National Military Command Systems Support Center, and U. S. Forest Service; Mass Fire Interaction; Scaling of Mass Fires; Fire Density; Results of Flambeau. Summaries of discussions are included.

Subject Headings: *Mass fire, symposium; Symposium, on mass fires.*

R. M. Fristrom

Rogowski, B. F. W. and Lewis, A. S. (Joint Fire Research Organization, Boreham Wood, England) "References to Scientific Literature on Fire," Part XIV (1962)

Crees, J. C. (Joint Fire Research Organization, Boreham Wood, England) "References to Scientific Literature on Fire," Part XV (1963-1964)

These bibliographies list titles of articles published during 1962–1963–1964. The material is cross-referenced under author and subject. (See *Fire Research Abstracts and Reviews 7*, 206, 1965.

Subject Headings: *Bibliography, on fire; Fire, bibliography.*

R. M. Fristrom

Lawson, D. I. (Joint Fire Research Organization, Boreham Wood, England) "Distortion of Doors in Fires by Asymmetric Heating," *Fire Technology* **3**(1) 29–32 (1967)

The author presents a mathematical analysis of the extent to which a door will be deformed by exposure to fire and develops expressions for calculating the distortion of unrestrained and restrained doors caused by asymmetric heating. For the temperatures encountered in fires, the distortion of restrained doors is much greater than for unrestrained doors of the same dimensions.

Subject Headings: *Distortion, of doors by fire; Doors, distortions by fire.*

R. M. Fristrom

Livingston, W. L. (Factory Mutual Research Corporation, Norwood, Massachusetts) "How Economics Guide Applied Research on Fire Protection Systems," *Fire Technology* **3**(3) 194–201 (1967)

The FM Research Corporation uses economics to guide its applied research activities, which are directed toward long-range goals as well as immediate problems. Economics, considered here as an analytical description of the production, distribution, and consumption of goods and services, is fundamental to applied research.

Subject Headings: ***Economics, and fire research; Fire research, and economics.***

Author's Abstract

McGuire, J. H. (Division of Building Research, National Research Council, Canada) "Smoke Movement in Buildings," *Fire Technology* **3**(3) 163–174 (1967)

Recent analysis of the leakage characteristics of several large buildings indicates that the leakage between adjacent stories appreciably exceeds that from any one story to the exterior. Gas movements between a localized area of a building and the exterior cannot, therefore, be discussed individually but only as a part of the flow complex throughout the building.

Most gas movements in a building may be discussed in terms of their influence on chimney effect. It is interesting that gas flow from a compartment on fire to an adjacent one is not likely to be more than double the value resulting from building heating under severe winter conditions in the absence of fire. Even though the temperature differential created by the fire may be sixteen times that resulting from normal building heating, it will establish less than double a typical winter pressure differential. Prior to breaking windows or establishing other conditions uniquely associated with a fire, the smoke movement may be discussed in terms of the normal gas movements within the building.

Subject Heading: ***Smoke, movement in buildings.***

Author's Summary

Miller, C. F. (Stanford Research Institute, Menlo Park, California) "World War II German Fire Document Translations," *Report under Contract N0022866C0317 with the Office of Civil Defense, SRI Project No. MU-5865* (July 1967)

This report describes the general content of several World War II German documents on war-caused fires. Major emphasis was given to the translation of reports of the Hamburg police president and the Hamburg fire department action reports.

The translated version of an evaluated report written by Hans Rumpf, colonel of the German fire protection police, on the fires resulting from the German attack on Rotterdam on May 14, 1940, is appended to illustrate points of practical information in regard to fire protection methods, fire damage, behavior of people in fire situations, and other factors relating to the spread of fire (e.g., methods of construction).

Subject Headings: *Fire, World War II in Germany; Fire fighting, German, World War II; Fire department, records, German, World War II; Fire storms, World War II, Germany; Hamburg fires, World War II.*

Author's Abstract

Renner, R. H., Martin, S. B., and Jones, R. E. (U. S. Naval Radiological Defense Laboratory, San Francisco, California) "Parameters Governing Urban Vulnerability to Fire from Nuclear Bursts (Phase I)," *Report under Contract OCD-PS-64-200 with Office of Civil Defense, USNRDL-TR-1040* (January 3 1967)

The parameters affecting the fire vulnerability of U.S. urban areas from nuclear bursts need to be identified, defined, and evaluated in terms of their relative importance, interactions, and sensitivity characteristics. The resulting information will be useful in fire-vulnerability assessment studies.

The parameters that govern urban vulnerability to fire from nuclear bursts have been identified and defined (Appendices: A. Target Parameters, B. Weapon Burst Parameters, C. Atmospheric Transmission Parameters, D. Fundamental Processes of Ignition and Combustion, E. Fires from Causes other than Thermal Radiation, and F. Macro-Scale Fire Phenomena). Sections 2 to 9 of the body of the report present the reliability of estimates and the ranking of parameters for each of the stages (in quasi-chronological order) of nuclear-burst-caused urban fire. Section 1. concludes with a comprehensive listing of parameters in decreasing order of importance and the ranking of these parameter groups for the following categories of urban fire response:

Type 1. Fire Vulnerability is Determined Primarily by the Extent of Fires Caused by Thermal Radiation. (Category A. Limited Thermal Shielding, Category B. Extensive Thermal Shielding.)

Type 2. Fire Vulnerability is Determined Primarily by Spread or Magnitude of Fire. (Category A. Spreading Fire of Conventional Magnitude, Category B. Conflagration, Category C. Firestorm.)

Type 3. Fire Vulnerability is Determined Primarily by Fires Resulting from Blast or Other Causes. (Category A. Blast-Caused Fires, Category B. Panic or False-Alarm-Caused Fires.)

Further research efforts should be made in sensitive areas where major information gaps exist such as the transmission of thermal radiation through clouded and

hazy atmospheres, the detailed description of fuels (especially the fields of view or location of fuels), the mechanics of fire growth in enclosures, the mechanics of firespread (particularly fire-brand propagation), and the fire behavior of large-scale convection columns and coalescence of fires. At the present time it is possible to assess incendiary vulnerability only via intuitive-stochastic approaches based on fire experience, and this approach is of doubtful reliability for civil defense purposes.

Subject Headings: *Fire, vulnerability; Fire, urban; Fire research; Parameters, fire vulnerability.*

Authors' Summary

BOOKS, JOURNALS, AND MEETINGS

Books

Fundamentals of Combustion—Roger A. Strehlow, International Textbook Co. Scranton, Pennsylvania 18515 $12.50*

The title of this book is well chosen. It is a textbook rather than a research monograph. The coverage is broad and reasonably well balanced. It is written for engineering students on the advanced undergraduate or beginning graduate level. The requirements for understanding this book are a knowledge of fluid dynamics and mathematics through differential equations and advanced calculus (of the engineering, rather than mathematical variety). Problems are found at the end of every chapter, but answers are not provided. The references are adequate and reasonably current but not extensive. A bibliography of pertinent books is included at the end of each chapter.

The reviewer was initially taken aback by the scope of the table of contents:

(1) Atomic and Molecular Structures, 23 pages; (2) Kinetic Theory and Statistical Thermodynamics of a Dilute Gas, 51 pages; (3) The Physical Properties of Real Gases, 18 pages; (4) Chemical Reactions in Gases, 66 pages; (5) One-Dimensional Reactive Gas-Dynamics, 19 pages; (6) General Combustion Phenomena, 29 pages; (7) Premixed Gas Flames, 51 pages; (8) Aerodynamics of Flames, 38 pages; (9) Detonation, 65 pages; (10) Solid and Liquid Propellant Combustion in Rockets, 20 pages. Appendices—(Tables) 80 pages.

Half of the book is taken up by an extensive set of tables and introductory material with which a well-prepared graduate student would be familiar. After reading the lucid presentation, however, the reviewer concluded that the average graduate student would welcome the review material and the tables would be a great convenience for the problems. A suggestion for a second edition would be to drop the atomic and molecular structure chapter, since science and engineering majors should have been exposed to this material at least twice before graduation, and substitute a chapter on compressible gas dynamics. Answers to the problems would also be of great assistance. They could be published separately with the tables as a booklet.

The penalty which must be paid for this extensive introduction is the foreshortening of the specialized material which is the ultimate objective of the book. The treatment of many important topics is limited and almost no discussion is given of the experimental techniques. This is particularly unfortunate in the case of Dr. Strehlow's specialities where he has no doubt exercised great restraint in keeping coverage at a minimum.

The book is not perfect. There are several trivial errors, mainly misspellings. Some debatable statements are made without proper qualification. Those which the reviewer found particularly disturbing are that modifying the rate equation is

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* Book review for *Combustion and Flame*. Reprinted with permission.

preferable to introducing a heat sink (p. 210) and the implication that conduction enthalpy is crucial to flame propagation (p. 217).

Despite these objections the reviewer feels that the book can be recommended as a test and introduction for the nonspecialist. It is specifically aimed at the engineering community. The chemist or chemical engineer would need auxiliary material on gas dynamics and find the chapters on chemical subjects superfluous. Even the specialist may find some unfamiliar new material and perhaps a new insight into old material.

Subject Heading: *Combustion.*

R. M. Fristrom

Directory of Fire Research in the United States, 1965–1967 (Fourth Edition) National Academy of Sciences Publication 1590. Available from the Office of Printing and Publishing, National Academy of Sciences, 2101 Constitution Avenue, N. W., Washington, D. C. 20418

Published biennially under the auspices of the Committee on Fire Research of the Division of Engineering. This edition has 226 pages describing the work of 85 laboratories—government, military, university, private research groups, industry. Three hundred and three projects are included, 177 of them sponsored research and 126 in-house research supported by the laboratory reporting the work. Three indexes list projects according to categories describing the nature of the work, the names of sponsors and the projects they sponsor, and in-house projects in the various laboratories. Heads of the laboratories, scientists responsible for each project, purposes and descriptions of the projects, reports and publication are given. The compilation of this directory by Mrs. Emma Jane Whipple of the staff of the Committee on Fire Research is a service to the fire research community. It gives a perspective of the scope of fire research in this country and provides a reference for locating workers in the field.—R. M. Fristrom

Journals

Oxidation and Combustion Reviews, edited by C. G. H. Tipper, University of Liverpool, England

Volume 1—Contents

Application of the Theory of Branched Chain Reactions in Low-Temperature Combustion—R. Ben-Aim and M. Lucquin
Oxidation Reactions Induced by Ionising Radiation—G. Hughes
Gas Phase Photo-Oxidation—G. R. McMillan and J. G. Calvert
Oxidation Reactions Involving Nitrogen Dioxide—J. H. Thomas
Oxidative Degradation of High Polymers—W. L. Hawkins
The Heterogeneous Selective Oxidation of Hydrocarbons—R. J. Sampson and D. Shooter

Author and Subject Index. 6 x 9″, vii+344 pages, 29 tables, 45 illus., 815 lit. refs., 1965, Dfl. 47.50, U.S. $17.00

Volume 2—Contents

Thermal Explosion Theory—P. Gray and P. R. Lee
Some Fundamentals of Combustion Instability—R. F. Salant and Tau-Yi Toong
The Use of Adiabatic Compression and Mass Spectrometry in the Study of Combustion—A. Martinengo and K. H. Homann
Trapped Radicals and Combustion—A. Thomas

Author and Subject Index. 6 x 9″, vii+301 pages, 19 tables, 64 illus., 311 lit. refs., 1968, Dfl. 60.00, U.S. $21.00

Volume 3 No. 1—Contents

The Mechanism of Combustion of Droplets and Sprays of Liquid Fuels—A. Williams
The Low Temperature Gas-Phase Oxidation of Lower Aliphatic Aldehydes—J. F. Griffiths and G. Skirrow, page 47

Volume 3 No. 2—Contents

Ammonium Perchlorate as an Oxidizer—A. R. Hall and G. S. Pearson
Ionization in Combustion Processes—W. J. Miller

One volume per year in 2 issues. Subscription price: Dfl. 45.00, f5.4.9. U.S. $12.50 per volume (plus postage) Elsevier Publishing Company, P.O. Box 211, Amsterdam, The Netherlands.

Meetings

Western States Section of The Combustion Institute—Spring Meeting University of Southern California, Los Angeles, California (April 29–30, 1968)

Dr. Melvin Gerstein, Chairman

Introductory Remarks—Dr. Alvin S. Gordon, Section Vice-Chairman
The Need for Fire Research from the Viewpoint of a Major Urban Fire Department Raymond Hill, Chief, Fire Department, City of Los Angeles
Paper 68-5: A Simple, Sensitive Graphical Method of Treating Thermogravimetric Analysis Data—A. Broido, Pacific Southwest Forest and Range Experiment Station, U.S. Forest Service
Paper 68-3: A Proposed Measurement of the Heat of Pre-ignition of Fine Forest Fuels—William H. Frandsen, Intermountain Forest and Range Experiment Station, U.S. Forest Service
Paper 68-9: Isothermal Pyrolysis of Cellulose-Kinetics and Gas Chromatographic and Mass Spectrometric Analyses of the Degradation Products—A. E. Lipska and F. A. Wodley, U.S. Naval Radiological Defense Laboratory

Dr. A. Broido, Chairman

Paper 68-1: Electronic Simulation of Mass Fires—Lester A. Eggleston, Southwest Research Institute
Paper 68-3: Surface Temperature Distributions ahead of Spreading Flames—Robert F. McAlevy III and Richard S. Magee, Stevens Institute of Technology

Paper 68-10: Combustion of Vertical Cellulosic Cylinders in Air—Franklin J. Kosdon, University of California, San Diego
Paper 68-6: The Interaction and Merging of Flames from Burning Liquids—K. G. Huffman, J. R. Welker, and C. M. Sliepcevich, University of Oklahoma
Paper 68-11: Gas Fires with Pool-Like Boundary Conditions—Further Results and Interpretation—R C. Corlett, University of Washington

Dr. Robert F. Sawyer, Chairman

Paper 68-12: Investigation of Flame Arrester Fundamentals—Russell Laustsen, The Boeing Co.
Paper 68-15: Study of the Ignition Mechanism of Painted Surfaces—Norman L. Helgeson and Bernard P. Breen, Dynamic Science Corporation
Paper 68-14: An Experimental Test of Mass Fire Scaling Principles—W. J. Parker, R. C. Corlett, and B. T. Lee, U.S. Naval Radiological Defense Laboratory
Paper 68-7: Identification of Important Chemical Reactions in Liquid Propellant Rocket Engines—Steven S. Cherry and Leslie J. Van Nice, IRW Systems
Paper 68-4: A Study of the Premixed Flame of Cyanogen-Oxygen-Boron Trichloride as a Luminous Source—Robert L. Tischer and Karl Scheller, Air Force Aerospace Research Laboratories
Paper 68–8: The Effect of Water Vapor on the Burning Rate of Aluminum and Magnesium Wires in the Pressure Range of 15 to psia—C. Hardy Long, Virginia Polytechnic Institute and Hans Sebald, Cornell

Dr. P. Roy Choudhury, Chairman

Paper 68–2: Computed Rate Constants and Activation Energies for the Abstraction Reaction of Ground State and Excited Oxygen with Fuels—S. W. Mayer and L. Schieler, Aerospace Corporation
Paper 68–16: Ignition of Wood by Flame Radiation—A. N. Koohyar, J. R. Welker, and C. M. Sliepcevich, University of Oklahoma
General Discussion on Fire Problems—Organized by Dr. Melvin Gerstein

Comments on the Meeting

Thermodynamics and Kinetic Flame Studies

Equilibrium combustion chambers require only the provision of data for an occasional new species to calculate the adiabatic flame temperature and equilibrium composition by accepted computer routines and the JANAF thermochemical tables. Ten years ago, this was a prime topic for the Combustion Institute; today, kinetics gets the attention so time is part of the process description. A rocket has a sonic throat constriction which assures a reference dimension and velocity with a reasonable stay time in the chamber. This assures completion of the equilibrium reaction and the combustion source material becomes immaterial except for its ultimate composition and heat of formation. Thus, subsequent to the sonic throat in an isentropic expansion cone, thermodynamic equilibrium calculations are quite reliable with even a reasonable approximation in the case of condensed species involving two-phase flow.

Cherry and Van Nice (TRW) discuss the identification of chemical reactions in the exhaust section of a liquid propellant rocket engine. By taking the reasonable estimate of the expected and maximum value of the rate constants for various possible reactions, they rank the significance of the reactions in terms of the effect on prediction of specific impulse of a total system to ±1%. Due to the almost unlimited number of postulatable reactions, this technique ranks those urgently requiring investigation. Mayer and Schieler (Aerospace Corporation) describe a fundamental study of a particular reaction: the abstraction of ground state and excited oxygen with hydrocarbon fuel species.

Isolated Model Flames

As contrasted to the confined equilibrium combustion, two isolated model flames are studied. Tischer and Scheller (Air Force Aerospace Research Laboratories) use radiometric measurements of the luminous intensity for premixed flames of the cyanogen-oxygen-boron trichloride system over a range of pressure, composition, and burner size. Efficiency increases asymptotically with burner size.

Another flame of strict definition is the burning of aluminum and magnesium wires in oxygen with various contents of water vapor and a range of pressure from 15 to 2000 psia. Long and Sebald (Virginia Polytechnic) note that condensed combustion products affect the reaction rate through their resistance to the diffusion of oxygen. This accumulation of combustion product unfortunately results in considerable irregularity in the burning rates. Increasing moisture decreases burning rates and quenches it for aluminum at 13% to 15% water content, while magnesium endures even 25% water vapor. Fragmentation of the tip droplet may be critical.

McAlevy and Magee (Stevens Institute) concern themselves with flame spreading over a condensed phase, in which ignition is postulated to be due to a continuous diffusive phase. Polymethylmethacrylate in atmospheres of O_2/N_2, O_2/He, and O_2/Ar gave flame spreading rates of 0.2–2.0 in./sec. Using a 15 micron thermocouple, flame front discrimination as fine as 50 microns was detected. Variation of pressure permits resolution of radiative and conductive heating, and the moving front is compared to the steady-state surface pyrolysis condition.

Pool Fires and Merging Flames

Burning liquids are the next phase in generalization from confined equilibrium flame to unrestrained wildfire. A pool fire can be simulated by supplying the fuel vapor from a water-cooled porous horizontal burner. This permits calorimetric determination of the heat transfer from the flame to the burner (representing the pool or a liquid fuel reservoir). Corlett (University of Washington) shows molecular and radiative heat transfer results for a wide variety of fuels and fuel-diluent combinations. Molecular heat transfer correlation tendencies are observed in the limit of low and high fuel supply velocities. These limiting cases are discussed as a basis for the development of a theory.

Passing from a single flame to a merging of flames, Huffman, Walker, and Sliepcevich (University of Oklahoma) get into the dimensional scaling of empirical observation. A nine-burner pattern of buoyant diffusion flames from liquid pools will show a phenomenal increase in flame height and burning rate of the interior burners at a critical spacing where presumably the radiative heat from adjacent burners becomes conservative (allowing the interior burners to approach adiabaticity). This large increase in interior flame partially reduces again at still closer spacing, when all burners merge into a single effect. Dimensionless factors and empirical correlations of the effects are suggested.

The Combustion of Cellulose

Vertical cellulosic cylinders burning in air are a similar attempt at modeling a dimensional element of combustion by Kosdon (University of California at San Diego). The object is to determine conditions under which fire will spread from a burning fuel element to an adjacent combustible. Small, vertically oriented, pressed α-cellulose (filter paper) cylinders of circular cross-section, 1 inch in diameter and $1\frac{1}{2}$ to 4 inches long, were burned in air under conditions that enabled flame stand-off distances and rates of weight loss to be measured simultaneously. The gas-phase rate of heat transfer and mass transfer, which determine flame shape and the stand-off distance (separation distance between the luminous front and the vertical side of the cylinder). It is interesting that the heat released in the gas-phase reaction and the properties of the fuel vapor may be effectively represented by formaldehyde vapor. By iterating the temperature and velocity fields, a theoretical prediction of $\frac{1}{4}$th power variation of the flame standoff distance with respect to the distance from the leading edge is obtained. Experimental verification is within a factor of 2. Agreement with literature on burning fuel-soaked wicks of similar dimensions is notable. The similarity flame-sheet theory is a reasonable description of the gas-phase aspects of quasi-steady, flaming, cellulose combustion.

The actual pyrolysis of cellulose, in the solid phase, under nitrogen environment at 315°, 335°, and 360°C shows the usual three distinct phases of pyrolysis during the temperature range 276° to 298°C, but at 350°C the initial weight-loss region is foreshortened and disappears at 360°C. Time of flight mass spectrometry confirms the phases of degradation reported. Thus Lipska and Wodley (U.S. Naval Radiological Defense Laboratory) infer from experiments with added $KHCO_3$ that the effect on pyrolysis is not so much a change in type of degradation product as a change in rate of generation of the products and the physical presence of residual char.

Broido (Pacific Southwest Forest and Range Experiment Station) uses thermogravimetric (TGA) analysis on cellulose to extract kinetic data. Graphical methods based on taking slopes from rapidly changing curves are of questionable accuracy. A linearization method is introduced that permits identification and correction for a number of experimental complications.

Ignitability Measurements and Flame Arrestors

Typical of the difficulty of working with natural substances is the effort of Frandsen (Intermountain Forest and Range Experiment Station) to obtain the heat of pre-ignition of fine forest fuels such as twigs, needles, leaves, and grass dispersed on a forest floor. A forest fire grows through the flow of radiant and convertive heat flux from the combustion zone into the potential fuel with heat from the combustion zone supplying that necessary to lead the ignition front. The experimental determination of the ignitability to radiant flux of the critical element—a ponderosa pine needle—is described. Different rates of heating may cause total dehydration and ignition or at higher rates only surface ignition may occur on a partially altered core. This condition affects the quotation of heats of ignition.

Another subject of ignitability is a painted surface. Helgeson (Dynamic Science Corporation) studied cured paint as a solid combustible material under a radiant heat source. Thermocouple measurements on the initial supporting plate, on the paint surface and in the vapor phase one-quarter inch from the surface shows that surface temperature at ignition is quite unreproducible but the time to ignition is partially correlatable. The paint surface thermocouple gave no indication of the moment of ignition (which is clearly shown by the vapor phase thermocouple), except for being preceded by a slow rise in temperature interrupted by a 2–3 second plateau (presumed to be an endothermic pyrolysis period) just before ignition.

The propagation of a flame is studied from another point of view in flame arresting foam structures. Laustsen (Boeing) uses Safom (reticulated polyurethane foam) in couple with a metal screen as a flame arrestor in ducts. Fuel mixture ratio, organ-pipe oscillation, and system configuration are involved in the flame quenching capability of the metal screen. Zones where arrest cannot occur are detected, and the combination Safom and screen arrestor is recommended.

Mass Fire Modeling

The development of an electronic mass fire simulator is described by Eggleston (Southwest Research Institute) from concept through component and system design stages to a workable model which when checked against a researched conflagration in Boston showed good agreement in duplicating what had actually happened. The simulator is based on an electrical analog of the chemical processes of ignition and combustion and is intended to act in all important aspects exactly as would a real fire. The need for further work is pointed out together with the possible technique for simulating wind effects and burning brand phenomena.

Mass fire modeling based on a partial scaling principle in which Grashof number is ignored has been performed in a direct electrical analogy by Parker, Corlett and Lee (U.S. Naval Radiological Defense Laboratory). Heat release per unit area is proportional to the square root of the ratio of linear dimensions of the model and the prototype. Under the hypothesized scaling principle, the temperature will be same at homologous points while the ratio of velocities will be proportional to the square root of the linear dimensional model ratio. Inflow air velocities at the edge of the electrical burner (4.4 kw) and in the updraft are measured by a hot wire anemometer, and temperature by thermocouple. Dioctyl phthalate spray on the burner element produces a simulated smoke column. Conditions at 18 minutes after ignition in the 1966 Flambeau fire were favorably simulated. The potential for scaling of mass fire predictions should be investigated.

The Urban Fire Department Viewpoint

With this wealth of investigation, Hill (Los Angeles City Fire Department) discusses the need for fire research from the viewpoint of a major urban fire department. The fire practitioner does not enjoy the controlled experiment or planned experimentation that the researcher expects. His solutions in prevention and suppression are frequently politically and economically restrained. Quantity and speed of application of water is still the prime criteria of urban fire suppression.

Insurance rating schedules are based on prevention of conflagration: building codes, water supply, training and mobility, weather. Some criteria are traditional, and might be reoriented by fundamental knowledge of fire behavior. Indispensable in the morale and training of the suppression force. Education for prevention, legal and suasion, is the most efficient expenditure for fire control. Fire incidence is usually the confluence of several factors, which individually could probably be arrested with minimum loss. Fire growth prediction would be the most significant research contribution to suppression logistics, which could be coupled with system analysis and economic factors for higher cost/benefit of manpower and equipment in urban protection.

J. S. Billheimer
U. S. Department of Agriculture, Forest Service
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Berkeley, California

Western States Section of The Combustion Institute 1968 Fall Meeting—Stanford Research Institute, Menlo Park, California (October 28-29, 1968).

Specialists Session on Kinetics Calculations—University of California, Berkeley, California (October 30, 1968).

Annual Registration, 1968: Individuals and organizations may obtain preprints by mail. The fee for 1968 is $10.00 (plus foreign postage of $4.50) sent prepaid to the Preprints Chairman, Dr. R. F. Sawyer, Mechanical Engineering, Thermal Systems, University of California, Berkeley, California 94720.

Central States Section of The Combustion Institute 1969 Meeting—"Fire Research—Experimental and Analytical Modeling of Fires." (Free burning fires and fires in enclosures)

March 18–19, 1969 University of Minnesota, Department of Mechanical Engineering.

Abstracts should be submitted to the program Chairman:

Dr. Hugo Nielson
IIT Research Institute
10 W. 35th Street
Chicago, Illinois 60616

Eastern Section of The Combustion Institute—Fall Meeting—University of Massachusetts, Amherst, Massachusetts (October 21–22, 1968).

Heterogeneous Combustion

Papers dealt with: Oxidation, combustion, and reduction of carbons and coals: Combustion of polymers, including charring ablation with external flow; and Flames in dust clouds.

Southwest Regional Meeting of the American Chemical Society—Austin, Texas December 4–6, 1968.

Symposia: Fundamental Processing in Gas Kinetics—Dr. J. M. White, Department of Chemistry, University of Texas, Austin, Texas 78712.
Physical Chemistry of Gaseous Fuels Oxidation—Dr. G. L. Schott, Los Alamos Scientific Laboratory, P. O. Box 1663, Los Alamos, New Mexico 87544.

International Symposium on Corrosion Risks in Connection with Fire in Plastics

In connection with a Fire Protection and Prevention Congress and Exhibition. (Official language will be English.) April 25, 1969.

Sponsored by the Research Foundation of the Swedish Fire Insurance Companies and the Swedish Fire Protection Association.

Short summaries of proposed papers should be sent to:

Swedish Fire Protection Association
Brunkebergstorg 15
Stockholm, C. Sweden

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ABSTRACTS AND REVIEWS

Volume 10 Number 3

Fire Research Abstracts and Reviews

Committee on Fire Research
Division of Engineering
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FOREWORD

It is with regret that we report the retirement from the Committee on Fire Research of Dr. Walter Berl of the Applied Physics Laboratory, The Johns Hopkins University. Dr. Berl was the pioneer editor of *Fire Research Abstracts and Reviews* and the organizer of a number of fire research meetings and symposia. He has been a staunch supporter of basic research in fire studies. Your editor feels he speaks for the entire fire research community in thanking Dr. Berl for his many contributions to the field.

As the replacement for Dr. Berl, we welcome Dr. R. Keith Arnold, Dean of the School of Natural Resources, University of Michigan, to the Committee on Fire Research. His experience and ability should provide a new source of strength for the Committee.

The issue begins with an interesting survey by I. Glassman and J. G. Hansel of Princeton University entitled "Some Thoughts and Experiments on Liquid Fuel Flame Spreading, Steady Burning, and Ignitability in Quiescent Atmospheres."

R. M. Fristrom *Editor,*

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MEETINGS

REVIEWS

Some Thoughts and Experiments on Liquid Fuel Spreading, Steady Burning and Ignitability in Quiescent Atmospheres*

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I. *Introduction*

The combustion process associated with large pools of flammable liquids can be divided into three phases: ignitability, flame spreading, and steady burning. The nature of the research being undertaken by the authors relates mainly to flame spreading and burning under quiescent and natural convection conditions. However, initial results on flame spreading have indicated some possible important effects concerning ignitability.

Early photographic observations by T. Eklund[1] were instrumental in the formulation of some preliminary models of flame spreading and subsequent thinking on burning and ignitability. A copyrighted thesis[2] published in 1959§ by A. F. Roberts of Imperial College, London (now of Safety in Mines Research Establishment, Buxton) shows that Roberts had earlier undergone the same type of thinking. Roberts' excellent work is thus reviewed directly and indirectly. The models proposed herein are a logical consequence of observations of simple experiments and were developed independently of and extend the work of Roberts. Perhaps others have put forth similar thoughts, although a preliminary search of the literature has not revealed any very direct correspondence. This report represents a critical literature review and the current thinking of the authors on liquid fuel flame spreading and steady burning and some comments on ignitability.

II. *The Relation of the Flash Point to Liquid Pool Flame Modeling*

Two empirical tests that are quite pertinent to the explanation of what governs the spread of a flame across a fuel surface will be discussed initially.

The first and perhaps most important is the flash point.[3] The flash point is that temperature at which the liquid fuel will ignite in air when a pilot flame is passed near and at a fixed distance above the fuel surface. It is meant to specify the temperature at which the liquid can exert a vapor pressure so that a mixture of fuel vapor

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§ Attention was drawn to this thesis by Roberts' comments on the paper by Tarifa and Torralbo[8] in the 11th Combustion Symposium. The date of the thesis in these comments was erroneously reported as 1966 and so referenced in earlier versions of this document.

and air will be just within their flammability limits. Obviously the flash point will vary somewhat according to the position of the ignition source. The further the source from the liquid surface, the higher the surface temperature. Diffusion of the vapor into the air controls the difference.

The fire point[4] is the temperature at which the liquid will not only ignite (i.e., flash), but will continue to burn. Fundamentally it is the temperature that will create a mixture ratio near the surface so that the transfer number will be sufficiently great that the rate of energy release due to combustion will be at least equal to the rate of energy feedback necessary to sustain evaporation of the condensed liquid.

In estimating the mixture ratios mentioned above, it would appear sufficiently accurate for purposes here to assume that near the surface the partial pressure of the fuel in air is equal to the vapor pressure.

If a fuel is at its flash point or above (really at its fire point),* and if ignited, a flame can spread over the liquid without requiring further vaporization. It is likely in such cases that phenomena in the gas phase will be controlling and the rate of spreading will be of the order of the laminar flame speed.

One knows, however, that a liquid below its flash point will sustain a spreading flame and subsequently burn. The logical process of sustaining the spreading flame is to have the liquid ahead of the flame heated to its flash point, so that when the flame arrives at that position it will be sustained. The methods by which the liquid ahead of the flame may be heated are: conduction through the gas ahead of the flame, radiation from the flame to the forward fuel surface, and heating from the flame and combustion gases behind the flame through the liquid. Estimates of the thermal conductivities of the gas mixture and the liquid indicate that it is a very good assumption to ignore conduction in the gas phase. Most models of flame spreading consider only the latter two mechanisms, and for nonluminous, small flames, radiation may be neglected as well.

As mentioned before, liquids at or above their flash point will support a spreading rate of the order of the laminar flame speeds. Liquids below their flash points will have spreading rates less than the laminar flame speeds because they must be heated to the flash point through the liquid ahead of the propagating flame. One then would expect an important, but milder, variation of spreading rate with temperature when the initial temperature of the liquid is below the flash point.

It is interesting now to give consideration to the spreading rate when the initial liquid temperature (T_L) is above the flash point (T_{LFl}). Recall that the flash point is thought to give a mixture ratio near the liquid surface that corresponds to the lean flammability limit. As the temperature is raised the partial pressure near the surface, which as mentioned before is taken as a good approximation for purposes here to be the vapor pressure of the liquid at the specified liquid temperature, rises. Thus, as the temperature is raised, the air–fuel mixture ratio near the surface moves from the lean inflammability limit towards the stoichiometric ratio and then to fuel rich mixture ratios. Then, one would expect that the spreading velocity would increase sharply from the value at the flash point (T_{LFl}) and reach a maximum for the liquid temperature which gives a vapor pressure corresponding to the fuel fraction required for a stoichiometric mixture in air. This liquid temperature related

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* The fire point is only of the order of a few degrees higher than the flash point: reference will be made mostly to the flash point which traditionally has been the limiting temperature with respect to safety applications.

to the stoichiometric condition in the vapor is specified as T_{LSt}. Since T_{LSt} is very much below the saturation temperature (T_{Sat}), it is possible to continue to raise the liquid temperature. Temperatures above T_{LSt} give fuel rich conditions near the surface. However, because the partial pressure of fuel above the liquid decreases with distance, there is always some point above the liquid surface where a stoichiometric mixture exists. A flame propagating through a stratified air–fuel mixture system will be led by that part of it which flashes through the stoichiometric zone. Thus one can conclude that as the temperature is raised from T_{LFl} to T_{LSt}, that the flame spreading velocity will increase sharply, but that above T_{LSt} there will essentially be no change in the flame spreading velocity (V_F). If the Lewis number is equal to one, that is, if the mass diffusivity (D) equals the thermal diffusivity (α), this latter statement should hold well. With this background one can draw a qualitative curve of the expected variation of V_F with T_L, as shown in Fig. 1.

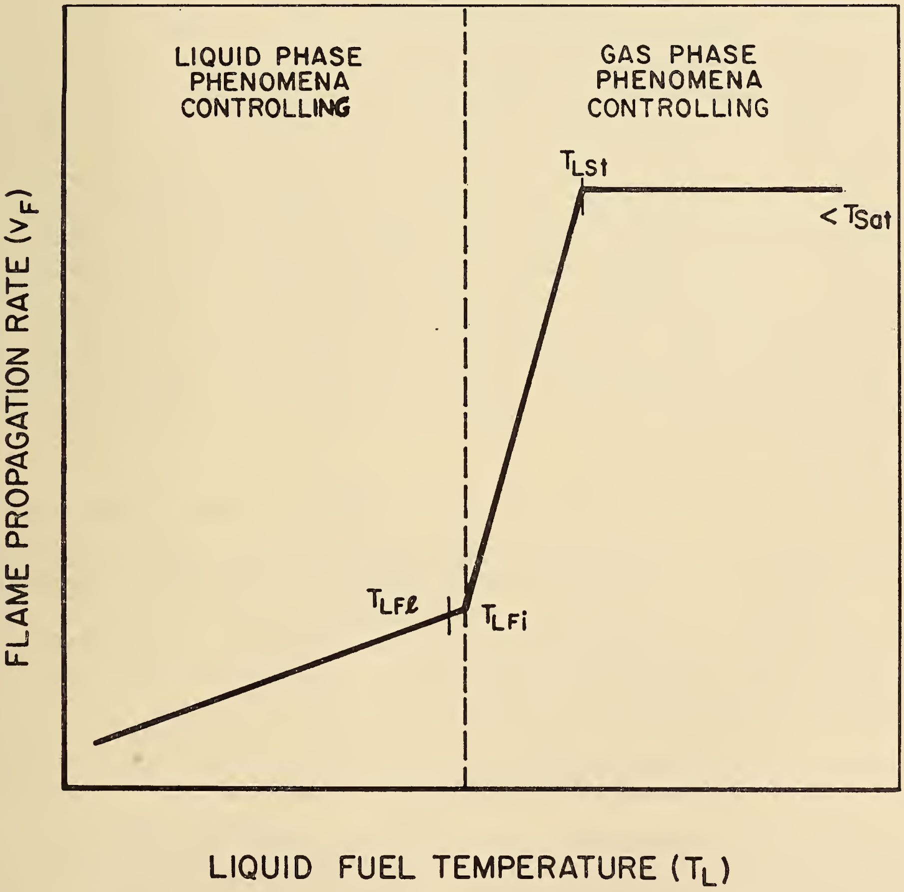

FIG. 1. The flame spreading rate (V_F) in air across liquid fuel surfaces as a function of the bulk liquid temperature, T_L. (T_{LFl} is the liquid flash point, T_{LFi} is the liquid fire point, and T_{LSt} is that temperature of the liquid which gives a sufficient vapor pressure to create a stoichiometric fuel vapor–air mixture above the surface.)

It was found that Roberts[2] previously had given such curves and the experimental evidence to support them.

Since a truly stabilized flame can only exist when the real fire point is reached, the rapid rise in flame spreading rate designated in Fig. 1 was begun a few degrees higher than T_{LFl} at the possible liquid fire point (T_{LFi}).*

Thus one would expect that the maximum flame spreading rate for a liquid would be the laminar flame speed of a stoichiometric fuel vapor–air mixture at an unburned gas temperature corresponding to T_{LSt}. It is assumed, of course, that there are no movements of the *gases* to or from a direction normal to the spreading flame front, i.e., there are no gas phase forced convection effects. All the conclusions, including the last one, will also hold even if radiative heat transfer from the flame to the fuel surface is considered. If, however, the optically thick flame can intensively heat by radiation the fuel–air gas mixture above the liquid surface, then the gas mixture could be ignited ahead of the flame and the flame speed is not the upper limit. This radiative ignition obviously could not be photolysis, but must be thermal in character and then would not seem to be a possibility here.

These above postulates would appear to be in conflict with some results on flame spreading across solid fuels. A possible explanation is as follows. Certain polymers when raised to elevated temperatures can be pyrolyzed upon evaporation or sublimation as in the case of, for example, a solid propellant binder under heating. Particular fragments of the pyrolysis can be very reactive and thus act as an ignition source in the gas phase. In such cases, one would not necessarily expect the laminar flame speed to be an upper limit for the flame spreading which occurs over the solid polymer surface. It would, however, demand a strong radiative heating ahead of the flame; otherwise, the spreading rates would be much less than laminar flame propagation rates. Since most liquid hydrocarbons of interest do not pyrolyze upon evaporation, this type of ignition is not a factor and the conclusions with respect to the flame speeds hold. The authors believe, further, that the mechanism for flame spread across solid fuels must be much like that for liquids below their flash point.

III. *Theories of Flame Spreading Across Fuel Surfaces in Quiescent Atmospheres*

There are three theories† of flame spreading in quiescent atmospheres: Magee and McAlevy,[5,6,7] Tarifa and Torralbo,[8] and Roberts.[2] The first two approaches were developed for spreading with solid propellant and solid propellant materials (i.e., polymers) in mind and postulated to hold for liquids as well. Magee and McAlevy, in their latter publications, no longer state that their theory applies to liquids in which induced liquid convection can take place.[6,7]

Based upon solid propellant ignition work, Magee and McAlevy[7] propose the following model of flame spreading. "Ignition starts at a certain surface location in advance of the flame when it experiences a temperature increase due to the ap-

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* Observations in the present experiments as well as those of Roberts show under many occasions that something which very much has the appearance of a cool flame, really a precursor flame, will precede the main propagating flame, consume some vapor, disappear, and reappear as the flame progresses. One could argue that these precursor flames occur when the flash point is reached, but cannot sustain combustion until the liquid is heated further to the fire point; then the flame arrives.

† Recently Friedman[9] reviewed the first two of these theories.

proaching flame; at a sufficiently high temperature the surface pyrolyzes and emits vapors. As the vapors diffuse away from the surface they react chemically with the active component in the environment, liberating heat, and increasing the local temperature and, hence, the heat feedback to the surface. The advancing flame, having now moved closer to this location of interest further accelerates the vaporization rate and thus the vapor transport rate; the heat release rate is continually accelerated by the increasing vapor flow rate to the site of active chemical reaction, leading to a temperature 'run-away' to ignition. Ignition occurs just as the flame reaches the location. Thus, flame spreading is described as continuous, diffusive, gas-phase ignition."

Magee[6] in his thesis states that the reaction in the gas follows an Arrhenius kinetic rate law and has a high activation energy. This would appear to be inconsistent with the above model. The vapors arising from the surface are not likely to react with the oxygen in the atmosphere if the activation energy of the reaction is high. Only, if the pyrolyzed fuel fragments are quite reactive and thus give a gas phase reaction of low activation energy, does the second sentence in the above quote seem probable. Or else, the position at which McAlevy and Magee[7] state ignition commences ahead of the flame must be "very close" to the flame so that the gases there be heated by conduction. In fact, this distance would have to be less than the thickness of a laminar flame.

McAlevy and Magee find excellent agreement between their experiments with solid propellants and solid propellant binders in oxygen atmospheres and a parameter which evolves from their analysis, $Y^{c}_{\mathrm{ox}}P_t$. Y_{ox} is the oxygen mole fraction, c is a constant about 2 when He is the inert and 3 when N_2 is the inert, and P_t is the total pressure. However, in simplified theories of thermal ignition based upon the approach of Frank-Kamenetskii[10] a parameter of the form of $Y^{2}_{\mathrm{ox}}P_t$ can arise as well. Thus, it appears difficult to assess the validity of the McAlevy–Magee model. In particular, it is difficult to understand the variation of the exponent c with the inert. In other experiments,[11] those authors found approximately the same flame spreading rates with Ar as the inert as they did with He. Since the diffusivities of Ar and N_2 are close and the molar heat capacities of Ar and He are the same, it would appear that the molar heat capacity plays the more significant part. Generally, this result indicates a higher temperature with the monoatomic gas, but again, which temperature is difficult to assess. McAlevy and Magee ignore the possibility that heat transfer from the flame behind the propagating front to and through the solid as the method which controls the supply of fuel vapor. Tarifa and Torralbo[8] feel that this step must be a critical aspect of a flame spreading model since they have determined that this route is faster than conduction through the gas ahead of the flame front. The authors feel that certainly in nonluminous flames heat transfer in the condensed phase must be a dominant mechanism.

Roberts' model considers the flame to be a strip source of heat moving across the surface of the liquid. The source of heat is taken as being at the surface. The two-dimensional equations of heat conduction are written for the liquid state. The flame spreading rate is given by the condition that the flame reaches a certain point when the temperature of that point reaches the flash point (T_{LFl}). Of great interest here is that Roberts observed the flow of liquid ahead of the flame front and wrote of possible convective currents in the propagating direction. He thus solved the two-dimensional heat conduction equation for an essentially anisotropic medium. Although the thermal transfer from the combustion zone to the liquid and within the liquid itself were greatly simplified, he obtained an excellent qualitative correlation between his analytical results and experiments.

Tarifa and Torralbo modeled the problem more correctly in considering the flame to be a surface discontinuity with combustion gases behind the discontinuity. The heat transfer to the fuel ahead of the flame is considered to come from two paths: (1) radiation from the flame to the fuel ahead and (2) convection and radiation from the combustion gases behind the flame to the solid (or liquid) and then conduction through the solid (or liquid). Path (2) is considered faster than conduction of heat ahead of the flame because of the low thermal conductivity of gases. The propagation condition is the same as that of Roberts except Tarifa calls the required surface temperature, the ignition temperature. For liquid fuels he uses the flash point temperature and simplifies the problem by dealing only with large flames in which radiation is the only mode of heat transfer. His models are stated correctly, mathematically; however, his treatment of the liquid case is limited in the sense that he considered only radiation and did not consider the anisotropicity in the liquid. This latter effect is believed to be a major one.

Both Roberts and Tarifa inherently assume that the time required for vaporization, diffusive mixing, and combustion is small compared to the time required to heat the fuel to the flash point. They have, in essence, mathematically uncoupled the gas phase from the liquid phase conditions.

There appears to be sufficient evidence to support the general concepts of the Tarifa and Roberts' models. By the general concepts it is meant that the heat is transferred through the liquid and when the temperature on the surface reaches the flash point, the flame can be considered to have traveled to that point. The fire point (T_{LFi}) sustains the flame in the propagating model; whereas the oxygen mole fraction and total pressure do not affect the lower inflammability limit appreciably and thus the flash point, they should affect the fire point since they control the rate of energy release.

IV. *Some New Experiments on Flame Spreading—The Effects of Viscosity and Surface Tension*

In preliminary experiments to estimate flame propagation rates across kerosene surfaces, it was decided to use only films of the fuel as economic and safety measures. As Tarifa had done, these films were floated on water. The container used was a metal tray 15 cm wide, 122 cm long and 2.5 cm deep. During the observations of the flame spreading process it was noticed, as Roberts apparently had, that the liquid ahead of the flame moves in the same direction as the flame. This observation was verified by noting the movement of styrofoam chips floating on the fuel surface during the flame propagation experiments. It was then speculated that convective currents, or more truly cells, were established in the direction of propagation. An iron oxide powder was then dispersed on the kerosene-water interface (probably supported by interfacial surface tension). During an actual experiment, one readily could observe the styrofoam chips to move in the direction of the flame, and the powder under the surface to move in the opposite direction. The powder moved much slower than the chips. Since quantitative effects were not sought, no efforts as yet have been made to refine this type of experiment. Obviously the thickness of the fuel film and the interface play a part in the particle movements. Nevertheless, it was concluded that convective currents were established in the direction of the flame propagation and were a most important factor in determining the propagation rate. This conclusion was supported by two other experiments. An early one, in which the fuel was absorbed in metal and refractory wicks, was designed originally to verify Tarifa's model that conduction through the liquid was important. It was reasoned that the metal wick had a higher thermal conductivity and thus the flame should propagate at a faster rate. However, without the benefit of convection, the flame, established in a plane on the wick with an ignition source, propagated so slowly across the metal wick that it could be considered trivial with respect to regular fuel propagation rates. The liquid in the refractory wick was transferred, in essence, to a stationary flame through capillary action. In the second group of experiments a barrier was placed in the experimental tray. The height of the barrier was such that it almost pierced the fuel–air surface; i.e., the fuel just wetted the top of the barrier. Barriers with thermal conductivity equal to the fuel (cardboard) and barriers with thermal conductivity greater than the fuel (steel and glass) were used. In this experiment the flame would propagate at its normal speed until it would reach the barrier and then stop. All barrier materials performed in the same way. If allowed to burn for awhile, the fuel on the other side of the barrier would eventually ignite and propagation begin again. If the barrier were lowered a little below the fuel surface, the flame propagated normally and crossed the barrier. Thus it was concluded that if convective cells did exist their height was small.

There are two possible means by which a convective cell can be established. Either by surface tension induced flows (Marangoni effect)[12] or buoyancy effects (gravity flows). One should recall the early experiments of dispersing particles on the surface of water and observing them race from the point at which a drop of detergent (or any surface tension reducing agent) is placed on the surface. Since surface tension decreases with temperature, the flame could act as the "detergent" in a propagation experiment. Whether surface tension or buoyancy effects or both determine the convective movements in these flame experiments, it was realized that these effects could be reduced by increasing the viscosity of the fuel. This logic is supported by the fact that the viscous forces oppose the surface tension induced and buoyancy forces in a convective system as represented by the Grashof number (ratio of buoyancy forces to viscous forces) and the Marangoni number (ratio of the surface tension induced convection to conduction:

$$\mathrm{Gr}=\frac{g(\Delta T)\beta h^3\rho^2}{\mu^2},$$

$$\mathrm{Ma}=\frac{-(\Delta T)(d\sigma/dT)h^2}{\mu k},$$

where β = volumetric coefficient of thermal expansion, k = thermal conductivity, μ = viscosity, ΔT = temperature gradient, σ = surface tension, h = height, and ρ = density. The Marangoni number is sometimes called the Thompson number.[12]

Experiments were then performed with kerosene in which thickening agents (particularly Vistanex,* a polyisobutylene of molecular weight ~200,000) were added in small percentages. Such thickening agents are not expected to alter the vapor pressure of the kerosene and indeed thickened fuels had the same flash

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* Vistanex is the trade-mark used by the Enjay Chemical Company.

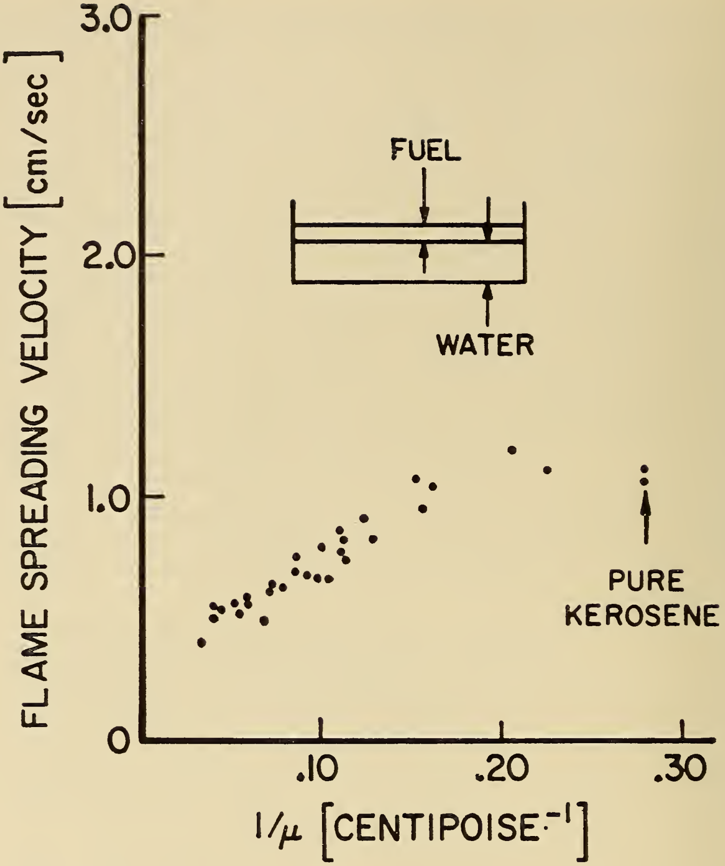

FIG. 2. The flame spreading rate across thickened kerosene surfaces at room temperature (~21°C) as a function of reciprocal viscosity. A 3.5 mm kerosene layer floated on 14.75 mm of water.

point as the unthickened fuels. It is not known how they affect the surface tension. Both the vapor pressure and surface tension of a thickened fuel will be measured in future experiments. As expected, it was found that, as the viscosity of the fuel was increased, the flame propagation decreased. The effect was significant, as shown in Figs. 2 and 3†. Examination of Figs. 2 and 3 did show that the depth of the fuel does affect the results with pure kerosene and with the thickened fuels. This result also is consistent with the convective cell concept.

Whether simply adding a surface tension reducing agent will alter the flame propagation rate cannot be assessed at this time. The Marangoni number contains

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† The experiment related to Fig. 2 has been repeated using dipentene (Kodak-technical grade) with very similar results. The viscosity data reported in Figs. 2 and 3 were obtained in these preliminary studies with a student falling ball viscosimeter. Such viscosimeters usually read high in the low range of viscosities and low in the higher range of viscosities. Figs. 2 and 3 are meant to be qualitative only.

the gradient of the surface tension (σ) with respect to temperature (T), i.e., $d\sigma/dT$, and not the absolute value of the surface tension. Experiments with surface tension altering agents will be tried.

V. *Ignitability*

In performing the experiments with the thickened fuels, the ignitability characteristics of these fuels were noted and found to be consistent with the concepts of convective fluid movements postulated in the previous section. Again the experiments were preliminary, not refined, but revealing.

It was required to ignite pure kerosene in the spreading experiments by first pouring a small amount of a low flash point fuel (usually hexane) at one end of the tray and then igniting with a secondary source. However, with the thickened fuels, a low flash point fuel was not required for ignition. A pilot flame can be used as the initial ignition source. When this flame is directed at the pure kerosene surface, one observes the surface liquid to move away from the heat source, and ignition does not occur. As in the discussion of flame spreading, it is apparent that heat is

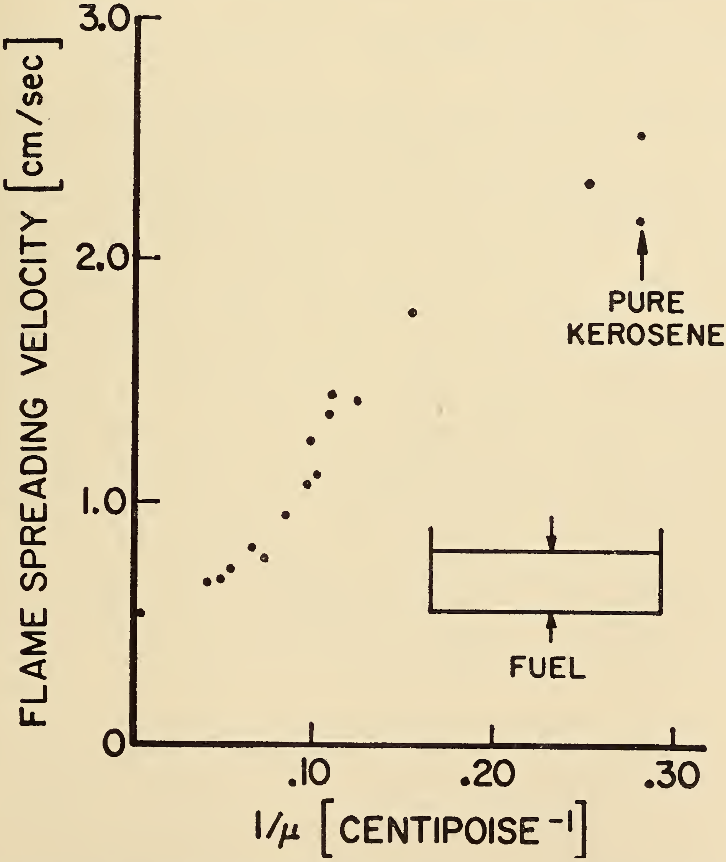

FIG. 3. The flame spreading rate across thickened kerosene at room temperature (~21°C) as a function of reciprocal viscosity. A 10.5 mm depth in metal tray, no water present.

convected away from the ignition source and ignition cannot occur. When the fuel is thickened, there is less convection, more heat is retained at the source and ignition occurs with a simple pilot flame. Again one can actually observe the slower surface currents in the thickened fuels.

The thickened fuels then act very much like thick wicks. A thick wick ignited at one edge will not propagate to the other. As mentioned earlier, fuel will flow to the edge which has been ignited. Convective currents are not possible in such wicks. If there is any propagation, it is only that the wick can become heated by conduction. One can ignite kerosene in a wick with a pilot flame, but not without the wick, unless the kerosene is thickened. Thus thickening the fuel reduces the rate of flame spreading across its surface, but increases its ignitability.

VI. *Steady Burning*

There exist too much data on the burning of pools of liquid fuels to discuss all the work in this area. What will be discussed is the early work (1957) of Blinov and Khudiahov,[13] as reported by Hottel,[14] and considered by most authors to be one of the most significant since it was in essence the first to show the effect of pool size on burning rate. Also, the recent work of Akita and Yumato[15] with segmented circular pools and the work of Blackshear[16,17] on fuel soaked wicks will be reviewed briefly.

Although all the vast literature in this area may not have been reviewed, the authors do not recall any one stating the possible difference in the burning rate of fuels in pans and in horizontal fuel soaked wicks in the context of the part that hydrodynamic effects actually play. It has been well established that in large pools of liquids the burning takes place at the edge of the retaining pan. Although there is evaporation of the fuel in the center of the pool, appreciable combustion does not take place until the fuel reaches the edge of the hollow cone flame formed above the pool, and thus the amount evaporated from the center is appreciably less than that at the edge. Many have realized that there is a likely flow in the liquid from the more dense center to the pan edge. This point apparently was considered as a simple buoyancy effect (gravity flow). However, when one considers that the surface tension is less at the pan edge than in the center, there could be a surface tension induced flow away from the pan edge on the surface with a return flow below the surface as discussed in previous sections. These hydrodynamic effects could be important to the burning rate and it appears well worthwhile to establish experiments which will permit observation of these currents.

It would seem then that experimental results with fuel-soaked horizontal wicks should yield different results than pools. Blackshear states "the fuel consumption rates in wick burning are found to be nearly the same as in comparable burning experiments in which liquid fuels burn in horizontal pans."[16,17] Without knowing the extent of the convective effects it is difficult to say how they will alter burning rates; nevertheless, one feels compelled to say that Blackshear's statement cannot be explicitly correct for large pools. Experiments to be carried out by the present investigators will determine the difference between the burning rate of a fuel in a pool with and without level control (where, in the former case, there is a forced liquid flow), the same fuel in a wick of the same size as the pool, and lastly of a fuel in a pool with various amounts of thickener and surface tension agents. With this background, no further comment will be made on wick experiments.

Although there have been many models and theories dealing with the flame plume, there have been only two fundamental approaches to determine the burning rate of liquid pools, namely, those of Hottel and Spalding. These will be discussed in the following pages. Recall the fundamental problem in determining the burning rate of a condensed fuel in a quiescent gaseous atmosphere. Only the spherical-symmetric problem is tractable. The one-dimensional or cylindrical symmetric systems cannot be solved.[13,19] In order to solve these problems, one must impose a convective condition in the atmosphere in order to establish a "boundary-layer thickness" or "stagnant film" which determines the distance between the conditions of the free atmosphere and the condensed plane surface. Using methods developed by Spalding,[20] it can be shown[21] that the burning rate for stagnant film conditions can be written as

$$\mathrm{G} = (\rho D/\delta)\ln(1+B) = (k/c_p)\cdot(1/\delta)\ln(1+B) \tag{1}$$

where G is mass flux, δ is the boundary layer or stagnant film thickness and B is the transfer number. This expression may be written in terms of the Nusselt number (Nu) as

$$GXC_p/k \ln(1+B) = \mathrm{Nu} \tag{2}$$

where X is the critical dimension of the system. The Nusselt number may be determined from either the Reynolds or Grashof number depending upon whether the convective atmosphere is forced or natural. Spalding[22] has adopted this approach to explain the diameter effect on the burning rate of liquid pools.

Hottel[14] developed a semi-qualitative approach from reviewing the work of Blinov and Khudiahov.[13] The Hottel developments have recently been modified by Akita and Yumato[15] to correlate with their experimental results.

The Hottel approach is best developed by first discussing the experimental results of Blinov and Khudiahov. Their results "... 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."[14] Figure 4 taken from Ref. 14 reveals that Blinov and Khudiahov results show a decrease in burning rate with pan diameter in the laminar region, a variation in burning rate through a transition region, and a burning rate independent of pan diameter in the turbulent region. Since the work of Blinov and Khudiahov, others have verified experimentally the diameter effect of the burning rate.

Hottel attempted to correlate the results of the Russian investigators by an expression

$$q/\tfrac{1}{4}(\pi d^2) = [k(T_F - T_L)/d] + \bar{U}(T_F - T_L) - \sigma F(T_F{}^4 - T_L{}^4)[1 - \exp(Kd)] = GLv \tag{3}$$

which simple states that the heat flux to the liquid per unit surface area is equal to the heat gained from the pan rim, the convection from the flame, and the radiation from the flame, respectively. k, the thermal conductivity, $\bar{U}$ the convective coefficient, F, the view factor and K, Beer's extinction coefficient were all assumed constant. The expression was said to explain the diameter effect, since for small d's the first term is the only one of importance. At large d's the first term is negligible,

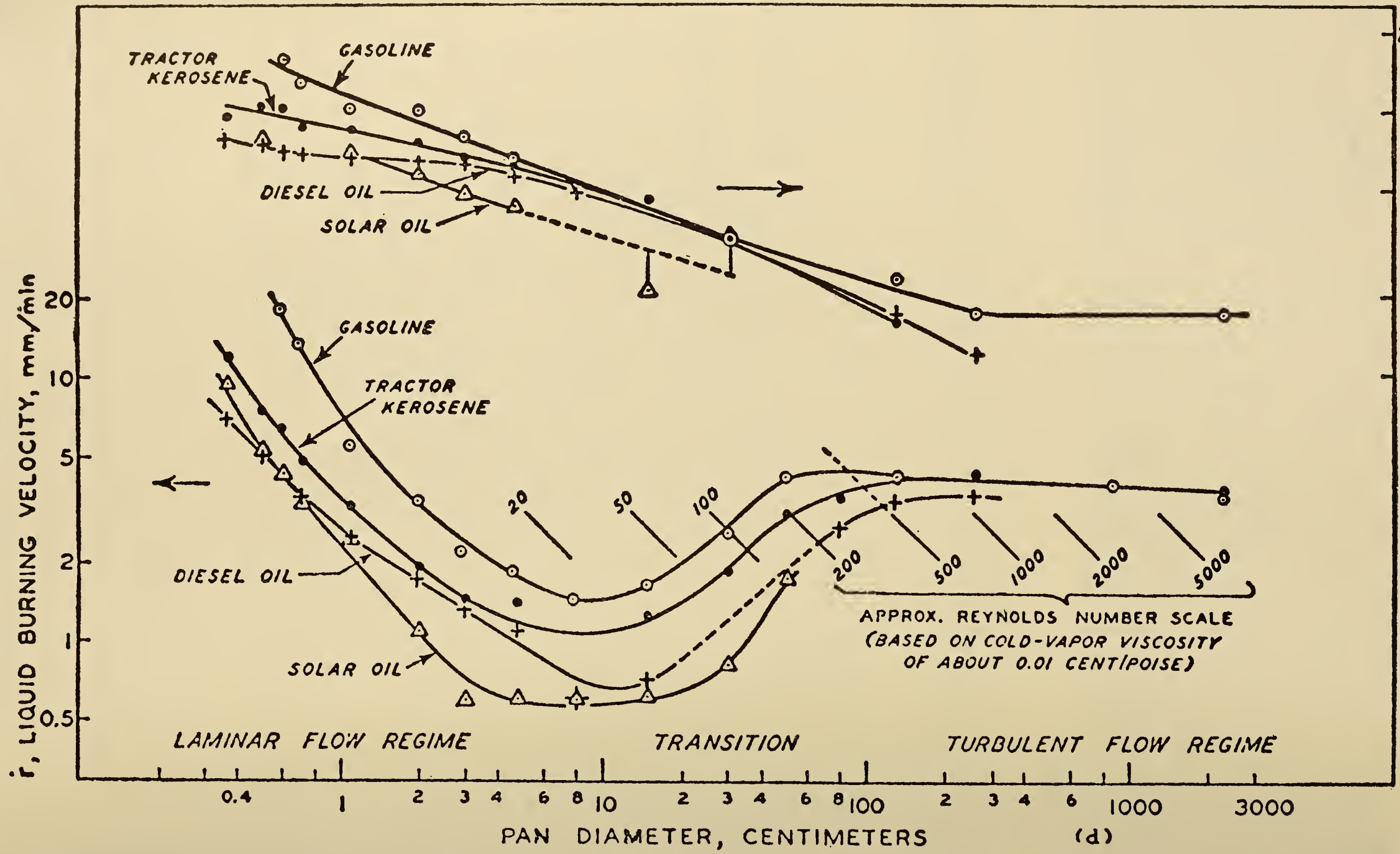

FIG. 4. Linear liquid burning velocity as a function of pan diameter. Data of Blinov and Khudiahov (11), figure from Reference 14.

the second is constant, and the third term will dominate and it is constant because Kd is so large. This argument is very qualitative and the fact that such an expression can be fitted to experimental data may be purely fortuitous when one considers the number of physical constants which are in essence handled as arbitrary constant terms adjusted according to the experimental conditions.

Akita and Yumato[15] made some relative minor modifications to the Hottel expression, by writing k and $\bar{U}$ as a function of d and dropping the radiation term. Since these authors dealt with non-luminous methanol flames, the last modification was certainly valid. They claim good agreement with their data, but again such agreement is fortuitous because of the presence of the large number of physical constants, which again are handled as arbitrary constant terms.

Spalding[20] has suggested that his work on burning rates in free convection both with vertical flat plates and spherical surfaces could also be adapted to the horizontal pan or wick. The expression for the pan burning rate which then develops from the previous expression given in terms of a stagnant film and the Nusselt number is

$$\frac{\dot{r}\rho_l d}{(k/c_p)} = AB^{3/4}[gd^3/\nu^2]^n \tag{4}$$

where A is a constant and n is the coefficient of the Grashof number. $\dot{r}$ is the linear regression rate, B is the transfer number as before, and ν is the kinematic viscosity. The Grashof number in the above expression does not contain a density difference. In flames burning in air the density of the flame zone is about one-seventh to one-fifth that of the surrounding air which suggests that an adequate approximation of the buoyancy force in the flame zone is to assume the density to be vanishingly small, thus, permitting writing the Grashof number as shown.

For laminar conditions, heat transfer experiments show A and n to be 0.45 and $\frac{1}{4}$ respectively; for turbulent conditions they take the values of 0.117 and $\frac{1}{3}$. Thus one sees immediately that for the turbulent condition, $n=\frac{1}{3}$, Spalding's expression gives $\dot{r}$ independent of d. For laminar conditions, $\dot{r}$ should be proportional to $d^{-1/4}$. Akita and Yumato results experimentally predict $n=0.20$, which does not appear too bad, although they deem it unsatisfactory. Blackshear and Murthy[16] found $n=\frac{1}{4}$ and $n=\frac{1}{3}$ respectively for burning on vertical wicks for the small and large size condition respectively. Others have supported the Spalding approach.[23,24] Apparently there are other factors to be considered under the small diameter condition.

Additional evidence may be offered to support the semi-empirical approach of Spalding. Burgess, Grumer, and Wolfhard[25] relate the liquid burning rate (linear regression rate, $\dot{r}$) at large tray diameter to two physical properties of the fuel, the heat of combustion in air (Q) and the heat of vaporization (L_v), (which includes the heat capacity term from ambient temperature to the saturation temperature), by plotting $\dot{r}$ as a function of Q/L_v. They argue that the percent of heat radiated to the surface from the flames of many different fuels (methanol, UDMH, hydrocarbons and liquid hydrogen) are approximately equal and that the burning rate must then be proportional to the heat of combustion. Since experiments show the burning rate to be inversely proportional to the heat of evaporation, they contend that the burning rate should be inversely proportional to L_v/Q. This conceptual reasoning is said to be expressed in more detail in reports of the Fire Research Station at Boreham Wood, England. Burgess, *et al.*, find a good linear correlation

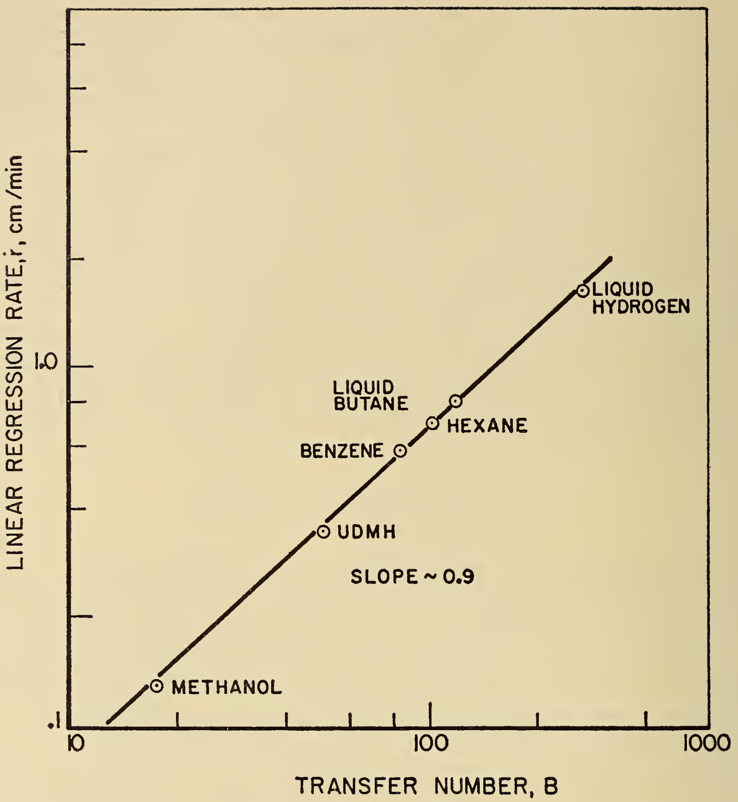

FIG. 5. Relationship of linear regression rate at large tray diameter to the transfer number, B. Data from Reference 25.

and state "the approach to linearity . . . is somewhat disconcerting in view of the crude reasoning in which the correlation is based."

The Q/L_v and $\dot{r}$ can be correlated in another manner. Q/L_v as calculated by Burgess, *et al.*, is the transfer number B for the fuel burning in air. Spalding's formulation suggests $G=\rho_l\dot{r}\sim B^{3/4}$. Since the densities of most of the hydrocarbon-type fuels are the same, one would expect $\dot{r}\sim B^{3/4}$. Figure 5 gives a plot of log $\dot{r}$ vs log B. Although it was difficult to pick data from Burgess' figure, the linearity found in Fig. 5 is even better than that found in Ref. 25, in that the liquid hydrogen aligns more closely. The slope obtained is, however, 0.9 somewhat higher than 0.75 suggested.

It was at first thought that the hydrogen agreement was fortuitous, since its liquid density is much less than the others. However, there is the gas phase term k/c_p $(=D\rho)$ in Spalding's expression and an estimate of this term indicates that it is appreciably lower for hydrogen and very nearly compensates for the liquid density factor. Because omitted terms are self-compensating, the agreement is not as fortuitous as might be expected.

Equation (4) and Fig. 4 show the consumption rate to be independent of pan size when the pan is large. Recall that the significance of this trend is that the natural convective field has become turbulent. Further, the fact that the convective heat transfer is independent of the critical dimension and that a radiant component would also be independent of the size of the horizontal pan makes it difficult to assess the relative importance of these two modes of heat transfer. However, it has been shown by one of the authors and detailed in a student thesis[21] that when the radiative mode must be accounted for in problems of heat and mass transfer, only the transfer number need be modified in most cases. The effective transfer number with radiation becomes

$$B_{\text{eff}}=\frac{B}{1-(R/\dot{r}\rho_l L_v)}$$

where R is the radiant flux.

One must question the extent of the radiant flux in flames of the fuels listed in Fig. 5. The luminosity of hydrocarbon flames are certainly much greater than that of either the alcohol or hydrogen. Yet, the linear regression rate appears to correlate with B and not B_{eff}.

Some of Akita and Yumato's other experiments[15] are worth reviewing in a little more detail. They performed a series of tests in circular pans which were divided into three concentric rings of equal area. They found that the burning rate is the largest in the outer ring which is next to the flame base (at pan edge) and the rate decreases with the distance in from the outer rim. As the vessel becomes larger, this effect decreases. Also of interest is that the average burning rate of the three concentric zones is generally less than the burning rate found in vessels not subdivided and of equivalent size of each of the sub-divisions. These results would seem to support the strong influence of liquid convection in burning experiments.

In conclusion, the experiments suggested earlier in this section, in which the burning rate of thickened fuels would be measured, and the currents of pure and thickened liquids observed, seem very valid and should give further understanding of the burning of liquid fuels. It is important, as well, to reflect on the experiments in which the experimental burning rate is determined by the rate of feed to keep the surface at a stationary height with respect to a container rim. Practically all the published data for the steady burning of liquids were obtained by this technique or some modification of it. Knowing that the hydrodynamics in the liquid can play a part in determining the burning rate, one must question whether such experiments will give the same results as stagnant pools. For this reason the authors will attempt to measure burning rates with stagnant pools and with the liquid level control.

VII. *Conclusions*

The flame propagation rate of liquid fuels is determined by gas phase phenomena when the temperature of the fuel is greater than its flash point and by liquid phase phenomena when the fuel is at a temperature less than its flash point. The maximum flame propagation rate across a liquid surface is the laminar flame speed of the stoichiometric fuel vapor-air mixture at the liquid temperature which gives a vapor pressure sufficiently high to form a stoichiometric mixture, i.e., T_{LSt}. For the $T_L<T_{LFl}$, in which liquid phenomena control, the important heat transfer mode is apparently a convective fluid motion in direction of the flame propagation. This fluid motion is generated by surface tension and/or buoyancy (gravity) effects. Increasing the viscosity of the fuel, then lowers the rate of flame propagation and

burning, but increases its ignitability. The effects of surface tension are yet to be determined.

It is apparent that hydrodynamic considerations are important (if not the most important) factors in determining the ignitability, burning and flame spreading rate of pools of liquid fuels at temperatures below their flash point. In fact, they establish the difference between the combustion of large pools of liquid and small liquid droplets. Their relative importance to a large, sooty flame where radiation ahead of the flame may be a major mode of heat transfer, is yet to be evaluated.

VIII. *Practical Implications*

If the modeling described in the previous sections is correct and if the experimental observations have been interpreted properly, then it is possible to speculate as to the applicability of the results to certain practical problems. But, first, the reader must be reminded that much remains to be verified.

The problem which arises when oil tankers meet disasters and affect neighboring land areas is best exemplified by the so-called "Torrey Canyon" incident. Efforts to burn the oil from the Torrey Canyon on the water just off the coast of southern England met with failures. To the best of the authors' knowledge, flares, torches, bombs, etc., were tried, but to no avail. From the work presented here, one could analyze the difficulty. The temperature of the ocean is such that one is sure that the oil was below its flash point. More than likely, the oil, as well, has a flash point well above standard conditions. One then concludes that propagation must be controlled through the liquid phase. As discussed in the body of the report, if the oil slick is thin, then propagation is difficult and not likely. The thin slick permits the ocean to be a large heat sink and also alters the "convective" situation necessary for propagation. Thus, a region ignited by the flare or other device does not spread. The manner by which one possibly should proceed would be to spray or coat the oil with a volatile hydrocarbon (gasoline, for example) that has a low flash point, i.e., one below the ambient conditions (say the ocean temperature). Since the flame for such compounds propagates in the gas phase, it is a simple procedure to ignite at one location and have the flame propagate rapidly across all the coated area. Once ignited in this fashion, the oil should burn.

The use of foamed plastics to inhibit the propagation of condensed phase flames in closed spaces (i.e., a partially empty fuel tank) deserves some comment. If the plastic does not completely fill a volume; that is, a gap can exist, then the effectiveness of the foam depends upon whether the fuel under consideration is above or below its flash point. The foam would prevent propagation near any gaps if the ambient temperature is below the flash point, but may be completely ineffective if the ambient temperature is above the flash point and propagation can take place through the gap in the vapor phase. This situation is very similar to the spreading problem when wicks are used and has been discussed in the body of the report.

Although thickened fuels no doubt have slower flame spreading rates than pure fuels, the thickened fuels would appear to be ignited more readily by hot projectiles, or for that matter any ignition source.

Related to the concept of ignitability, one may also speculate about the merits of thickened fuels from the point of view of pool fire extinguishment techniques using water. In fire-fighting practice, moderately sized pools of burning liquids whose flash point are above normal environmental temperatures, may be extinguished by driving the flame across the surface with the aid of water (and thus steam). The water cools the liquid surface by direct contact and also creates motion within the fuel to bring cooler fuel to the surface. In this regard, the technique is directly opposite to the process of flame spreading. The thickening of a fuel inhibits the fuel motion; thus, it would appear that, other factors being equal, a large, thickened-fuel fire may be more difficult to extinguish with water.

IX. *Acknowledgments*

The authors wish to acknowledge the aid offered by three Princeton University undergraduates who have worked or are currently performing research in the Combustion Research Laboratory; namely, Messrs. T. Eklund, D. Hensler, and M. R. Hough. Many interesting discussions were held with Professor W. A. Sirignano. Professor S. H. Lam provided the first insight concerning the possible importance of surface tension induced flows in the kerosene experiments. Dr. Robert MacKinven has been most helpful in performing some of the recent experiments.

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Subject Headings: *Flame propagation, in liquid fuels; Fuel spreading; Ignitibility; Liquid burning; Liquid fuels.*

ABSTRACTS

A. Prevention of Fires and Fire Safety Measures

Alvares, N. J. and Wiltshire, L. L. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Ignition and Fire Spread in a Thermal Radiation Field" *Report USNRDL-TR-68-56, DASA, NWER A-8, Subtask RLN 5032* (July 12, 1968)

An investigation has been made of the radiant ignition and fire spread characteristics of some composite cellulosic fuels. The composite specimens consist of cotton cloth covering one side of a 1 in. thick cotton batting panel. Black, white, and natural cotton fabrics were used for this purpose. The panels were orientated vertically for the ignition measurements so that the cloth surface faced the front of a calibrated thermal radiation source. Ignition measurements were also made of the fabric alone, and with the cloth surface of the panels half covered by newsprint. Preliminary measurements of fire spread along a fuel element were made by use of the composite panels. The panels were ignited at one end by a small amount of kerosene and the rate of fire spread across the panels was determined by a continuous recording of the panel weight versus time. Fire spread measurements were made both with and without irradiance from the thermal source.

It has been found that the ignition thresholds of cotton cloth are decreased when the cloth is either backed by cotton batting or in contact with newspaper. The effect of external radiation from a tungsten lamp bank on the ignition and fire spread in the cellulosic fuel combinations is influenced by the optical characteristics and impurity content of the cloth material. It has been observed that very small amounts of cloth finishing impurities induce dramatic changes in the fire spread characteristics of the fuel combinations.

Subject Headings: *Burning rate, of cotton; Cotton ignition, fire spread on; Fire spread, on cotton; Ignition, of cotton; Thermal radiation, ignition of cotton.*

Authors' Abstract

Banik, E. (Lübeck, Germany) "A Study of Safety Distances in the Planning, Erection, and Operating of Explosives and Powder Factories Producing Smokeless Powders" (in German), *Explosivstoffe* **9**: 200–205 (1967)

In addition to devising safe operating practices in explosives factories, safe methods of construction of buildings, limitation of number of persons employed, automatic equipment, shields, etc., are important. Safe distances between buildings in the factory and their distances from neighboring residential areas are the subject of this paper.

Two types of factories are dealt with—those producing high explosives, and those producing smokeless powder. For the former, the minimum distance to a residential area should be one kilometer in the case of an explosive like nitroglycerin, although large-scale detonations have been known to propagate several kilometers. For smokeless powder, there is less risk, so a minimum distance of 500 meters is prescribed.

Within the factory, relationships are described which estimate safe distances between buildings. For example, the "cone radius" for 1000 kg of nitroglycerin is 7 meters, the safe distance for enclosed warehouses from each other is 17 meters, and the distance for breaking window panes is 196 meters (pressure $=60$ g/cm^2). The cone radius varies as the cube root of the mass of the explosive, and the distance at each pressure point varies as the square root of the mass of the explosive. Damage is attributed to spherical shock waves which may be reflected and bound around buildings.

Different types of building construction are described. These include fire-resistant materials, blowout walls to relieve pressure and to make sure that no heavy objects can be tossed about. A diagram is given, illustrating the following formula used:

$$E=k(M)^{1/2}$$

where E = required safety distance in meters, k = a constant dependent on method of construction, and M = mass of explosive in kg. The safe distance to buildings in the blowout direction should be increased by 50%. The distances may be shorter for those buildings covered by at least one meter of earth.

Safety distances which are too great make the duties of the industrial watchmen very difficult, and also make it difficult to relieve the shift workers.

Relations are also given for the storage sites of explosives packaged for shipment. Some explosives, such as nitrotoluene, are relatively less sensitive and safer to handle.

In the case of smokeless powder, detonations are much less likely, and fire protection only is needed. For the latter, a minimum distance between buildings of 10 meters is needed, and 50 meters to the factory fence. For 150 tons (metric), packaged, the distance should be 150 meters. This distance is always about 2½ times that for quantities not yet packaged for shipment.

It is asserted that these relationships are fairly reliable and based on considerable experience. In the long run, observing these quantities will be found to be economical.

Subject Headings: *Building separation, for explosives; Explosives, safe distances for; Safety, with explosives; Smokeless powders, safety procedures.*

J. K. Richmond

Brenden, J. J. (Forest Products Laboratory, U.S. Forest Service, Madison, Wisconsin) "Effect of Fire-Retardant and Other Inorganic Salts on Pyrolysis Products of Ponderosa Pine at 250° and 350°C," *Forest Products Laboratory, U.S. Forest Service Research Paper FPL 80* (1967)

Basic information was obtained on the pyrolysis reaction and products formed when wood treated with fire-retardant and other salts was pyrolyzed at 250° and 350°C. This information will be useful in the systematic evaluation and selection of improved fire-retardant treatments for wood.

Fourteen inorganic chemicals were used to treat wood shaving samples, which were then pyrolyzed in vacuum at 250° and 350°C. The pyrolysis products of untreated wood and chemically treated wood were separated into four fractions by vacuum distillation. The fractions were: a char residue, low vapor pressure tars, water, and "noncondensable" gases. The flammability of wood is normally associated with the volatile tar fraction.

When treated and untreated wood were pyrolyzed at 350°C, the chemicals increased the yield of the char, water, and gas fractions at the expense of the flammable tar fraction. This effect was greater for chemicals that are usually considered to be fire-retardant than for non-fire-retardant chemicals. Also, at a pyrolysis temperature of 350°C, very small amounts of chemical (on the order of 1 per cent of the treated sample weight) markedly affected pyrolysis, increasing yields of char, water, and gases, and decreasing tars.

When treated wood was pyrolyzed at 250°C, most chemicals reduced the tar and char fractions of the pyrolysis products and increased the water fraction. An important exception was diammonium phosphate, which produced a higher proportion of tars in the pyrolysis products than was observed for untreated wood. The relation of these data to the fire-retardant characteristics of diammonium phosphate may be explained on the basis of the low temperature at which the tars were released (250°C), and the fact that the tars were diluted with a relatively large amount of water vapor. Thus the result was a nonflammable composition.

In general, small concentrations of the various chemicals were less effective at 250°C than at 350°C in altering the composition of the pyrolysis products.

Subject Headings: *Fire retardants, effects on pyrolysis of pine; Ponderosa pine, pyrolysis produced by; Pyrolysis products, of pine; Salts, effects on pyrolysis of pine.*

Author's Summary

Burgoyne, J. H. (Imperial College, London, England) "Designing for Protection against Dust Explosions," *Chemistry and Industry* No. 21 854-858 (May 1967)*

This article is a survey in somewhat general terms of design aspects for a dust handling plant, with particular emphasis on the considerations involved in designing a new plant from scratch. As such it contains little that would be un-

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* Paper presented at the Symposium on "Design for Safety" in London, December 6, 1966.

familiar to those experienced in dust explosion protection precautions, but it is nevertheless a useful survey article either for those entering the field, or as a check-list for those with considerable experience already in the field.

The essence of the article is essentially contained in the author's useful summary, which follows:

(1) A plant handling combustible powders should be designed with the minimum of building enclosure so as to reduce, as far as possible, the danger of secondary explosion.

(2) The plant itself should be operated as far as possible under induced draught, in order to reduce the escape of dust and to facilitate the sealing of explosion reliefs.

(3) All voluminous units of the plant (in excess, say, of 100 cu ft) should be protected, either by explosion reliefs designed in accordance with the strength of the unit, or by automatic explosion control systems, as may be most economical. Reliefs must discharge to a safe place in the open air.

(4) Plant details should be systematically considered to avoid the introduction of potential sources of ignition.

(5) Although it is probable that the ideal plant, from the point of view of minimizing the dust explosion hazard, can only be designed "from scratch", the same ideals should be kept in view in designing modifications to an existing plant.

This summary may be amplified by additional material from the article, which is divided into four main sections as follows: (1) structural arrangement (design); (2) plant arrangement (layout); (3) design of explosion relief systems; (4) ignition sources.

(1) *Structural Arrangement*—This is concerned with the design of structures. The author discusses the relative merits of open-air construction, in contrast to the light frame structure, or enclosed systems in explosion proof walls. The suggestion is that wherever possible the open-air structure should be adopted. Also included is a brief discussion of problems of surfaces and ledges design, and their elimination by appropriate design; together with the necessity for smooth surface finishes on walls, floors, and ceilings to assist cleaning and to prevent accumulation of deposits. In relation to this there are further comments concerning characteristics of dust explosions, notably that they feed themselves and generally accelerate as they progress, often with maximum damage some distance from the point of ignition.

(2) *Plant Arrangement*—This is concerned with the plant layout, in which it is assumed that most plants can be regarded as a sequence of storage volumes connected by more or less restricted channels. The points emphasized here are the need for design that will give dust-tight units, and the enclosure of troublesome escape points in units that can be properly ventilated. Also, the desirability of using subatmospheric pressures for conveying, appropriate siting of filters, and the choking of channels connecting isolated units. Other aspects also to be considered should include overflow control, pressure containment, the supply of fluid suppressants triggered by depressurization in large volumes, and possibly the value of inerting by washed flue gas.

(3) *Design of Explosion Relief Systems*—Here some more specific points are

dealt with, notably the following: assessment of the mechanical strength of the units; assessment of the relief area required to reduce the explosion pressure to below the strength of the unit; design of reliable closure units for relief openings; correct design of relief ductwork. This includes a discussion of the strength and coupling characteristics of typical units frequently found in existing plants, pointing out that many contain flat surfaces, particularly the tops of cyclone units, which have rather poor buckling characteristics. Mention is made of the suggested design pressure for the relieved explosion pressure: 1 psig is recommended. Mention is further made of the need for security of inspection panels, filters, and other similar units so that in the event of an explosion that these do not become missiles. There is also need to look to the design of relief closures, which must be robust and reliable.

A particularly interesting point is associated with comments about the literature of dust explosion relief investigations. This is described as "chaotic." "Efforts to distill any general relationships between relief area and maximum explosion pressure from the empirical data available are not particularly rewarding." In consequence the author recommends that a suggestion by Maisey[1] should be adopted, that dusts should be compared in some standard test, e.g., the Hartman bomb, against gases. This is because the literature of gas explosion relief, at least at low pressures, is in better shape. Four standard gases or reference gases are suggested, methane, propane, ethylene, and hydrogen; since, on these four gases, the highest average rate of pressure rise, and maximum pressures resulting exist already in the literature, and are very reproducible. The suggestion is to correlate dust behavior with the pressure and pressure rise of these reference gases, and then design as if the plant was to be operated using the reference gas.

(4) *Ignition Sources*—As the author points out, the elimination of ignition sources is often a matter of close attention to detail in basic design and in operation. Specifically, he mentions the following six points to which particular attention should be given. (a) The possibility of ignition of deposits, since thick deposits often show quite surprisingly low ignition temperatures, often between 100° and 200°C. (b) Elimination of foreign matter that can cause fouling, by appropriate screening grids and separators. (c) Permanent lighting of silos, bins, etc., and the strict avoidance of wander leads and inspection lamps. (d) Metal units earthed to avoid static. (e) Electrical equipment outside the operating plant, and properly dustproofed. (f) Naked flames, where these are necessary for some ancillary process, isolated from dust panels.

On the basis of this article, readers' attention could usefully be directed to the mentioned article by Maisey.[1] In addition, a source of material similar to the information provided in the article reviewed above has just been published in a CEP (*Chemical Engineering Progress*) technical manual titled "Loss Prevention", Vol. 2, published by AIChemE. This contains articles given at the 2nd Loss Prevention Symposium, St. Louis, Missouri, in February of 1968. Of the articles in Vol. 2 the following listed below are pertinent to dust explosions.

(1) Bisphenol—A Dust Explosion—by Richard L. Yowell, pp. 29–33.
(2) Testing Explosiveness of Dusts by Joseph Gillis, pp. 34–36.
(3) Interpretation of Dust Explosion Test Data by R. F. Schwab, pp. 37–43.
(4) Dust Explosion Research, by R. H. Essenhigh, pp. 44–49.
(5) The Dust Problem: Discussion, pp. 49–53.

Reference

1. Maisey, H. R.: *Chem. Process Engng.* (1965) pp. 527, 662

Subject Headings: ***Dust explosions; Explosions, of dust; Safety protection, against dust explosions.***

R. H. Essenhigh

Eickner, H. W. (Forest Products Laboratory, U.S. Forest Service, Madison, Wisconsin) "Fire-Retardant-Treated Wood," *Journal of Materials* 1(3) 625–644 (1966)

There has been increasing acceptance and use of fire-retardant-treated wood in construction, especially in the framing of interior partitions, in roof framing and decks, and as interior finish material. This paper summarizes information on the chemicals and treating processes used, theories on fire-retardant action, performance in test fires and actual fires, and treatment effect on various wood properties.

Full-cell pressure treating of wood with water solutions of the chemicals is the generally accepted practice. Required average dry-salt retention in lumber depends on lumber thickness with $2\frac{1}{2}$ to 3 lbs/ft^3 for 2 in. lumber and thinner, lesser amounts in thicker lumber. Minimum penetration required is $\frac{1}{2}$ in. In plywood, treatment pressures and temperatures are generally lower than for lumber. Solution retention of at least 25 lbs/ft^3 or a dry-salt retention of at least 3 lbs/ft^3 is necessary for good penetration and distribution.

Chemicals generally used in fire-retardant formulations include mono- and diammonium phosphate, ammonium sulfate, zinc chloride, borax, and boric acid. A number of the formulations used commercially for fire-retardant treatment include a combination of the above salts; these are listed by the author. Fire-retardant additives have also been used in combination with oil-borne preservatives. Included in this category are a triaryl phosphate compound, borax-boric acid, and sodium calcium borate.

Fire-retardant treatment formulations have been based both on basic and empirical investigations to result in the best over-all performance. In developing the formulation, consideration is also given to its effect on other properties of the treated products such as durability, strength, gluing, painting, etc.

A number of theories have been advanced on how a chemical reduces flammability in wood. Several are listed by the author. These include:

1. The chemical acts as a mechanical barrier to the escaping flammable products and prevents entry of air to the wood surface.
2. An insulating layer in a form of a coating, glaze, or foam prevents pyrolysis of the wood.
3. Treatment increases the thermal conductivity of the wood resulting in greater heat dissipation.
4. Fire-retardant chemical acts as a heat sink after undergoing chemical and physical changes.

5. Fire-retardant chemical decomposes and releases nonflammable gases which dilute the combustible gases of the wood.
6. Ion radicals are released by the chemical at pyrolytic temperatures; the radicals restrict the flammability range for the combustible gas-air mixtures.
7. Pyrolytic temperatures are lowered by the chemical resulting in greater water and charcoal formation and less flammable gases and tars.

Theories on glow retardation include the physical theories on flame reduction and several chemical theories related to increasing the molar ratio of carbon monoxide to carbon dioxide in the combustion process. The author states that studies using thermogravimetric, differential thermal, and decomposition product analyses confirm primarily the seventh theory. A lowering of the initial pyrolysis decomposition temperature for wood occurred for most of the effective fire-retardant chemicals. This decreased flammable gas and tar production and increased the amount of charcoal. Flaming is primarily attributable to decomposition of the cellulose fraction of the wood and glowing to lignin fraction.

The extent to which the various fire-performance characteristics have been improved over untreated wood is the basis for accepting and using fire-retardant-treated wood. The decrease in the surface-flammability characteristic is the principal advantage of fire-retardant treatment of wood. A second advantage is that treated wood contributes less heat, especially from volatiles, during initial stages of the fire. A number of studies are cited by the author demonstrating these advantages.

Treating wood with properly formulated fire-retardant chemicals will result in self-extinguishment, both flame and glow, once the primary source of heat and fire is removed or exhausted. Some chemicals will retard both flame and glow, others are more specific, retarding one but not the other. Combinations of chemicals are therefore used in many formulations.

Smoke development is also discussed by the author. A number of factors affect the amount of smoke produced by a material. These include area, rate and type of heating, and air available for burning. For fire-retardant-treated wood smoke production is dependent on both the level of treatment and the type of chemical used. In some cases a given chemical treatment may produce less smoke but its retardant action may be less effective than others which are smokier. Production of toxic products from burning treated wood does not appear to be a problem. Amounts produced are small and these react primarily within the wood.

Fire-retardant treatment has only a slight influence on rates of char and fire penetration. This is probably the result of the greater depth of insulating char which develops. Notable improvements in fire endurance have been recorded for wood composite doors when edge rails and frames are treated. The author also notes that the use of treated studs can improve fire endurance in walls. In actual fires fire-retardant-treated wood has performed very well. Two cases are described in the paper.

A number of tests cited by the author has shown that fire-retardant-treated wood retained its fire-retardant properties indefinitely under normal use conditions. Such use is restricted primarily to the interior since the chemicals are water soluble and can be leached by running water.

The effects of fire retardant treatment on a number of wood properties are discussed. There is some evidence to indicate that a small reduction in strength occurs. The largest decrease was for impact loading where decreases of 32% or less resulted. Modulus of elasticity decreased 5 to 8% and modulus of rupture 10 to 17%. Such decreases are taken into account in allowable unit stresses for design. There is no evidence to indicate that wood treated with fire-retardant chemicals undergo further deterioration with age.

Treated wood is usually more hygroscopic than untreated wood, particularly at higher relative humidities (RH). Increases in equilibrium moisture content for treated wood depend on the type of chemicals, level of retention, and size and species of wood. Most current fire-retardant formulations result in a negligible increase in equilibrium moisture content, especially at lower levels of RH. Zinc chloride formulations add appreciably to the equilibrium moisture content in the range of 30 to 80% RH; ammonium phosphate does not generally increase the moisture content; and ammonium sulfate increases the moisture content only above 65% RH. Substantial increases in moisture content occur for wood treated with borax or boric acid during the initial desorption cycle, becoming less in subsequent sorption cycles.

Some earlier types of fire-retardant treatments were very corrosive to metal fittings in contact with the treated wood. This corrosivity depended on relative humidity conditions, the metal involved, and the types and retention of fire-retardant chemicals. Current formulations using corrosion inhibitors have overcome this problem. Even with inhibitors, prolonged exposure to high humidity conditions should be avoided, since various forms of electrolytic corrosion can occur.

For drying fire-retardant-treated wood, the same general schedule for untreated wood can be used. Two exceptions are noted by the author. These are: the maximum temperature should not exceed 160°F, and the initial relative humidity should be below the equilibrium relative humidity of a saturated solution of the chemicals. The first limitation minimizes any combined effect of chemical and heat on the strength properties of the wood, and the second prevents surface condensation and leaching and corrosion of the kiln. The hygroscropic nature of treated wood permits it to be dried with more severe conditions of rapid reduction in humidity in the early stages of drying than with untreated wood. Final conditioning to relieve casehardening is usually not required.

Because of the presence of salt crystals in the wood there is an abrasive effect on cutting tools. The use of abrasive-resistant cutting and shaping tools is recommended. Tool wear can also be minimized by cutting the wood to approximate finished size before treating.

Results in gluing fire-retardant-treated woods have only been partially satisfactory. While they can be glued using conventional assembly glues or using hot-press phenolic glues for plywood, the bonds are not comparable to those obtained with untreated wood. In general the type of bonding obtainable is not recommended for structural assemblies but is satisfactory for decorative purposes.

Generally, treating the wood has not interfered with the adhesion of surface coatings except when associated with higher moisture contents of the treated wood. Some test results have indicated an improvement in paint durability. A moisture content of 12% or less for the treated wood is recommended for applying paint.

Fire-retardant-treated wood is not recommended for exterior use where it may be exposed to rainfall owing to the soluble nature of the salts in the retardant formulations. Sealer treatments have been used to improve the leaching resistance of treated wood. Results from tests using a sealer are cited in the paper.

Subject Headings: *Fire retardants, in wood; Wood, fire retardants in.*

W. Y. Pong

Fahnestock, G. R. (Pacific Northwest Forest and Range Experiment Station, Portland, Oregon) "Fire Hazard from Precommercial Thinning of Ponderosa Pine," *U.S. Forest Service Research Paper PNW-57* (1968)

Slash from precommercial thinning of ponderosa pine stands in the Pacific Northwest can be a high to extreme fire hazard for 5 years or longer.

Subject Headings: *Fire hazards, of pine slash; Pine slash, fire hazard of; Thinning of pine, fire hazard.*

Author's Summary

Fish, A. ("Shell" Research Ltd., Thornton Research Centre, Chester, England) "The Cool Flames of Hydrocarbons," *Angew. Chem. internat. Edit.* 7(1) 45–60 (1968)

The oxidation of hydrocarbons and other related species, e.g., ketones, is a process of extraordinary complexity. One of the most interesting aspects of this process, from the chemist's point of view, occurs between about 250° and 400°C for mixtures of oxygen and various hydrocarbons. A blue luminosity is observed which propagates through the mixture and may or may not lead to ignition to a hot flame. This phenomenon is referred to as a cool flame.

The luminosity of such cool flames has been found to be due to electronically-excited formaldehyde. There are many other interesting features of cool flames which are not at all well-understood. These features are now being investigated in various laboratories by ever more sophisticated means, and the present review is thus a timely one.

The general factors that influence cool flames are the nature of the oxidant (air requires much more drastic conditions of temperature and pressure than does oxygen) of the fuel and of the surface. The last is believed to play its role by destroying chain carriers with varying efficiency. The influence of the other two factors is discussed briefly.

When a cool flame traverses a system, pressure and temperature pulses are observed. The significances of the absolute pressure change, the maximum rate of pressure increase and the temperature change are discussed briefly.

Cool flames are characterized by induction periods. For the neopentane system—oxygen system, for example, these are of the order of several seconds. Data are presented for this system and the general significance of induction periods is described.

It has long been believed that a radical–radical reaction must account for the generation of excited formaldehyde molecules in view of the energy requirements. The reaction $RCH_2O+OH\rightarrow CH_2O^*+ROH$ is suggested here; the exothermicity of 75 kcal/mole is about right for the transition in formaldehyde. The multiplicity of products that can be formed in cool flames is strikingly illustrated by a table of products of the 2-methylpentane-oxygen system cool flame that includes 45 products.

The periodic nature of cool flames is a fascinating phenomenon. A series of cool flames may traverse a system in succession. The author reviews two explanations that have been offered for this phenomenon. The "chain-thermal" theory considers a single intermediate for which the relative temperature dependences of its formation and destruction determine the periodicity phenomenon. The "two-product" explanation involves the competition between the formations of different intermediates. The author concludes that neither theory can explain all the features of cool-flame periodicity in a satisfactory fashion.

The chemistry that has been proposed to explain cool flames generally involves alkyl hydroperoxides as critical intermediates via

$$RH+O_2\rightarrow HO_2+R$$

$$R+O_2\rightarrow RO_2$$

$$RO_2+RH\rightarrow ROOH+R$$

The author points out the variety of paths open for further reaction of hydroperoxides which can account for the kinds of reaction products that are observed. He also points out the important roles of the HO_2 radical, alkyl radicals, and the hydroxyl radical and suggests how the differing reactivities of these species can be used to account in a qualitative fashion for the occurrence of cool flames and their transition to hot flames.

The last section describes briefly the present view on the connection between cool flames and engine combustion processes, in particular the phenomenon of "knocking" in the gasoline internal combustion engine.

Subject Headings: *Cool flames, of hydrocarbons; Flames, cool, of hydrocarbons; Hydrocarbons, cool flames.*

J. B. Levy

Gunners, N. E. (Royal Institute of Technology, Stockholm, Sweden) "Methods of Measurement and Measuring Equipment for Fire Tests. Joint Inter-Scandinavian Fire Tests on Lining Materials for Buildings at Copenhagen Fire Test House," *Royal Institute of Technology Civil Engineering and Building Construction Series No. 43* (1967)

Inter-Scandinavian tests concerning the characteristics of the process of fire development are carried out by the Liaison Committee of Scandinavian Fire Prevention Laboratories. The purpose of these tests is to investigate the thermal effects which a fire in an individual room produces on the surface layers of lining materials in a corridor that is connected by means of a door opening with the room where the fire is initiated.

The paper presents a study of the types and scopes of the separate measurement systems which are required for this investigation in order to determine the rate of combustion, the temperature fields, the heat flow due to convection and to radiation, the velocity of gas flow, and the composition of gases. New cylindrical pressure probes for measurement of the velocity of gas flow are proposed and the construction of a new total hemispherical radiation meter is presented.

Subject Headings: *Building materials, fire tests of; Fire resistance, of lining materials; Copenhagen fire test house.*

Author's Abstract

Hoyle, H. and Bray, G. (Mather & Platt, Ltd., Manchester, England) "Hydraulic Performance of Sprinkler Installations," *Fire Technology* **3**, 291–305 (1967)

This paper, presented at the 71st Annual Meeting of the National Fire Protection Association in Boston, May 1967, deals with a new approach for the design of sprinkler systems. The authors claim that the conventional design approach involving handbook "rules and pipe schedules" is often uneconomical compared to the more tedious approach of individually calculating each system. The authors present a compromise method which involves a modification of pipe-size rules together with the simplest application of hydraulic data. This method circumvents the defects of the conventional method while preserving the economies of the calculated approach without significantly altering system performance.

The defects of the conventional method are:

(1) The larger the size of the system, the lower the rate of discharge from any given number of the most unfavorably placed sprinklers in operation with a given water supply pressure at the valves.

(2) If pipe sizes are adequate to supply water to sprinklers at the highest level of a multi-storey building, the pipes for the sprinklers at the lower levels are larger than required, which unnecessarily increases system cost.

A sprinkler system should be designed so that the water application rate per unit area (discharge density) is adequate over the anticipated area of sprinkler operation in order to effect control or extinguishment for the potential fire hazards involved. Three fire hazard levels are defined:

Extra light hazard:	minimum discharge density, 0.06 gpm/sq ft
Ordinary hazard:	average discharge density 0.12 gpm/sq ft (with a minimum discharge density of 0.084 gpm/sq ft for the most unfavorably placed sprinklers in operation)
Extra high hazard:	average discharge density above 0.12 gpm/sq ft

Cost reductions are made possible by setting sprinklers at the maximum spacing consistent with the average discharge density for the hazard level involved.

The discharge density is a function of the water pressure available at the sprinklers, the orifice size and design of the deflector. Where higher discharge densities are desired, a more economic arrangement of sprinklers is made possible by making small increases in the size of the orifice. The authors state that for an increase in sprinkler diameter bore from $\frac{1}{2}$ in. to $\frac{17}{32}$ in., the sensitivity of fire detection is practically unaffected.

The study of sprinkler system hydraulics revealed that for a given supply pressure the performance of the most unfavorably placed sprinklers varies widely with the layout and number of adjacent sprinklers in operation. From the results obtained thus far, the authors concluded that the requirements for a sprinkler system could be achieved most effectively and economically by the following:

(1) A revision of the pipe-size tables with separate tables for range pipes and distribution pipes according to the hazard class of the occupancy.

(2) The adjustment of pipe sizes to achieve more uniform performance irrespective of layout.

(3) Limiting such pipe-size tables to the number of sprinklers anticipated to operate.

(4) Determining the size or sizes of the distribution pipes connecting the valves to those most unfavorably placed sprinklers anticipated to operate by simple hydraulic calculation or reference to tables.

Based on the above, the authors derived range and distribution pipe sizes which are proposed for use in standard piping designs for so-called ordinary hazard occupancies. In a system incorporating the derived rules operating under increased water supply pressure, it was possible to improve installation cost and to make the performance of the most unfavorably placed sprinklers less dependent upon sprinkler layout.

The authors also defined the pump characteristics necessary to achieve the pressure/flow requirements for various conditions within the ordinary hazard category.

Based on experience, the anticipated area of sprinkler operation was estimated for required discharge densities of 0.12 gpm/sq ft (ordinary hazard) and 0.72 gpm/sq ft (extra high hazard). The anticipated area of sprinkler operation was scaled between these two limits. Sprinkler system design and water supply requirements can be formulated from such a diagram.

Since no common system of piping could be devised to meet the wide range of hazard conditions with reasonable costs and water supply requirements, three schedules were proposed with separate pipe-size tables for range and distribution pipes with up to a maximum of 48 connected sprinklers.

The point on the distribution pipe beyond which there are 48 sprinklers was defined as the "48 sprinkler point." Calculations were made to determine water pressure required at the 48 sprinkler point and the total flow rate under each condition to provide the stated average discharge density from the four most remote sprinklers with $\frac{1}{2}$ in. and $\frac{17}{32}$ in. sprinklers. These sprinklers were spaced from one per 60 sq ft to one per 130 sq ft in 10 sq ft increments for each of the pipe-size tables.

The pipe sizes and hence the pressure loss may be chosen to achieve an installation pressure/flow characteristic which matches that of an available water supply. Alternatively, the water supply can be designed to meet the conditions required with the chosen pipe sizes.

The installation of sprinklers at intermediate levels between ceiling and floor enables considerable reduction of the average discharge density required from ceiling sprinklers. Where such an arrangement is possible, it is proposed that the anticipated area of sprinkler operation under the ceiling or roof shall be that corresponding to the nature of the materials and stack height above the floor, but the required discharge density shall be that corresponding to the height of the stack above the uppermost level of the intermediate sprinklers. The average discharge density from the intermediate sprinklers should be related to the nature of the stored combustibles and their height above the floor or the sprinklers on the next lower level.

Subject Headings: *Hydraulic performance, of sprinklers; Sprinklers, hydraulic performance of.*

A. L. Goldstein

Palmer, K. N. and Tonkin, P. S. (Joint Fire Research Organization, Boreham Wood, England) "Effect of Diluent Dusts on the Explosibility of Some Plastics Dusts," *Joint Fire Research Organization Fire Research Note No. 667* (June 1967)

The proportions of barium sulphate and magnesium oxide dusts required to prevent explosions in phenol formaldehyde resin and polyethylene dusts dispersed in air in a large-scale vertical tube have been determined. The behavior of the dust mixtures in the routine small-scale classification tests has also been studied. In further experiments with small-scale apparatus, the explosibility of mixtures of phenol formaldehyde resin with other diluents has been observed.

The results have been used to test further a theory developed previously for determining the percentage of diluent required to prevent explosion when dispersed with the combustible dust. The theory was based on a heat balance in which the function of the diluent dust was to act solely as a heat sink. The theory was in good agreement with the results obtained with the large-scale apparatus, and with most of the results from the small-scale apparatus. A diluent which was markedly more effective than predicted was sodium iodide.

Subject Headings: *Dust diluents, explosibility; Explosibility, of diluted plastic dusts; Plastic dusts, diluting of.*

Authors' Summary

Tinson, R. ("Shell" Research Ltd., Thornton Research Centre, Chester, England) "The Electrostatic Hazard during Loading of Petroleum Products into Glass-Reinforced Plastic Tanks," *Journal of the Institute of Petroleum* **53** (525) 303–311 (1967)

There is considerable interest in the use of plastic tanks for the transportation and storage of petroleum products; however, occasional fires have occurred during loading. It is thought that these fires have been caused by electrostatic discharge. In a typical case, a vehicle with a glass-reinforced plastic (GRP) tank was being filled with gas oil, the previous load having been gasoline. Shortly after loading commenced, a spark passed between the drop-pipe and the metal dome causing a fire. It was subsequently found that there was no electrical connection between the metal manhole fittings and the chassis of the lorry, other than through the tank material.

This paper gives an investigation into the possible electrostatic hazards that might exist during loading of a GRP tank.

Two tanks made of glass-reinforced plastic, one standing free on the ground and the other mounted on a road vehicle, have been loaded with aviation kerosene and with gas oil at filling speeds of up to 480 IG/minute. The fuel was filtered through either a basket strainer or a microfilter situated immediately upstream of the loading arm. Both tanks had metallic fittings and connections which were insulated from earth by the tank material.

At filling speeds of 450 to 480 IG/minute, the charging current in the fuel was as high as 0.8 μamp when the strainer was used, and up to 22 μamp when the microfilter was used. Gas oil became more highly charged than kerosene during microfiltration.

During fuelling, potentials of up to 11 kV built up on insulated metal connections to the tanks. When fuel was filtered through the strainer, potentials in excess of 1 kV built up only on connections which were well insulated from earth, but when the fuel was microfiltered, the potentials of connections were prevented from rising above 1 kV only by earthing them individually. With an earthed probe, sparks could be drawn from all metal connections with potentials above about 1 kV. No discharges were detected from the surface of the tanks.

It is concluded that if, in the design of tanks made from glass-reinforced plastic or other materials of very high resistivity, provision is made for proper electrical bonding, the electrostatic hazards during the loading of petroleum products should not be different from those in similar tanks made from conducting materials.

Subject Headings: *Fire, electrostatic discharge; Fire hazard; Glass-reinforced plastic tank.*

W. C. Johnston

B. Ignition of Fires

Alvares, N. J. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Oxygen Concentration and Pressure Effects on the Ignition of Cellulosic Fuels by Thermal Radiation," *Report USNRDL-TR-67-25* (February 17, 1967)

Measurements of the ignition time and surface temperature, at the time of ignition for cellulosic fuels in varying atmospheric environments, were made in order to help illuminate the mechanism responsible for the spontaneous ignition of these materials exposed to thermal radiation. It was assumed that the mechanism would fall into one of three categories, and these were: (1) A piloted self-ignition, which is dependent in some way upon the temperature of the pyrolyzing solid. (2) A thermal self-ignition which is governed mainly by gaseous heat transfer. (3) A free-radical chain branching self-ignition which should be quite pressure dependent. The varied environmental atmospheric parameters were: (1) total atmospheric pressure, holding the oxygen concentration constant; (2) oxygen concentration with the total pressure held constant; (3) the thermal conductivity of the atmospheric environment by use of different diluent gases with both the total pressure and oxygen concentration held constant. Both the surface temperature and ignition response data provide evidence which indicates the thermal self-ignition to be the most likely mechanism responsible for these phenomena.

Subject Headings: *Cellulose, ignition of; Oxygen concentration, cellulose ignition; Pressure dependence, of cellulose ignition; Radiation, thermal, ignition of cellulose.*

Author's Summary

Nettleton, M. A. and Stirling, R. (Central Electricity Research Laboratories, Leatherhead, Surrey, England) "The Ignition of Clouds of Particles in Shock-Heated Oxygen," *Proceedings of the Royal Society* **A300**, 62–77 (1967)

This paper presents the results of an experimental study of the ignition of clouds of coal particles in an oxygen atmosphere heated by the passage of an incident and reflected shock wave. The shocked gas temperature and pressure were calculated from the Rankine-Hugoniot equations, taking dissociation into account, for each set of initial conditions and measured incident shock velocity. Either pressure transducers or heat transfer gauges were employed to determine the times at which incident and reflected waves passed an emission station and these records in conjunction with light emission records were used to determine ignition delay times. The ignition temperature was defined as that temperature at which a complete flame envelope first developed. Several different kinds of coal of different size range were tested.

The experimental results indicate that the gas temperature at ignition is a function of the pressure until high pressures are reached, when it approaches a limiting value, and a function of particle size at all pressures. Also, the gas temperature at ignition is shown to be related to the particle temperature at ignition, which in turn depends on the volatile content of the coal and is very near the temperature at which the particles first lose volatile matter at an appreciable rate. The studies indicate that ignition occurs after only small amounts of volatile matter have been lost by the particles and that the particle surface may catalyze the ignition.

Ignition delay times are presented for the various coal samples and sizes at oxygen pressures of 1.5 to 30 atms and temperatures of 700° to 1600°K. The results generally confirm the conclusions drawn from the ignition studies and, in addition, indicate that the ignition delay was essentially unaffected by radiant heat transfer from flames established at the shock reflecting face.

A model for the ignition process is proposed in which the ignition delay is associated with the time required to heat the particles to ignition temperature by conduction only. This model appears to describe the experimental delays properly. In order to test the limits of validity of the model, experiments were carried out on completely volatile particles and nonvolatile particles. In the latter case, it was found that the ignition process is more complex in that the effects of chemical reaction must be included.

Subject Headings: *Ignition, of particles, by shock in oxygen; Oxygen, ignition of particles, by shock wave in; Particles, ignition by shock, in oxygen; Shock ignition, of particles, in oxygen.*

T. C. Adamson

Simms, D. L. and Law, Margaret (Joint Fire Research Organization, Boreham Wood, England) "The Ignition of Wet and Dry Wood by Radiation," *Combustion and Flame* 11(5) 377–388 (1967)

The effect of moisture on the temperature/time profiles of oven-dry woods and of woods containing up to 30% moisture has been measured by Williams.[1] Previous work[2,3] has shown that the ignition times can be correlated with the thermal properties. The assumptions made are that the materials are inert and that they ignite at a fixed temperature which is independent of density and species. The theory uses thermal conduction, taking into account the change in properties due to moisture.

Specimens of wood were oven-dried and then conditioned to moisture content. Specimens were exposed to decreasing levels of radiation until it was reasonable to assume that ignition would not take place because the evolution of volatiles was too low. Both pilot and spontaneous ignition data were taken and the ignition time recorded. The effect of moisture for any given wood is to increase the ignition time, the total ignition energy, and the minimum intensity for both spontaneous and pilot ignition.

The presence of moisture increases the ignition time by changing the heat transfer and hence the temperature rise in at least three ways: (1) Moisture increases the value of the thermal conductivity and the volumetric specific heat. (2) Heat is transferred directly by molecular diffusion of the water. (3) Evaporation cools the hotter regions and condensation heats the cooler regions. Williams[1] found it possible, within a wide scatter, to correlate his results (temperature/time profiles) with the thermal properties, making appropriate allowance for moisture content and the desorption of water. Gardon[4] found little effect due to moisture migration and correlated his results similarly to the method used by Williams. Williams has also calculated the rate at which the zone of vaporization moves into the solid. He finds further evidence that the effect of moisture migration may be neglected.

The results of this investigation have been correlated on the assumption that the material is inert and ignites at a fixed temperature. Simple heat transfer theory has been used to calculate this temperature, taking values for the thermal properties. Allowance has been made for the given moisture content and the thermal capacity required to remove the water.

For pilot ignition the correlating temperature was found to be 380°C, corresponding to a critical radiation intensity of 0.31 cal/cm^2 sec. The only exception to this was fiber insulating board which appeared to ignite at a lower temperature of 330°C. Earlier results with smaller specimens gave similar results of the pilot ignition temperature, however, the present data extend times up to 59 minutes. The results show that the choice of 0.3 cal/cm^2 sec as the maximum acceptable level of radiation for building purposes gives a larger margin of safety than was originally thought.

For spontaneous ignition, the correlating temperature was found to be 545°C, the same as found previously for smaller areas, corresponding to a critical radiation intensity of 0.74 cal/cm^2 sec. The present correlation extends the range of times and suggests the fact that the area correction is connected with the density of the material.

References

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2. Simms, D. L.: *Combustion and Flame*, *7*(3), 253 (1963).
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4. Gardon, R.: "Temperature Obtained in Wood Exposed to High Intensity Thermal Radiation," *M.I.T. Fuel Research Lab. Tech. Report No. 280* (1953).

Subject Headings: *Ignition, by radiation; Ignition, spontaneous; Ignition, of wet and dry wood.*

W. C. Johnston

C. Detection of Fires

Campbell, R. B. and Chang, H. C. (Westinghouse Research and Development Center, Pittsburgh, Pennsylvania) "Solid State Ultraviolet Devices for Fire Detection in Advanced Flight Vehicles," *Final Report under Contract with U.S. Air Force, AF33(615)-3624, AFAPL-TR-67-23* (May 1967)

Improvement has been made in both theoretical analyses and fabrication techniques of siliconcarbide photovoltaic diodes. A *P-I-N* junction theory of photodiodes has been developed which includes all carrier transport parameters. This

general theory is compared with the simple model developed previously for the explanation of the dependences of the peak response wavelength on the junction depth and temperature. During this program, eight siliconcarbide ultraviolet detectors were fabricated. Using improved fabrication techniques these detectors had a lower electrical impedance and higher response than detectors previously fabricated. Rise times of 10 to 100 microseconds were measured at 30°C, with a slight decrease at 500°C. An alumina encapsulation with a quartz window was used for these devices. The feasibility of using aluminum nitride, a high temperature semiconductor with a band gap wider than siliconcarbide, in the fabrication of ultraviolet detectors was also studied. The sublimation technique was used to grow small hexagonal crystals about 2 mm across, and several epitaxial methods were used to grow single crystal layers of AlN on both SiC and AlN. Definitive electrical properties were not obtained on these crystals, possibly due to low mobility in the samples. The detector structures prepared showed no photoconductive or photovoltaic effect up to 800°C.

Subject Headings: *Fire detector, solid state ultraviolet; Solid state ultraviolet fire detector.*

Authors' Abstract

O'Dogherty, M. J., Young, R. A., and Lange, A. (Joint Fire Research Organization, Boreham Wood, England) "Experiments on Detection of Insulating Oil Fires in a Transmission Cable Tunnel," *Joint Fire Research Organization Fire Research Note No. 686* (January 1968)

This note describes experiments carried out in a 132 kV transmission cable tunnel to examine the problem of detection of fires in cable insulating oil. Fires of various surface areas were used, and measurements of smoke density and air temperature rise made up to a distance of 115 m (377 ft) from the fire, with and without the ventilating air current flowing. The results enable the response times of heat and smoke detectors to be compared for a range of conditions, and indicate how systems using the two methods of detection can be designed to have an equivalent performance.

Subject Headings: *Fire detection, in oil fires; Oil fires, in transmission cable tunnels, detection of; Transmission cable tunnels, oil fires, detection of.*

Authors' Summary

D. Propagation of Fires

Thomas, P. H., Simms, D. L., and Law, Margaret (Joint Fire Research Organization, Boreham Wood, England) "The Rate of Burning of Wood," *Joint Fire Research Organization Fire Research Note No. 657* (September 1967)

Vertical pieces of wood about 2.5 cm thick and 12 to 15 cm square have been exposed in normal ambient surroundings to the radiation from a hot source and weighed while charring. The rates of weight loss for various degrees of charring have been measured for woods of different density and permeability. The effective permeability has been altered by various devices such as sealing the edges of the wood specimens and inserting an impermeable layer between two pieces of half thickness.

The rate of weight loss increases with the intensity of radiation, the density and the actual or effective permeability. Provided the charring is not too shallow the results can be interpreted in terms of a mass transfer theory in which "Q", the amount of heat required to produce 1 gm loss of weight, is independent of the heating rate. In the absence of measurements of surface temperatures the calculations are perforce somewhat crude but the order of magnitude of Q (assuming the specific heat of the volatiles is about 550 for some woods of high permeability when the weight loss is about 10% (about 4 mm char). The rate of weight loss decreases and Q increases as charring proceeds.

The variation of weight loss with time and least squares formulae relating the rate of weight loss at particular times to density, incident radiation and permeability are given for various experimental conditions.

Subject Headings: *Burning rate, of wood; Wood, burning rate of.*

Authors' Summary

E. Suppression of Fires

"Proceedings of Fire Hazards and Extinguishment Conference," *Aerospace Medical Division, Air Force Systems Command, Brooks Air Force Base, Texas, Special Report AMD-TR-67-2* (May 1967)

Subsequent to the fire in the space environment simulator at Brooks Air Force Base on 31 January 1967, the Aerospace Medical Division developed fire extinguishing systems and protective clothing for use in oxygen enriched atmospheres. As this was a subject of intense general interest, it seemed appropriate to host a conference to describe and demonstrate these fire extinguishing systems and protective clothing.

Subject Headings: *Space environment simulator, combustion in oxygen enriched atmospheres; Toxicity, of halogenated hydrocarbons; Protective clothing, for oxygen enriched atmospheres.*

Abstract from the Proceedings

Butlin, R. N. (Joint Fire Research Organization, Boreham Wood, England) "High-Expansion Air Foam—A Survey of Its Properties and Uses," *Joint Fire Research Organization Fire Research Note No. 669* (May 1967)

This note examines the present state of knowledge regarding the use of high-expansion air foam, and suggests areas in which development of this agent and its uses may proceed.

Subject Headings: *Foam, extinguishment by.*

Author's Summary

Fittes, D. W. (Joint Fire Research Organization, Boreham Wood, England) "Some Notes on the Properties of Foams Produced by a Gas Turbine Operated Foam Generator," *Joint Fire Research Organization Fire Research Note No. 668* (June 1967)

This report gives details of the physical properties of the protein-based foams produced by an experimental gas-turbine operated foam generator at different rates of delivery of foaming solution. The relation between critical shear stress and foam drainage is also shown. Some experiments using a detergent-based foam are reported.

Subject Headings: *Foam generator; Foam, properties of; Gas turbine foam generator.*

Author's Summary

McGuire, J. H. and Sumi, K. (National Research Council, Ottawa, Canada) "Field Testing Inert Gas and High Expansion Foam," *Division of Building Research, National Research Council Research Paper No. 325—Reprint from Fire Fighting in Canada* **11**, No. 3 (June 1967)

In this paper, the authors report fire extinguishing tests and demonstrations of inert gas and high expansion foam. These tests were conducted in the three floor concrete block Fire Test Building of the Ontario Fire College at Gravenhurst, Ontario. [The following abstracts in *Fire Research Abstracts and Reviews* are pertinent to the background and historical development of these fire extinguishing media, and the techniques for their application: *6*(1) p. 47; *6*(2) pp. 172–176; *6*(3) p. 274; *8*(1) p. 37; *9*(3) p. 230.]

The building used in these tests was 30 ft high, with a floor area of 28½ by 23 ft. The ground floor consisted of three rooms and an enclosed stairwell. The second and third floor comprised two rooms and enclosed stairwells. These enclosed stairwells leading from the first floor to the third floor proved to be significant in demon-

TABLE 1.a

Inert Gas Generator Tests

Number of Tests: 4 plus one control. Inert Gas Generation Rate: 3300 cu ft/min, with gas at 90°C, about 68% water vapor, 28% Nitrogen and 4% CO_2.

Observables	Test number				Control
	1	2	3	4	
A Test fire configuration	Small wood cribs and $3\frac{1}{4}$ inch diam. cans of gasoline fuel located on 2nd and 3rd floors.	4′×4′ wood cribs	See test 1	1 sq ft tray of gasoline on 3rd floor.	See test 4
B Roof vent		Open for preburn then closed.			
C Door schedule	All exterior doors closed, all interior doors open.	Main door open for preburn then closed.		All exterior doors closed, door to 3rd floor closed.	See test 4
D Window schedule	All windows closed.		11 sq ft opened on 3rd floor. See tabulation below.	All windows closed.	See test 4
E Preburn time		$3\frac{1}{2}$ min			N/A
F Time to extinguish flame	3 min	3 min in spite of $1\frac{1}{2}$ min malfunction.	3–4 min	15 min	N/A. Fire burned for 25 min.
G Total time of application (to suppress smoldering)	11 min	10 min			N/A
H O_2 concentration			See Tabulation below.		(Equilibrium)
time after start of generator:	11 min				25 min
Location:	3rd floor				(3rd floor)
Percent:	10%				18%

TABLE 1.b
Inert Gas Generator Tests

Oxygen concentration percent		Time after start of gas generator	Notes
Top floor	Ground floor		
—	—	−4	Fire started.
—	—	0	Injection started.
18.5	—	3	
17.0	—	4	Fire extinguished.
15.0	—	5	
13.5	—	6	
12.0	—	8	
11.2	—	10	
—	9.5	14	Additional 11 sq ft low level opening on 1st floor
12.0	—	16	
12.3	—	18	
13.6	—	22	
—	13.0	24	
—	12.8	26	

The door to the third floor did not fit closely, gap at sill was about 1 inch, and 0.25 inch elsewhere, which allowed sufficient flow of inert gas or foam to effect extinguishment in the times indicated.

TABLE 2

High Expansion Foam Tests

Number of Tests: 4. Foam Injection Rate: 29 U.S. gal per min liquid, containing 0.4% sodium lauryl sulfate plus butyl carbitol solvent: 3400 cu ft/min airflow.

Observables	Test number			
	1	2	3	4
A Test fire configuration	None, foam flow only.	2′×2′ Tray. 1 inch gasoline over water located on third floor.	2 ea 4′ cube wood crib fires located on ground floor.	1′×1′ Tray of gasoline.
B Door schedule	All interior doors open, all exterior doors closed.	All interior doors open, all exterior doors closed.	Exterior doors open for preburn then door nearest foam generator closed for extinguishment.	All exterior doors closed, door to third floor closed, except for gaps.
C Window schedule	All windows closed except some of the third floor windows.	All windows closed.	—	All windows closed.
D Roof vent	Open.	Open.	Open.	(Open?)
E Foam filling by floor				
1st: Time:	1′:25″	—	—	
Rate:	2900 cu ft/min	—	—	
Efficiency:	90%	—	—	
2nd: Time:	2′:05″	—	—	
Rate:	1900 cu ft/min	—	—	
Efficiency:	60%	—	—	
F Preburn	N/A	—	3 min	
G Extinction time	N/A	4′:40″	3 min	15 min

The door to the third floor did not fit closely, gap at sill was about 1 inch, and 0.25 inch elsewhere, which allowed sufficient flow of inert gas or foam to effect extinguishment in the times indicated.

TABLE 3

Combined Inert Gas Generator and High Expansion Foam Injection Test.
Number of Tests: One only.

Injection Rates:

a. Initial Conditions: Ca. 1500 cu ft/min cold air and 3300 cu ft/min hot inert gas giving a mixture with resultant gas temperature of 78°C, the high expansion foam was produced by the foam generator using the inert gas and cold air mixture (See Table 2).

b. Final Conditions*: 3300 cu ft/min hot inert gas at 85°C, the high expansion foam was produced in the foam generator using the hot inert gas (See Table 2).

Observables	Test data
A. Test fire configuration	No fire, foam flow and filling test only
B. Door schedule	All interior doors open, all exterior doors were closed
C. Window schedule	All windows closed
D. Roof vent	Open
E. Foam filling:	
(First and second floors)	
Time:	3′:45″ (i.e., the time that foam started to flow from the roof vent)*
Rate:	2200 to 3100 cu ft/min
Efficiency:	50 to 70 percent

* After about 3 min and 45 sec of combined foam and inert gas injection using 1500 cu ft/min of cold air in the gas mixture, the cold air flow was reduced to zero. The third floor was not at this time completely filled with foam. Foam continued to flow from the roof vent after cold air was cut off.

Note: In all tests injection of foam and/or gas was into a ground floor window opening.

strating foam mobility. To pass to the third floor from the point of injection on the first floor, foam flow required passage through five doorways and up two flights of stairs. The window openings of the test building were covered by $\frac{1}{4}$ in. plywood. The window closure was not complete however, since some leakage was possible. The roof vent, which could be opened to facilitate ignitions and preburn, also contributed to air leakage when closed.

Thermocouples were placed above the test fires to record the time of extinguishment. The building interior atmosphere was sampled by means of a $\frac{3}{8}$ in. diameter tube leading outside, where oxygen was determined by means of a "magnetic susceptibility" analyzer. The sampling rate was such that the authors estimated reporting errors of up to one minute.

The inert gas generator burned a stoichiometric propane-air mixture in a combustion chamber which exhausted the combustion gases into a water spray injection chamber.

The foam generator comprised a nylon regular pyramidal net (with base and slant dimensions of 29 in.), a full cone nozzle from which a solution of foaming agent was sprayed into the nylon net, and an axial flow fan by which air was blown into the net, which along with the solution spray produced the high expansion foam.

The inert gas generation rate was about 3300 cu ft/min at a temperature of 90°C, and the approximate gas composition was 68% water vapor, 28% nitrogen, and 4% CO_2.

The air flow in the foam generator was about 3400 cu ft/min, and the water solution of foaming agent was sprayed into the nylon net at the rate of 29 gal/min. The solution contained 0.4% sodium lauryl sulfate, plus butyl carbitol.

The tests conducted are summarized in Tables 1, 2, and 3. In all these tests, inert gas and foam were injected into a ground floor window of the test building.

The authors discuss the relationship between ventilation area and the minimum inert gas injection rate required for fire extinguishment.[1,2]

For predicting foam flow in compartmented configurations, the authors suggest treatment by analogy to electrical networks, where compartment opening areas correspond to circuit admittances. In this analogous treatment, effects of viscous forces and pressure heads are assumed to be negligible.

References

1. McGuire, J. H.: "Large-Scale Use of Inert Gas to Extinguish Building Fires," *Fire Research Abstracts and Reviews 8*, 37-40 (1966)
2. McGuire, J. H.: "Inert Gas Fire Extinguishment Excessive High Level Vents," *Division of Building Research, National Research Council Research Note 50* (November 1965)

Subject Headings: *Foam, inert gas, testing of; Inert gas foam, testing of.*

J. E. Malcolm

Shelberg, W. E. and Tracy, E. T. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Countermeasure Concepts for Use against Urban Fire from Nuclear Weapons," *Special OCD Summary for USNRDL-TR-67-100* (August 14, 1967)

The purpose of this report is to propose and to perform an initial evaluation of new concepts for the extinguishment and for the control of urban mass fires resulting from nuclear weapon attacks.

One of the primary objectives of civil defense is to minimize casualties and property damage from urban mass fires. Unfortunately, current metropolitan firefighting manpower, equipment and techniques will almost certainly be inadequate for extinguishing or controlling the multiple mass fires to be expected from a nuclear attack. Thus, there is merit in conceiving, evaluating and developing new procedures for dealing with these fires so that the civil defense objective may be realized.

Possible countermeasures for extinguishing or controlling urban mass fires were investigated and evaluated. The evaluations led to some recommendations for the direction of any future physical research, development and further evaluation.

The authors conclude that firebreaks can be effective in cities, provided that they are made correctly, rapidly and in adequate width, and provided that they are diligently tended by firemen.

The probability for controlling an urban mass fire by some combination of firebreaks and then letting it burn out is greater than that for extinguishing it in toto; however, extinguishment efforts for sections of a mass fire seem hopeful, particularly in connection with control efforts. Control countermeasures and extinguishment countermeasures should be applied cooperatively when possible.

Subject Headings: *Countermeasures against fires, urban mass; Urban mass fires, from nuclear weapons.*

Authors' Summary

F. Fire Damage and Salvage

Gross, D., Loftus, J. J., and Robertson, A. F. (National Bureau of Standards, Washington, D.C.) "Method for Measuring Smoke from Burning Materials," *Fire Test Methods—Restraint and Smoke, Special Technical Publication No. 422 of the American Society for Testing and Materials* (1967)

Based on a study of possible smoke-measuring methods, a laboratory test has been developed for the photometric measurement of smoke from burning materials. The method assumed the applicability of Bauguer's law to the attenuation of light by smoke, and smoke quantity is therefore reported in terms of optical density rather than light absorptance or transmittance. Optical density is the single measurement most characteristic of a "quantity of smoke" with regard to visual obscuration. Experiments have been performed on a variety of building finish materials under both flaming and nonflaming (smoldering) conditions, and the results are reported in terms of (a) maximum smoke accumulation, (b) maximum rate of smoke accumulation, and (c) the time period to reach an arbitrary "critical" smoke level.

Subject Headings: *Optical density, smoke measurement; Pyrolysis, and smoke production; Smoke measurement; Tests, for smoke.*

Authors' Abstract

G. Combustion Engineering

Bowes, P. C. (Joint Fire Research Organization, Boreham Wood, England) "Thermal Explosion of Benzoyl Peroxide," *Joint Fire Research Organization Fire Research Note No. 650* (February 1967)

The thermal explosion of benzoyl peroxide, in the form of the commercially pure solid and as a paste with plasticiser, has been studied experimentally with the object of determining the extent to which small-scale explosion trials are likely to provide a useful guide to the behavior of unstable compounds in storage or during transport.

A comparison of (1) self-heating and explosion data and (2) isothermal decomposition data, principally in terms of the derived activation energies and of heats of reaction estimated by different routes, has shown that the self-heating and explosion behavior is broadly consistent with expectation on the basis of the generalized stationary state thermal explosion model of Frank-Kamenetskii. In detail, the behavior is complicated by melting of the peroxide during decomposition and by mixing due to gas evolution.

It has been concluded that a simple graphical treatment of small-scale critical explosion data, based on the model, can give a useful guide to the practical hazard.

Subject Headings: *Benzoyl peroxide, thermal explosion of; Explosion, thermal, of benzoyl peroxide.*

Author's Summary

Bowes, P. C. (Joint Fire Research Organization, Boreham Wood, England) "Thermal Explosion of Unstable Compounds Experimental Equipment and Methods," *Joint Fire Research Organization Fire Research Note No. 626* (July 1967)

A detailed description is given of equipment used to determine minimum temperatures for thermal explosion of unstable compounds. Measurements of heat transfer coefficients controlling the explosion are also reported.

Subject Headings: *Explosions, thermal; Thermal explosions.*

Author's Summary

Butcher, E. G., Chitty, T. B., and Ashton, L. A. (Joint Fire Research Organization, Boreham Wood, England) "The Temperature Attained by Steel in Building Fires," *Joint Fire Research Organization Fire Research Technical Paper No. 15* (1966)

The report describes a series of fire tests in two large fire compartments, 7.7 m× 3.7 m×2.9 m high (25 ft 3 in.×12 ft 2 in.×9 ft 6 in. high) in which fire load densities ranging from 7.5 kg/m^2 (1.55 lb/ft^2) to 60 kg/m^2 (12.4 lb/ft^2) with two degrees of window opening were used.

Structural steel members of various sizes, some protected and some unprotected, were placed in and around the fire compartments in a variety of positions.

The temperatures reached in the fire compartments and by the structural steel for fire tests of varying severity were measured. The results are discussed and some of them are compared with those obtained in a few tests carried out according to B.S. 476: Part 1 (1953).

Subject Headings: *Building fires, steel temperature in; Steel temperature, in building fires.*

Authors' Summary

Chervinsky, A. and Timnat, Y. M. (Technion—Israel Institute of Technology, Haifa, Israel) "Experimental Investigation of Turbulent Swirling Flames," *Israel Journal of Technology* 5(1–2) 39–46 (1967)

A swirl burner was used to investigate the effect of swirl on a premixed flame. Liquified petroleum gas was introduced as a gas tangentially into an air stream. Downstream of the point of fuel addition, more air was added through tangential slots in the burner wall. The degree of swirl was thus controlled by the relative amounts of air flowing in the two air feed streams. The flame was unconfined for a length of 200 cm. The flame axis was horizontal. Axial, tangential and radial velocity components were measured at a number of positions in the flame using a water cooled impact probe. Temperature measurements were made using a bare Pt/Pt—Rh thermocouple. The pressure probe was calibrated in a wind tunnel, and corrections for radiation losses were applied to the thermocouple readings.

Although a theoretical analysis is given, the effect of heat addition to the flow was omitted. The constants occurring in the theoretical expressions were evaluated empirically. The degree of swirl was characterized by the dimensionless quantity $G = w_{m0}/u_{m0}$ where u_{m0} and w_{m0} are the maximum values of the axial and tangential components of the velocity at the burner exit. Velocity distributions, decay of velocity maxima along the axis, isotherms, temperature distribution, and temperature maxima data are given for three values of G: 0.22, 0.33 and 0.53. The axial velocity distribution at the burner exit is symmetric for $G = 0.22$ and asymmetric for $G = 0.53$. Twenty burner diameters from the exit, the axial velocity distribution is much flatter for the higher value of G, with a smaller value for the maximum axial velocity. The tangential velocity was zero on the jet axis, and at the jet boundaries, but attained values at intermediate positions that depended on G. The maximum axial velocity along the jet axis decayed more rapidly for $G = 0.53$ than for $G = 0.22$. A similar result was obtained for the maximum swirl velocity. Both these velocity maxima decayed less rapidly than the same velocity maxima of cold jets having the same values of G.

Isotherms showed the presence of a cold central core. The position of flame stabilization depended on G. For $G = 0.53$, the flame stabilized two burner diameters from the burner exit, whereas for $G = 0.22$ the flame stabilized at 5.5 diameters from the exit. The flame length was 40 burner diameters at $G = 0.22$ and 20 burner diameters at $G = 0.53$. Thus flame size, shape and position could be controlled by the degree of swirl.

The temperature maximum increased with increasing G. The authors interpreted this to mean that burning efficiency and heat release rates are greater in swirling flames. They comment, however, that further evidence is required on this point. The velocity data were interpreted to imply an increase in turbulent burning velocity as G increased. No data were given as to the initial stoichiometry of the flame, and no data were given on composition changes due to entrainment of surrounding air. Such compositional data will be required for a more complete characterization of these flames.

Subject Headings: ***Flames, swirling; Swirling flame burner.***

P. R. Ryason

Essenhigh, R. H. (The Pennsylvania State University, University Park, Pennsylvania) "Combustion Phenomena in Industrial Flames—The Rosin Equation," *Industrial and Engineering Chemistry* **59**(7) 52–59 (1967)

Rosin's equation, developed in 1925, is based upon a one-dimensional, or plug-flow, behavior of the combustion chamber. Upon entering the chamber fuel and oxidant are assumed to spread immediately and uniformly over the chamber cross section. The combustion chamber has dimensions of length, L_c, area A_c, giving a volume V_c. The flame is assumed to just fit within the combustion chamber length. Combustion intensity is defined as

$$I=(FB/V_cP)\ (\text{Btu/ft}^3\text{-hr-atm}) \tag{1}$$

where F is the fuel flow (lb/hr), B the heat of combustion at constant pressure (Btu/lb), and P the combustion chamber pressure (atm). The volume of gases passing through the combustion chamber is $(FQ/P)(1+E/100)(T_f/T_0)$ cu ft/hr where Q is the stoichiometric air quantity (cu ft air/lb fuel), E is the per cent excess air, T_f is the average flame temperature in the combustion chamber, T_0 the temperature of the air supply, and P the chamber pressure (atm). For a residence time in the combustion chamber of t_b (sec) the chamber volume is then

$$V_c=(FQ/P)(1+E/100)(T_f/T_0)(t_b/3600) \tag{2}$$

which, when substituted in Eq. (1) gives the basic Rosin combustion intensity equation:

$$I=\frac{B}{Q(1+E/100)(T_f/T_0)(t_b/3600)} \tag{3}$$

For hydrocarbon fuels (B/Q) is approximately 100 so

$$I=\frac{100}{(1+E/100)(T_f/T_0)(t_b/3600)} \tag{4}$$

For both coal and oil fired furnaces excess air is 10% or less, so $(1+E/100)$ lies between 1 and 1.1. Flame temperature and residence time, or burning time (t_b), are related empirically by

$$t_b=\frac{1}{A(T_f/T_0)^n} \tag{5}$$

where the parameter A is a function of fuel and oxidant concentrations, mean particle or drop size, velocity constants of reaction, turbulence levels, and other factors. The exponent (n), used for simplicity in place of the Arrhenius exponential form, can range between 1 and 10.

Data from combustion studies of single oil drops show that burning time varies as

$$t_b=100F_Dd_0^2 \tag{6}$$

where F_D is an excess air factor lying between 1 and 2, and d_0 is initial droplet diameter (cm). Two limiting values of combustion intensity can be found by taking n as large, so $1/n$ becomes zero, and small, so n is unity. These limiting values, assuming no excess air and $T_f/T_0=5$, are

$$3.6(10^2)/d_0^2<I<3.6(10^3)/d_0^2$$

The lower value is more realistic since oil drop combustion is essentially a diffusion process for which n is near unity. Taking 10^{-2} cm as an upper limit for d_0

$$3.6(10^6)<I<36(10^6)$$

which is compared to intensities of 10^6 Btu/hr-ft^3-atm obtained from medium (pressure and air atomized) and heavy (air and steam atomized) fuel oils.

Using 1 and 2 sec as limiting burn times, no excess air, $T_f/T_0=5$, and the limiting values of n, combustion intensity for coal combustion is

$$36(10^3)<I<36(10^4)$$

This is compared to values of 10^3 through 10^6 obtained with pulverized coal in industrial and experimental furnaces.

The good agreement of oil furnace experience with the combustion intensity computed from droplet experiments using the Rosin equation suggests that the model of combustion consisting of a perfectly stirred reactor followed by a one-dimensional, or plug, flow is closer to an over-all plug flow representation than might have been expected.

Subject Headings: *Flames, industrial, Rosin equation for; Rosin equation, and industrial flames.*

A. E. Noreen

Fells, I. and Harker, J. H. (The University of Newcastle upon Tyne, England) "A Method of Introducing and Determining the Concentration of Seed Additions to Flame Gases," *Journal of the Institute of Fuel* **40**(32) 477–478 (1967)

In this short paper the authors describe an apparatus for generating alkali metal seed aerosols in a gas stream and a means for rapidly determining their concentration. The first part of the paper describes their method for generating the aerosols in a gas stream by passing an inert gas (usually nitrogen) over a bath of the molten salt, which entrains the salt vapors and on cooling forms aerosols of the parent salt of extremely small size. The furnace used to contain the molten salt and the necessary hardware have been adequately described by the authors.

In the second part of the paper, the authors describe a less tedious and apparently reasonably accurate procedure for measuring the mass concentration of the alkali metal on the gas stream. The procedure involves vaporizing the alkali metal aerosols in a gas flame and measuring the electrical conductivity of the resulting plasma. The technique and equipment involved are relatively simple, involving two platinum electrodes inserted in the flame, a differential amplifier, and a means of recording the amplifier's output voltage. The recorded output is used to calculate a mean output voltage which serves as a measure of the alkali metal concentration. The authors applied the technique to the case of a potassium carbonate seed in a propane air flame and the agreement between their results and those of a previous investigator, using a similar arrangement, provides a reasonable test of the technique and demonstrates its validity.

Subject Headings: *Flames, seeding of; Seeded flames.*

H. E. Perlee

Hurle, I. R., Price, R. B., Sugden, T. M., and Thomas, A. ("Shell" Research Ltd, Thornton Research Centre, Chester, England) "Sound Emission from Open Turbulent Premixed Flames," *Proceedings of the Royal Society* **A303**, 409–427 (1968)

This paper describes a study carried out to investigate the mechanism of sound emission from premixed turbulent flames. To accomplish that, an optical technique for characterization of the combustion process was developed. The technique not only allowed for elucidation of the sound process but also allowed for generation of data concerning the basic structure of premixed turbulent flames.

According to simple acoustic theory, the instantaneous sound pressure (i.e., the fluctuating component of pressure), $p(t)$ measured at a distance, d, from a monopole sound source situated in a medium of density, ρ, is given by the equation

$$p(t) = (\rho/4\pi d)[(d/dt)(dV/dt)]_{(t-r)} \tag{1}$$

where dV/dt is the rate of volume generation at the source. The qnantity $d(dV/dt)/dt$ is called the strength of the monopole source and is evaluated at the retarded time $(t-r)$, where r corresponds to the time taken for the sound wave to propagate from the source to the point of measurement.

If, as suggested by Smith and Kilham,[1] a turbulent flame is regarded as being made up of a distribution of n combustion elements, each evolving an increased volume of heated gas and, therefore, acting as a monopole sound source, we may write for the ith element,

$$dV_i/dt = (E-1)q_i \tag{2}$$

where q_i is the volumetric rate of consumption of combustible gas mixture in the element, and E is the volumetric expansion ratio of burnt to unburnt gases and is a constant for a given flame. From Eqs. (1) and (2), the far-field pressure in the individual waves that emanate from the combustion element is given by

$$p_i(t) = (\rho/4\pi d)[(d/dt)(E-1)q_i]_{t-\tau} \tag{3}$$

In 1966 Thomas and Williams[2] carried out measurements on the sound waves radiated from the expansion of a spherical laminar flame front (not turbulent but time variant) confined within a soap bubble containing a homogeneous and centrally ignited combustible gas mixture. The time variant flame did indeed act as a monopole source of sound, the instantaneous sound pressure in the radiated sound wave (as measured by microphone) being proportional to the rate of change of the volume increase of the gases during combustion (as measured by streak schlieren photographs).

In the present paper Smith and Kilham's hypothesis was experimentally tested under turbulent flame conditions. In order to accomplish that, an optical technique was developed to measure the instantaneous rate of volume generation and its time derivative, the instantaneous rate of change of volume generation within a turbulent flame. The optical technique was based on measurements of the intensity of emission from the free radicals, C_2 or CH, generated within the flame. The technique basically consisted of recording the free radical emissions through use of a photomultiplier tube which viewed the entire flame through an interference filter.

The optical technique was based on the assumptions (1) that the CH or C_2 free radical emission intensities were proportional to the volume of the reaction zone, and (2) the volume of the reaction zone was a measure of the rate of consumption of combustible gas mixture.

Good agreement between experimentally measured sound pressure and sound pressure deduced from the optical measurements via Eq. (3) was found. It was therefore concluded that a turbulent flame may be represented acoustically as a collection of monopole sound sources distributed through the reaction zone.

Time averaged free radical emission intensities integrated over the flame were found to vary linearly with flow rate all the way from the laminar flow regime, through the transition region, and into the turbulent flow regime. Those results are highly significant from the standpoint of basic turbulent flame theory. They are consistent with a turbulent flame model wherein it is postulated that the primary effect of turbulence is to wrinkle a laminar flame, thereby creating additional surface area, the surface area being in direct proportion to the flow rate. They also indicate that the turbulence had no effect on the burning process within the wrinkled laminar waves.

The investigation reported in the present paper was continued and the latest results are described in Ref. 3. Methane/hydrogen/air turbulent diffusion flames and acetone sprays burning in oxygen enriched atmospheres were studied. Good quantitative correlations between the acoustic and optical measurements were again found.

Time averaged emission intensity measurements were also made on turbulent premixed flames wherein the scale and intensity of the upstream turbulence was varied. The emission intensities were again found to vary linearly with flow rate and were additionally found to be independent of upstream scale and intensity. However, the root mean square value of the rate of change of the rate of combustion (i.e., the rms sound pressure) was found to be dependent on the intensity of turbulence.

References

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2. Thomas, A. and Williams, G.: *Proc. Roy. Soc. A294*, 449 (1966).
3. Price, R. B., Hurle, I. R., and Sugden, T. M.: *Twelfth Symp. (Int'l) on Combustion*, The Combustion Institute, Pitts., Pa., 1968.

Subject Headings: *Flames, premixed, sound from; Sound, from premixed turbulent flames; Turbulent flames, sound from.*

R. N. Gurnitz

Kimsey, J. H., Downs, W. R., Eldred, C. H., and Norris, C. W. (Manned Spacecraft Center, Houston, Texas) "Flammability in Zero-Gravity Environment," *NASA-TR-R-246* (October 1966)

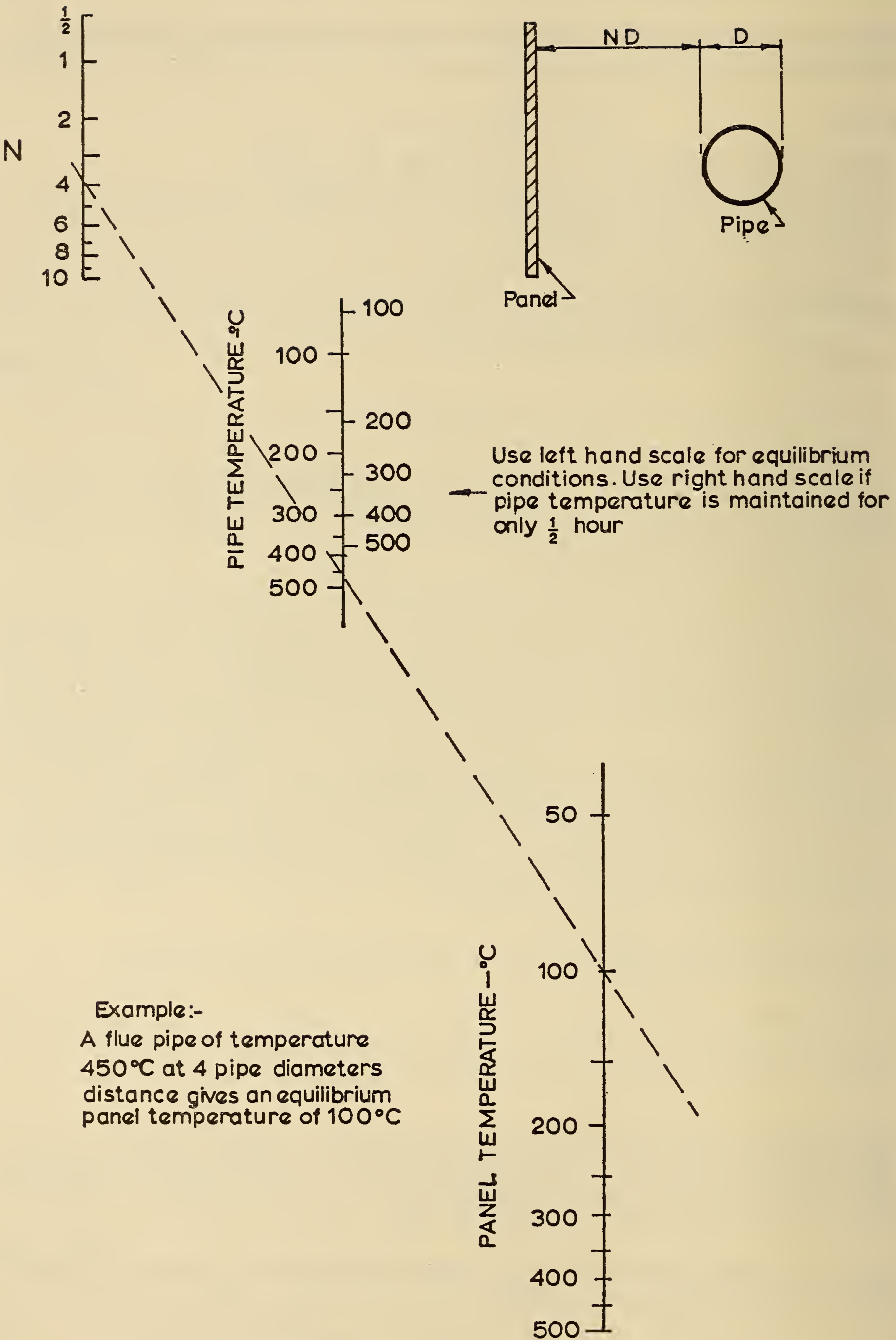
Paraffin and other combustibles were burned in a zero-gravity environment. Zero-gravity intervals of 12 seconds, maximum duration, were obtained in the cabin of an aircraft flying Keplerian parabolas. Experiments were photographed with infrared sensitive film at 100 frames per second and 16 mm color film (ER-B) at 200 frames per second. Test results indicate that ignition is essentially unchanged compared to a one-gravity environment but that combustion is suppressed, in some instances, to the extent that the fire appeared to be extinguished. In all cases, the flame was brightest during periods of acceleration, such as at impact of the test chamber with the aircraft and when returning to level flight. Flame conditions at zero gravity were typical of those expected of a pure diffusion flame in which steady-state conditions were not achieved.

Subject Headings: *Flammability, in zero gravity; Gravity, zero and flammability.*

Authors' Summary

Law, Margaret (Joint Fire Research Organization, Boreham Wood, England) "Nomogram for the Fire Danger of Flue Pipes," *Joint Fire Research Organization Fire Research Note No. 696* (February 1968)

An equation and nomogram (Fig. 1) are given for the temperature of a panel at different distances from a heated pipe.



Use left hand scale for equilibrium conditions. Use right hand scale if pipe temperature is maintained for only ½ hour

Example:-
A flue pipe of temperature 450°C at 4 pipe diameters distance gives an equilibrium panel temperature of 100°C

Fig. 1. Nomogram for the fire danger of flue pipes.

Subject Headings: *Fire danger, of flue pipes; Flue pipes, fire danger.*

Author's Summary

Martin, F. J. (General Electric Research and Development Center, Schenectady, New York) "A Model for the Candle-Like Burning of Polymers," *Combustion and Flame* 12(2) 125–135 (1968)

This is a report of an experimental study of the candle-like burning of organic polymer strips (0.6 cm×0.3 cm×8 cm) at atmospheric pressure in oxygen diluted with inert gases: helium, argon, nitrogen, and carbon dioxide. The limiting ratio of moles of oxygen to moles of inert gas (n_O/n_i) required to sustain steady burning was determined. The polymers burned were polyoxymethylene (Delrin), polyethylene (Marlex 5002), polymethylmethacrylate (Plexiglass G), chlorinated polyethylene $(C_2H_{3.80}Cl_{0.20})$, chlorinated polyethylene with 4 wt.% antimony oxide, polytetrafluorethylene (Teflon), polycarbonate (Lexan T), and polycarbonate with 1.9 wt.% Br.

The polymer strip was mounted vertically in a cylindrical Pyrex glass chimney. The oxygen-inert gas mixture rose in laminar flow past the strip at a mean velocity within the range of 3 to 10 cm/sec. Ignition was accomplished by inserting a hydrogen flame momentarily from the top of the chimney. The oxygen content was adjusted so that the sample would be able just to burn steadily.

For each polymer (except Lexan) an approximate linear relation was found between the ratio (n_O/n_i) and the mean heat capacity $\tilde{C}_{P,i}$ of the diluting gas (Ar, N_2, and CO_2). The values of (n_O/n_i) obtained with helium are too high to obey this relationship. In the burning of Lexan, solid carbon forms on the surface, whereas for each of the other polymers this is not observed. Since another extinction mechanism probably applies, the Lexan data are not considered further in the paper.

When a polyethylene strip burns, a clear molten dome is formed at the top, enclosed by a thin blue flame. The bottom (leading) edge of the flame reaches to less than 1 mm (quenching distance) from the polymer surface. The blue flame is topped by a yellow-white cap.

The blue flame is considered to be a diffusion flame sustained by gases generated by pyrolysis of the polymer. Oxygen from the ambient gas is assumed to be consumed primarily in the flame zone. Near the extinction limit the flame shape and its downward movement is generally steady. Thus the local gas flows, transport properties, and flame reactions can be assumed to be in a steady state.

If the (n_O/n_i) is reduced below the critical level the flame will go out in one of two ways. Generally the flame shrinks slowly until only a small blue cap exists just before extinction. But for polymers containing antimony oxide and halogen violent flickering occurs before eventual blow-off. In either case, stability of the leading edge is considered essential for continuous burning.

A model is proposed in which (n_O/n_i) must exceed some limiting value in order to maintain the necessary temperature within a critical control volume in the gas phase. This control volume is a narrow ring encircling the tip of the sample and containing the leading edge of the flame. Its cross section is approximated by a five-sided figure where the sides s, a, c, h, and g represent the surfaces of the volume. All fuel enters the control volume through the vertical inner surface s, the boundary along the polymer surface. All the oxygen-inert gas mixture present in the control volume enters at its bottom surface a, as a continuous gas film flowing upwards along the polymer surface. The outer vertical side of the control volume, surface c, is described by a streamline in the gas flow; no net mass transfer occurs across *c*. Surface *h*, the flat top of the volume, is intersected by the flame near its leading edge; all mass leaving the control volume passes through surface *h*. Surface *g* is described by a sloping streamline spanning the gap (approximately the quenching distance) from the polymer surface to the inner flame surface; no net mass transfer occurs across *g*.

The steady-flow energy equation (kinetic energy terms omitted) across the boundaries of the control volume is rearranged to yield the following expression for the mole ratio (n_O/n_i):

$$\frac{n_O}{n_i}=\frac{-Q_i+(H_{i,h}-H_{i,a})}{\Delta H_c-(\sum n_p/n_O)[-Q_p+(H_{p,h}-H_{p,a})]}, \tag{1}$$

where n_j is the mole rate of species j, $-Q_j$ is the heat loss per mole of species j, $H_{j,k}$ is the enthalpy per mole of species j at surface k, and ΔH_c is the heat of combustion per mole of *oxygen* i.e.,

$$\Delta H_c=(n_f/n_O)H_{f,s}+H_{O,a}-(\sum n_p/n_O)H_{p,a}$$

and where the subscripts represent

> control volume surfaces: s, a, h; and species: f (fuel), O (oxygen), i (inert gas), p (combustion products).

Introducing the mean heat capacity of the inert gas at constant pressure $\bar{C}_{P,i}$ into Eq. (1) yields immediately

$$n_O/n_i=[(T_h-T_a)/B]\{[-Q/(T_h-T_a)]+\bar{C}_{P,i}\} \tag{2}$$

where T_h is the flame temperature, B is the denominator of the RHS of Eq. (1), and Q replaces Q_i and Q_p which as a simplification are taken to be equal.

It is reasonable to assume that the flame stoichiometry with different diluting inert gases is the same. A constant limiting flame temperature T_h can be assumed, that is, $T=T$(stoich.). The heat loss term $-Q$ can be characterized by the ratio of the heat loss rate from the control volume to the mole flow rate through the volume. Therefore, $Q=Q$(stoich., T). Hence for a given sample, Q is constant when different diluting gases (except helium) are used. Also ΔH_c is a function of the stoichiometry, and the enthalpy difference is a function of temperature and stoichiometry.

Equation (2) may be written

$$n_O/n_i=(n_O/n_i)(\text{stoich.}, T, \bar{C}_{P,i}).$$

When the stoichiometry, T, and Q are all constant, then n_O/n_i is a linear function of $\bar{C}_{P,i}$. If a diluting gas having an appreciably different thermal conductivity (e.g., helium) is used, then the heat loss rate and Q change. In this case, n_O/n_i is a function of variable Q as well.

An attempt was made to test the above flame model in the following manner: Observed values of n_O/n_i for Ar, N_2, and CO_2 were substituted into Eq. (2). Then for a selected stoichiometry and assuming T_h and Q to be independent of the inert gas, values of T_h and Q were determined, which produce the best least-squares fit.

In the case of polyethylene, for example, the observed limiting n_O/n_i obtained with diluent Ar is 0.153; N_2, 0.212; and CO_2, 0.339. Assuming burning completely to CO_2 and H_2O, T_h is 1680°C and Q is 2.047 kcal/mole. For 50% conversion to CO and 50% to CO_2, T_h is 1545°C and $-Q$ is 1.726 kcal/mole. (The corresponding values of adiabatic flame temperature for complete combustion in oxygen–argon is 2030°C; for incomplete combustion, 50% CO, it is 1845°C.) Both sets of values of T_h and $-Q$ seem reasonable; the model does not enable a decision between the two stoichiometries. Nevertheless, the reasonably good fits obtained give support to the suitability of the model. Since experimental values of T_h and $-Q$ were not available, the model could not be checked further.

The lines obtained for the various polymers have different slopes $(T_h-T_a)/B$ and different intercepts $-Q/B$. The slopes are determined principally by T_h; the higher the T_h, the greater the slope. The differences in intercepts arise from the large variations in molar heat loss. For example, $-Q$ for polyethylene is 1.7; for chlorinated polyethylene, it is 7.0.

The model was applied also to those cases where helium had been employed as a diluent. The measured value of n_O/n_i for polyethylene in oxygen–helium is 0.229, 50% greater than that observed in oxygen–argon. Quantitative demonstration of the increased heat loss (presumably owing to a considerably higher thermal conductivity) is given by the calculation of $-Q$ using Eq. (2), given the observed value of n_O/n_i and the value of T_h calculated previously for gas mixtures containing the other three inert gases. For example, for polyethylene burning in oxygen–helium to equal moles of CO and CO_2, $-Q$ is 5.306 kcal/mole, three times the value determined when the other inert gases were employed.

The author investigated briefly another model for which the gases in the control volume are homogeneously mixed and where the flame temperature is specified by the maximum heat loss condition. He employed the following equation applicable to the maximum heat loss condition in a premixed flame, corresponding to the quenching limit:

$$E=2RT_h^{*\,2}/(T_{h,\mathrm{ad}}-T_h^*) \qquad (3)$$

where T_h^* is the flame temperature at the maximum heat loss condition and $T_{h,\mathrm{ad}}$ is the adiabatic flame temperature.

If E is taken to be independent of inert gas, then a variable T_h^* can be calculated using Eq. (3). For an assumed value of 70 kcal/mole for E, calculated values of T_h and $-Q$ for polyethylene burning in oxygen–argon completely to CO_2 are 1790°C and 1.55 kcal/mole. It is of interest here that for a given polymer the fraction of the heat of combustion lost at the maximum loss point is essentially independent of the inert gas (e.g., 0.13 for polyethylene).

Subject Headings: *Burning, of polymers; Candle burning, of polymers; Polymers, candle burning of.*

G. A. Agoston

Schaffer, E. L. (Forest Products Laboratory, U.S. Forest Service, Madison, Wisconsin) "Charring Rate of Selected Woods—Transverse to Grain," U.S. Forest Service Research Paper FPL 69 (1967)

Laminated wood slabs, 3 in. thick, of Douglas fir, southern pine, and white oak were vertically exposed to fire on one surface. The rate of char development was constant when the specimens were exposed to uniformly increasing fire temperatures; charring rates at three constant fire exposure temperatures were described by a pseudo-first-order reaction equation with an Arrhenius temperature-dependent rate constant. Rates of char development in each species were related to the specific gravity and moisture content of the wood. The springwood to summerwood ratio, volatile extractive content, and annual ring orientation were either directly related to specific gravity and moisture content or had no significant effect on the charring rate.

Subject Headings: *Charring rate, of wood; Pyrolysis, of wood; Rate of charring, of wood; Wood, charring rate of.*

Author's Summary

Tarifa, C. S., Notario, P. P., and Valdes, E. C. F. (Instituto Nacional de Tecnica Aerospacial, Esteban, Terradas, Madrid, Spain) "Open Fires" (Vol. I) and "Transport and Combustion of Firebrands" (Vol. II) *Final Report of Grants FG-SP-114 and FG-Sp-146 from U.S. Department of Agriculture, Forest Service* (May 1967)

Vol. I.

The research program has comprised the experimental and theoretical study of some basic laws of open fires. This study has been carried out by utilizing the pool fire technique, which consists in burning liquid fuels in cylindrical vessels, and in measuring and analyzing burning rates, energy balances, flame properties and fuel temperatures.

Several important conclusions have been obtained on burning rates, energy balances and flame characteristics including the influence of type of fuel, vessel size and vessel configuration.

Vol. II.

A theoretical and experimental study has been carried out on the combustion properties and flight paths of firebrands when they are carried upwards by convective currents and then forward by the winds.

The study has shown that the flight paths of firebrands can be accurately calculated by assuming that they fly at their terminal velocity of fall. This velocity of fall decreases continuously as the firebrand burns.

Several types of wind tunnels have been developed especially designed to study combustion of firebrands at their final velocity of fall.

The study has also shown that combustion and flight paths of firebrands can also be calculated from data obtained on the combustion of firebrands at constant wind speed.

The influence of the initial size and initial shape of the firebrands, kind of wood and initial moisture content has been studied, as well as the influence of several types of convection columns configurations.

Results of these studies enable the calculation of the maximum range of possible fire spread by firebrands of given initial characteristics, once the convective currents above the fire are known as well as the horizontal wind conditions.

Subject Headings: *Combustion, of firebrands; Fires, open, firebrands transport and production of; Transport of firebrands.*

Authors' Abstract

Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "Experiments on the Rate of Decomposition of Wood in Fires," *Joint Fire Research Organization Fire Research Note No. 672* (July 1967)

This report summarizes experimental results on the rate of weight loss of wood exposed to various levels of radiation, and the relation between the rate of burning of piles of wood and radiation in fully developed fires in compartments.

Estimates have been obtained of the amount of heat (calories) associated with the mass (gm) of decomposition.

Subject Headings: *Decomposition, of wood; Pyrolysis, of wood; Wood, decomposition of.*

Author's Summary

Warner, F. E. (Cremer and Warner, London, England) **and Szekely, J.** (Imperial College, London, England) "Underground Gasification of Coal: Part II," *Proceedings of the American Institute of Chemical Engineers and the Institution of Chemical Engineers Joint Meeting*, London, England (1965)

A model of the gasification process in underground coal gasification was developed. The theory is based on large-scale trials in Great Britain (described in Part I[1]) of gasification in blind and open borehole systems. Boreholes were 8 to 14 in. diameter and 180 to 400 ft long arranged singly or in parallel arrays. Calorific values of the gases ranged from 70–80 Btu/ft^3 in the open borehole system. Air rates used to carry the gases were 25,000 to 75,000 ft^3/hr in the closed system and up to 250,000 ft^3/hr in the open system.

The analysis of the underground gasification process was directed towards achievement of maximum calorific value at highest possible gas rates and economic spacing between boreholes. Calorific values were related to the effect of the dependent variables (temperature profile along the coal surface, length of combustion zone, rate of development of burnt-out cavity, and the movement of the combustion center). Essential to the development were the postulates that formation of carbon monoxide (the essential calorific constituent) is controlled by mass transfer rather by chemical kinetics at temperatures above 1000°C, and that the initial combustion cavity continuously enlarges as burning continues until a limiting size is reached.

The ultimate channel width and its dependence of the process parameters were computed from a procedure based on balance of heat loss to the strata and heat generated in the channel. Total rate of heat loss over an exposed face with constant channel size, and rate of movement of combustion zone is given by

$$Q_l=[4kT_w/(\pi D)^{1/2}](UY)^{1/2} \tag{1}$$

where k = thermal conductivity, D = thermal diffusivity, T_w = temperature at the wall in combustion zone, U = rate of movement of combustion, and Y = width of combustion channel. The rate of heat generation is

$$q_g=Ub\rho_c(CV) \tag{2}$$

where b = seam thickness, ρ_c = density, and CV = calorific value of the coal. At the critical point, when $q_g=Q_l$,

$$Y=U\pi Db^2\rho_c^2(CV)^2/16k^2T_w^2 \tag{3}$$

A correction for the increase in cavity size with time results in

$$Y=[b\rho_c(CV)/2kT_w\times 0.89](U_0D\pi/2k')^{1/2} \tag{4}$$

where the new terms are U_0 = initial velocity of the combustion zone and k' = a constant defined by $U=U_0/(1+k'Y)$. Thus, the width of the combustion zone is directly proportional to the seam thickness, the calorific value of the coal, and the square root of the initial speed of the combustion front. Results predicted from these calculations were consistent with the earlier experimental data and new data revealed by new excavations that showed the characteristics of the "affected zone" in the coal burn-out area. Additional theoretical computations were made for the combustion wall temperature and thickness of the "affected zone" based on consideration of: heat conduction ahead of the moving combustion front, and heat re-distribution following termination of combustion. Shape of computed temperature profiles attained in the seam and width of the "affected zone" were in reasonable agreement with theoretical expectations. The experimental evidence gave no positive guide to the reaction mechanisms involved in gasification.

Reference

1. WARNER, F. E., SZEKELY, J., AND MAH, R. S. H.: *The Chemical Engineer* No. 163, *A68* (October 1962)

Subject Headings: ***Coal, gasification of underground; Gasification, of coal underground; Underground gasification, of coal.***

J. M. Singer

Zabetakis, M. G. (Explosives Research Center, U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Fire and Explosion Hazards at Temperature and Pressure Extremes," *Institution of Chemical Engineers A.I.Ch.E. Symposium Series No. 2* (1965)

This paper gives a summary of the data taken at the Explosive Research Center, Bureau of Mines, Pittsburgh, over the previous ten years on the limits of flammability and the ignition energy requirements for paraffin hydrocarbon-nitrogen-oxygen mixtures.

An investigation of the minimum energy in an electric spark required to produce ignition of a number of hydrocarbon air mixtures at atmospheric pressure and 26°C showed that the least energy is required in the vicinity of a stoichiometric mixture. As the per cent hydrocarbon is increased or decreased from this point a higher energy spark is required until the flammability limits are reached in the limiting case.

The autoignition temperature (A.I.T.) of a number of hydrocarbons has been found to decrease as the pressure increases although general conclusions can not be drawn since the mechanism appears to vary from one hydrocarbon to another.

An intensive investigation of the flammability limits of hydrocarbon-nitrogen-oxygen mixtures resulted in the presentation of the following equations:

$$L_t/L_{25}=1-0.00721(t-25)$$

where: L_t=lower limit of flammability at the temperature t°C, L_{25}=lower limit of flammability at 25°C, and t=temperature in °C.

For natural gas-air mixtures only

$$L\ (\text{Vol}\ \%)=4.9-0.71\ \log P\ (\text{atm})$$

$$U\ (\text{Vol}\ \%)=14.1+20.4\ \log P\ (\text{atm})$$

A representative diagram giving the flammability limits and autoignition temperatures of a combustible vapor in air is presented to show the general trends of these quantities as a function of pressure and temperature in the case of the former and pressure and composition in the case of latter.

The paper concludes with a discussion of the extinguishment of a flame in a closed vessel by means of injecting an extinguishing agent. In order to prevent the pressure from rising about a fixed value, ΔP_c, corrective action must be taken by the time t_c which is given by the relation:

$$t_c=75[(\Delta P_c/\Delta P_{\max})V]^{-1/3}$$

where $\Delta P_{\max}$ is the maximum pressure rise if the entire mixture has burned adiabatically and V is the volume of the container in cubic feet. The constant is based on the burning velocity of a 9.6 vol % methane-air mixture.

Subject Headings: *Flammability, of hydrocarbons; Hydrocarbons, ignition energy of.*

F. R. Steward

H. Chemical Aspects of Fires

Corlett, R. C. (University of Washington, Seattle, Washington) "Chemical Kinetics and Pool Burning Rates," *The Trend in Engineering, University of Washington* **19**(2) 8–14 (1967)

This paper is essentially a review of the author's work in pool fires and pool-like gas fires. Little detailed information is presented and it is difficult, at times, to follow the reasoning which leads to the conclusions given.

It is pointed out that fires may be characterized by the amount of reaction that takes place at the fuel surface, and that pool fires are a limiting case in that no reaction takes place at the fuel surface, due to quenching. The physical structure of a pool fire is considered and the outstanding problems are discussed. The experimental equipment and procedures employed to study real pool fires are described, and results are given for acetone, ethanol, and methanol fuels, in pools 1 to 30 cm in diameter.

Fuels available for real pool fire experiments are few enough that only relatively small variations in parameters can be studied. Hence, gaseous fuels are considered, and a gas burner, designed to simulate the boundary conditions of a burning fuel system is described. In these experiments, the fuels are methane, propane, carbon monoxide, and various diluents, and the burner diameters are 2, 4, and 7½ in. in diameter.

The measurements include mean burning rates, heat transfer rates, and water absorption in the pools. It is concluded that the radiative heat transfer is of the same order of magnitude as what the author terms the molecular (convective) heat transfer (generally referred to as conduction) but that the latter controls the burning rate. In addition, it is concluded that the molecular heat transfer apparently depends on chemical kinetic factors.

Subject Headings: *Chemical kinetics, of pool fires; Pool fires, chemical kinetics of.*

T. C. Adamson, Jr.

Duval, A. and van Tiggelen, P. J. (University of Louvain, Louvain, Belgium) "Kinetical Study of Hydrogen—Nitrous Oxide Flames," *Bulletin de la Classe des Sciences Academie Royale de Belgique* **53**(4) 366–402 (1967)

Equations developed in a preceding paper permit experimental determination of activation energy and reaction order in an expression for burning velocity of a flammable mixture. The derived values are, of course, over-all apparent values for the process. The next step in the study of a chemical reaction lies in synthesis of a reaction mechanism. This step, to be successful, must be relatively simple, a difficult condition in a flame reaction zone where high temperatures permit formation of radicals and stimulate a multitude of processes.

The hydrogen-nitrous oxide system was selected to test the method proposed in the preceding paper as a system having suitable properties for experimental observation, namely, sufficient luminosity and moderate burning velocity.

The equation used in interpretation of the experimental data is

$$\log V_0 + \tfrac{1}{2} \log T_m - \tfrac{1}{2} n \log(1-\sigma_m) = K' - (0.4343E/2RT_m)$$

where V_0 is the burning velocity given by the ratio of the total gas flow to the total flame surface, T_m is the mean temperature in the flame reaction zone, n is the over-all reaction order, σ_m is the mean degree of conversion in the reaction zone, E is the activation energy, R is the gas constant, and K' is a function of initial conditions only.

Experimental data were taken for the following ranges of variables:

Ratio of moles of fuel to moles of fuel plus oxidizer from 0.4 to 0.7,
(0.5 being stoichiometric)
Burning velocity from 17 to 169 cm/sec
Flame temperature from 1975 to 2575°K
Initial temperature from 290 to 467°K

Nitrogen, argon, and helium were used as inerts.

The only rational correlation of the experimental data for stoichiometric mixtures was obtained for a reaction order $(n)=2$ with an activation energy $(E)=26.5$ Kcal. These values also correlated the data for lean mixtures, since excess oxidizer decomposes in the flame reaction zone, leaving essentially a stoichiometric mixture for reaction. Rich mixtures were not correlated by a single value of activation energy.

Partial reaction orders with respect to nitrous oxide (a) and hydrogen (b) were also determined from the experimental data by selecting data for different mixture ratios and initial temperatures, but with the same flame temperature. This approach yielded for lean mixtures $a \simeq 0.45$ and $b \simeq 1.68$, while for slightly rich mixtures $a \simeq 0.8$ and $b \simeq 1.25$. A second approach to obtaining partial reaction orders used a transformation of the basic equation into a form where the initial mixture ratio is a separate primary variable. Data for varying mixture ratios were then correlated graphically to give values of a from 1 for rich mixtures to 0.3 for lean mixtures, with b derived as $2-a$. The two techniques thus confirm each other.

A chain reaction mechanism was postulated involving the following reactions:

$$\left.\begin{array}{r} \dot{\mathrm{O}}\mathrm{H}+\mathrm{H}_2\rightarrow\mathrm{H}_2\mathrm{O}+\dot{\mathrm{H}} \\ \dot{\mathrm{H}}+\mathrm{N}_2\mathrm{O}\rightarrow\mathrm{N}_2+\dot{\mathrm{O}}\mathrm{H} \end{array}\right\} \text{Chain propagation}$$

$$\left.\begin{array}{r} \mathrm{N}_2\mathrm{O}+\mathrm{H}\rightarrow\mathrm{N}_2+\mathrm{OH}^* \\ \mathrm{OH}^*+\mathrm{H}_2\rightarrow\dot{\mathrm{O}}\mathrm{H}+2\mathrm{H} \end{array}\right\} \text{Chain branching}$$

Analysis of this mechanism resulted in a reaction order $(n)=2$ and $0 \leq a \leq 1 \leq b$, which are consistent with the results derived from the experimental data. Furthermore an activation energy of 27.5 Kcal was calculated using the postulated mechanism and a portion of the experimental data. This agreed well with the 26.5 Kcal obtained from the evaluation of the over-all process.

The experimental results also showed the influence of the inert gas on flame speed. The flame speed with helium was higher than with nitrogen, which was higher than with argon.

Subject Headings: *Flame, nitrous oxide, kinetics of; Kinetics, of nitrous oxide flame.*

A. E. Noreen

This research has been supported in part by the Air Force Office of Scientific Research through the European Office of Aerospace Research (OAR), United States Air Force, under Grant AF-EOAR-66-44.

Homann, K. H. (University of Göttingen, Göttingen, Germany) "Carbon Formation in Premixed Flames," *Combustion and Flame* **11**(4) 265–287 (1967)

This review paper is mainly concerned with the mechanism of carbon formation in the gas phase of laminar premixed flames of low molecular weight hydrocarbons. Items covered are: (1) the physical appearance of soot forming flames, (2) limits of carbon formation, (3) temperature and (4) pressure dependence of the limit and yield of carbon formation, (5) reaction intermediates, (6) final products from aliphatic and aromatic fuels, (7) influence of additives and electrical fields and (8) particle formation and growth. A substantial amount of the reviewed work was carried out at Göttingen.[1,2]

In Section 1, *the appearance of nozzle burner flames* (conical and polyhedral) and flat burner flames (normal and cellular) is discussed. In such flames the position of the yellow luminosity is determined by two main factors: The molecular weight of the fuel with respect to oxygen (determining the results of preferential diffusion and consequently the location of the first appearance of soot in two- or three-dimensional flame fronts) and the relative rates of oxidation vs carbon formation reactions (determining the separation between the oxidation and carbon forming flame zones). For example, the nozzle flames of acetylene and ethylene exhibit uniform soot luminosity around the conical flame front, but high molecular weight nonaromatic hydrocarbons initiate soot formation above the tip of the flame, with a nonluminous space between the oxidation zone and the beginning of the soot formation zone. The rate of soot formation in benzene flames, taken as representatives of aromatic fuels, is so fast with respect to the oxidation reactions that in flat flames the luminous zone begins before the end of the blue-green oxidation zone.

The *limits of carbon formation* are mainly determined by fuel properties (hydrogen content, molecular structure, aromatic character, etc.) and by flame properties such as structure, temperature and quenching distance. Also of importance (even in premixed flames) is the gas composition surrounding the premixed flame. Secondary air is excluded in most determinations of the carbon formation limits. The critical atomic ratio of carbon to oxygen, C/O, at which visible soot luminosity just begins, is one way for expressing the limit. This limit varies very little for *n*-paraffin-air flames—from 0.47 for ethane to 0.44 for *n*-cetane; for *n*-olefins it lies a little higher—from 0.60 for ethylene to 0.48 for *n*-heptane. Such values are of help in many practical applications. However, one should not overlook their relative value, i.e., flames of similar limits may have very different yields. For example, the premixed acetylene-air flame with a critical C/O ratio of 0.83 comes close to the equilibrium value (at flame temperatures) of $C/O=1$,[3] but a small acetylene diffusion flame has a much larger yield of soot formation than, e.g., a propane diffusion flame. The experimental values of $C/O<1$ indicate that the overall rate of soot formation is faster than the reactions leading to equilibrium. Thus, equilibria such as $CO+H_2O \rightleftharpoons CO_2+H_2$, $C(s)+CO_2 \rightleftharpoons 2CO$, etc. were found not to be established.

The *influence of temperature* on soot formation is determined by the temperature dependence of the different processes involved in soot formation. Overall, one might expect two temperature regimes: a high temperature region in which the driving force for formation of a solid phase becomes smaller with increasing temperature and a low temperature region with a reversed temperature dependence, limited by a minimum flame temperature. The first seems to correspond to the region where the temperature dependence of soot formation is governed by the reactions controlling the availability of oxidants and the second by the temperature dependence of pyrolysis and polymerization reactions. A third factor of influence in 2- and 3-dimensional flames is given by the temperature dependence of preferential diffusion processes. Experimental results indicate that the first factor becomes determining in relatively lean carbon-forming flames at high temperatures, with a negative temperature dependence, while the second, with a positive temperature dependence, predominates at lower temperature under very rich conditions such as being present near the rich flammability limit. Regarding the first factor, a higher temperature causes CO_2 to be produced in smaller concentrations, while increasing the availability of the oxidant OH. Experimentally, it is not easy to vary flame temperature without varying other parameters such as burner size, gas velocity, etc. Diluting the flame with equal amounts of gases of different heat capacity, changing the rate at which a turbulent flame loses heat by radiative transfer or preheating are some of the used methods. Only few quantitative determinations of the temperature dependence other than those of the pyrolysis process in shock tubes (40–50 kcal/mole) have been carried out.

An analysis of the *effect of pressure* has to differentiate between the influence on the limit and on the yield of carbon formation. Such an analysis is complicated by the fact that changes in pressure are associated with more or less large changes in one or more of other flame parameters such as mass flow, linear gas velocity, flame temperature, preferential diffusion, or interaction with the burner surface. This situation can be alleviated by using shock waves, which allow one to vary pressure independent of temperature. While in general the yield of soot in rich flames is reported to increase considerably with increasing pressure,* the critical C/O ratio only decreases moderately. This decrease is observable at constant mass flow rates but is negligible for flames at constant initial, unburned gas velocity.

The technique of sampling low pressure flames (the reaction zone thickness is approximately proportional to 1/pressure) has considerably advanced the knowledge

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* Around 0.1 atm and at a constant initial gas velocity of 50 cm/sec, the pressure dependence of the yield of soot as obtained by observation of the optical absorption and emission of soot in a flat C_2H_2—O_2 flame was found to be very slight.[4] However, flame temperatures showed a simultaneous increase with increasing pressure.

of *intermediate flame products*. In terms of such intermediates, the transition from non carbon forming to carbon forming flames is not abrupt but gradual. Both concentration and variety of hydrocarbon intermediates, especially those with a greater number of carbon atoms than the original fuel, increase steadily with increasing C/O ratio. The author compares intermediates (1) found in lean flames with those in rich flames, (2) found in the gas phase with such found as volatile components of collected soot, (3) of aliphatic fuels with aromatic fuels and (4) with respect to their sequence of appearance in the oxidation and luminous flame zones.

The author used a molecular beam flame sampling technique which was directly connected to the ionization chamber of a mass spectrometer. The interpretation of the mass spectra was facilitated by the high sensitivity of the mass spectrometer, which allowed the use of ionization energy levels below the appearance potentials of fragment ions. In addition to the species known to appear in rich flames, such as CH_4, C_2H_4, C_2H_2 and C_4H_2, the author identified polyacetylenes up to $C_{12}H_2$ and polycyclic aromatic compounds (up to seven condensed benzene rings—see Figs. 1 and 2), as the most abundant species to be found among the final products besides

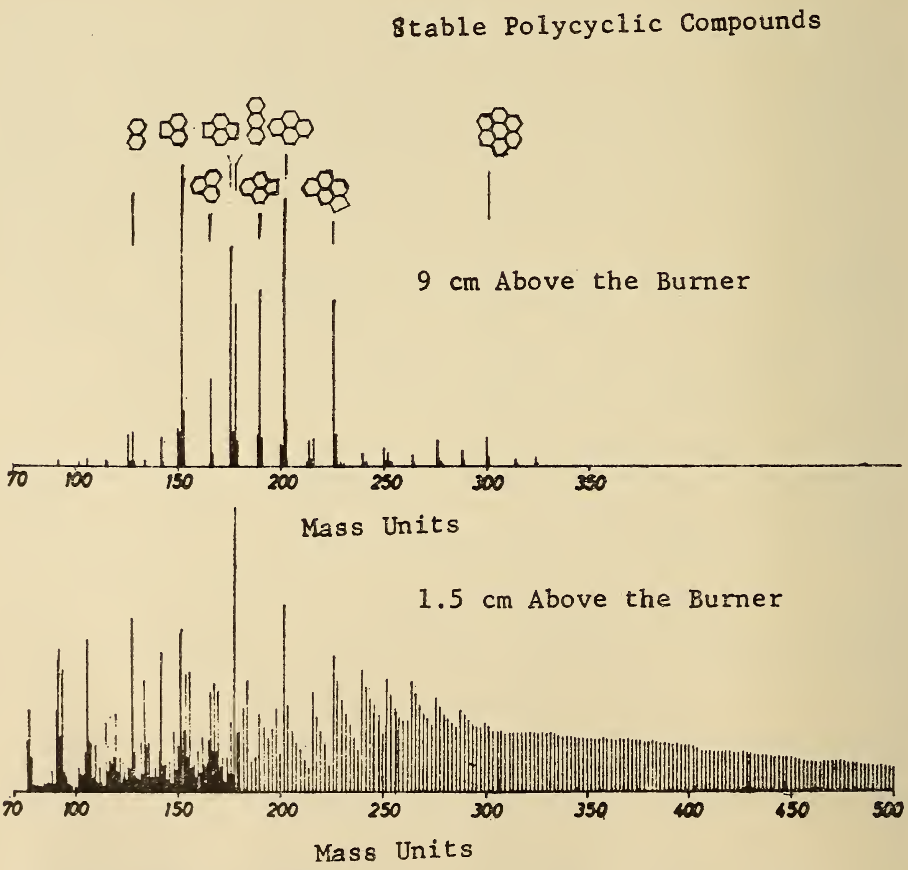

FIG. 1. Mass spectra of volatile components of soot collected from two heights in an acetylene–oxygen flame. $C_2H_2:O_2=1.37$; 20 mm Hg; $v_0=50$ cm/s.

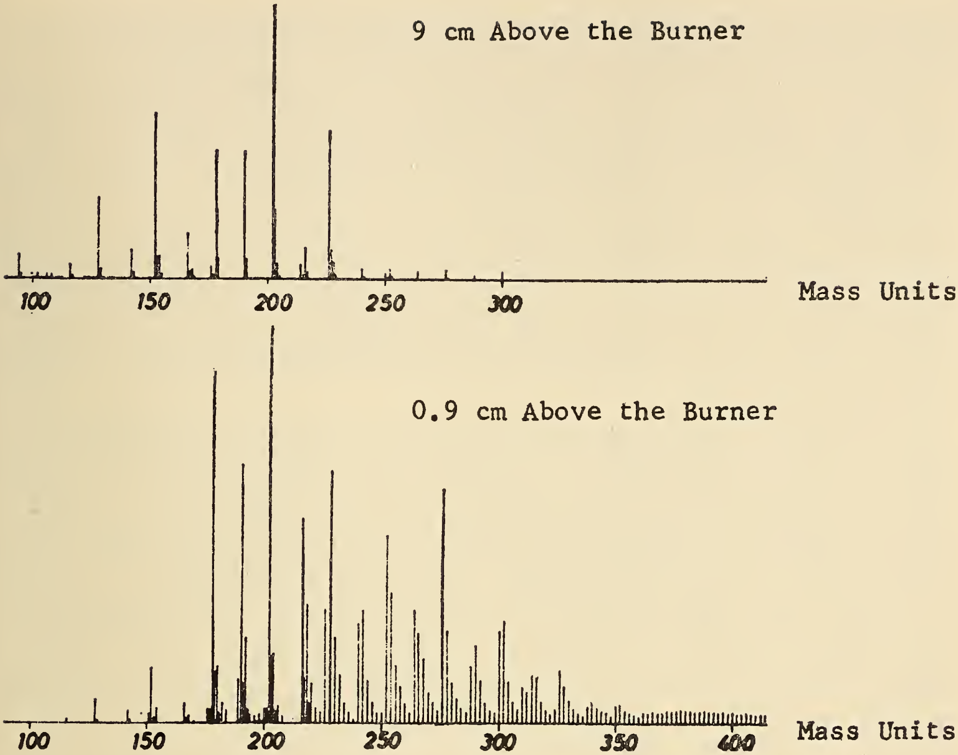

FIG. 2. Mass spectra of volatile components of soot collected from two heights in a benzene–oxygen flame. C_6H_6:O_2=0.2; 30 mm Hg; v_0=24 cm/s.

soot, H_2, H_2O, CO, CO_2. Polyacetylenes appeared earlier than aromatics and in relatively higher concentrations in flames of aliphatic fuels than of aromatic fuels, while more aromatic compounds were found in benzene flames. Polyacetylenes, because of their greater reactivity, appeared to react irreversibly with the *growing* soot particles. Unlike polycyclic aromatic compounds, polyacetylenes could not be identified as part of the volatile components of collected soot particles. The volatile components of soot collected from acetylene and from benzene flames are very similar: primarily, polycyclic aromatic compounds with no side chains were observed to evolve from the final or "old" soot (as had been observed previously by extracting the soluble fractions of soot with organic solvents), and polycyclic aromatic compounds with and without side chains, having a correspondingly higher atomic H/C ratio were well represented in the early, small soot particles, particularly of aliphatic fuel flames. The order of appearance of intermediates in the reaction zone of a representative rich, low pressure acetylene flame, was found to be the following: (1) in the blue oxidation zone, where the emissions of C_2, CH and OH reach their maxima and at the end of which all the oxygen has been consumed, hydrocarbon radicals such as C_2H and C_4H_3 in addition to HCO, H_2CO, CH_4, C_3H_4, etc., reach a maximum concentration and disappear again, (2) the concentration of polyacetylenes reaches a maximum and decreases again at the beginning of the luminous soot formation zone and becomes constant after the soot concentration has ceased to increase. The concentration of polycyclic aromatic compounds without side chains increases steadily behind the oxidation zone without going through any maximum, which is in agreement with the result of the analysis of the soot volatiles.

Compared to the processes occurring during *pyrolysis and polymerization* of hydrocarbons below 1200°C, flames show a more pronounced appearance of polyacetylenes and a greater concentration of intermediates formed by reactions with fuel fragments.

The influence of a number of *additives* on the formation of soot in premixed flames had been studied qualitatively by Street and Thomas[5] and by Gaydon and Wolfhard.[6] Among the strongest promoters of soot formation are SO_3 and halogen compounds. In these studies, no consideration was given, however, to simultaneous side effects like changes in temperature, preferential diffusion, flame structure, etc., so that no explanation could be given as to the way in which the additives affected the reaction mechanism.

The study of *electrical flame properties* uncovered a number of positive and, in smaller concentrations, negative hydrocarbon ions. Addition of substances like barium, nickel and alkaline earth salts, having a low ionization energy ("seeding"), reportedly decreased soot formation. But up to now there seems to be no indication that the presence of hydrocarbon ions influences soot formation appreciably in one way or another. A considerable fraction of soot particles has been found to carry a positive charge. Weinberg cites the number of carbon atoms per unit charge as being of the order of 10^4. The attachment of electric charges to soot particles has been used to control the soot particle residence time in different flame zones by applying suitable electric fields to the flame. In this way, soot particle aggregates of visible size have been obtained.

Particle Formation and Growth

Earlier hypothesis for the formation of carbon in flames such as "carbonization" of liquid polymer droplets and condensation of super-saturated carbon vapor are only mentioned briefly. The reader is referred to reviews by Gaydon and Wolfhard[6] and Palmer and Cullis.[7]

Carbon in flames is generally formed in long chains composed of beads from 100–2500 Å in diameter. In long residence time pyrolysis experiments, particle diameters of up to 6000 Å have been obtained. Each bead or particle is made up of 10^3 to 10^4 crystallites of about 20–30 Å in length. They may be formed by a kind of partial tempering process. Complete graphitization is obtained only if the particles go through a molten state. It is assumed that in the first phase of particle growth, molecules are not added in an ordered way. As mentioned earlier, differences observed in the soot formation in flames of different fuels are only quantitative. In acetylene, as a representative aliphatic fuel, as well as in benzene, as a representative aromatic fuel, the composition of the formed soot is similar, as indicated by Figs. 1 and 2, which show mass spectra of the volatile components of soot taken at different stages of soot formation. Hydrocarbons of relatively large H/C ratio (e.g., aliphatic saturated hydrocarbons, aromatic compounds with side chains, etc.) do not survive very long in the flame. Only polycyclic aromatic compounds of 5 and 6 membered rings are stable enough to survive and their concentration increases both in the solid and in the gas phase. Polyacetylenes are only observable in the gas phase and seem to react very rapidly after colliding with reactive, small soot particles. The reactivity of small soot particles was confirmed by ESR. "Older" soot particles gave no or a much smaller ESR signal indicating no or a much weaker radical character. This is in agreement with the results of gas analysis indicating only a very slow decrease in the polyacetylene concentration with time after radicals and reactive soot particles have disappeared.

After the initial formation of small particles with strong radical character, particle growth is governed by addition of polyacetylenes and polyaromatic compounds, with a rate determined by their concentration and their chemical stability. This hypothesis is supported by the elemental analysis of soot as a function of reaction time, which indicated a marked decrease of the atomic H/C ratio during particle growth.

In benzene flames, the concentration of aromatic compounds is relatively so large that even in spite of their low reactivity, they seem to accelerate soot formation enough for the luminous flame zone to appear before the oxygen is completely consumed.

The initial rate of overall growth is so fast that the collision effectiveness seems to be close to unity. Little is known, however, about the nature and growth rate of particles below about 40 Å, corresponding to about 40,000 mass units. The heaviest species identified by mass spectrometry correspond to about 500 mass units. Rapid build up of polyacetylenes can be explained by reactions between hydrocarbon radicals such as C_2H and C_2H_3 and acetylene and polyacetylenes. The immediate products of such reactions are again substances with radical character. Further addition of acetylene and polyacetylenes to the formed branched radicals, and cyclization eventually produces the first small soot particles. Their growth only slows down after a kind of "tempering" process, which removes their radical character. The importance of the radicals for soot formation has been underlined by experimental additions of fuel to different parts of the flame. Only if the added fuel is introduced at or upstream of the reaction zone, is an increase in soot generation noticeable.

The author also lists a number of suggestions for further work such as: determination of the relative reaction rate and temperature dependence of polyacetylene formation and oxidation by OH; to find out why cyanogen flames form carbon only on surfaces but not in the gas phase; the study of the influence of additives and electric charges on soot formation.

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Subject Headings: ***Carbon formation, in flames; Flames, premixed, carbon formation in.***

U. Bonne

Katō, Kunio (Central Research Institute, Japan Monopoly Corporation, Tokyo, Japan) "Pyrolysis of Cellulose. Part III. Comparative Studies of the Volatile Compounds from Pyrolysates of Cellulose and Its Related Compounds," *Agricultural and Biological Chemistry* 31(6) 657–663 (1967)

This paper describes a pyrolysis study of cellulose and its related compounds. The results consist of relative yields of pyrolysis products at 250°, 350°, and 500°C. The author uses these results to speculate on pyrolysis mechanisms. The apparatus consisted of a Shimazu-type PYR-1A pyrolyzer connected directly to a Shimazu GC-1B linear programmed gas chromatograph. The various compounds studied were prepared by methods described in the literature. The samples, consisting of 15 to 30 mg, were heated in a platinum boat at a rate of 5°C/min up to 200°C. The time spent at the pyrolysis temperature is given, but the rate of heating used between 200°C and the pyrolysis temperature is not reported.

The relative amounts of pyrolysis products obtained from cellulose, cellobiose, glucose, and levoglucosan are given for the three temperatures mentioned above. The products, identified by comparing chromatograph retention times with those of standard samples, are acetaldehyde, furan, propionaldehyde, acrolein, acetone, diacetyl, furfural, and 5-methyl furfural. Also reported are the relative amounts of these same eight products obtained by pyrolyzing the following saccharides pyrolysates at 350°C: *D*-xylose, *L*-rhamnose, chitose, *α*-*D*-glucosan, *L*-ascorbic acid, osone, gluconic acid, glucuronic acid, galacturonic acid, *D*-fructose, *D*-glucal, 2-desoxy-*D*-glucose and *D*-glucose.

The volatile compounds of cellulose were reasonably identical to those from cellobiose, glucose, and levoglucosan. The relative amounts of the low molecular weight compounds such as acetaldehyde, propionaldehyde, acrolein, and diacetyl increase with increasing pyrolysis temperature. The amounts of furfural decreased with increasing temperature.

The relative amounts of furfural and furan from cellulose pyrolysate are higher than those from levoglucosan. It is concluded from this that the pyrolytic degradation does not proceed through levoglucosan.

The data indicate that, in the pyrolysis of cellulose, the secondary degradation of 5-hydroxymethyl furfural to furfural plays a minor role, since the relative amount of 5-methyl furfural is much less than that of furfural from cellulose and other saccharides pyrolysates. It is also concluded that furfural, once formed from the saccharides, is relatively stable under the conditions of this experiment.

Scission of C—C bonds, formation of C═C bonds and formation of carbonyl and carboxyl groups in anhydroglucose units of cellulose appear to occur during cellulose pyrolysis. It is concluded from this that the relative amounts of low molecular weight compounds from pyrocellulose pyrolysate increase as the degradation of cellulose proceeds.

Two primary simultaneous reactions are accepted as being responsible for the volatile compounds from cellulose: (1) the initial scission of glucosidic linkages to produce radicals, and (2) chemical changes in anhydroglucose units of cellulose before scission of glucosidic linkages.

Subject Headings: *Cellulose, products of pyrolysis; Pyrolysis, products of, from cellulose.*

J. B. Howard

Lipska, Anne E. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Isothermal Degradation of Untreated and Fire Retardant Treated Cellulose at 350°C," *Report USNRDL-TR-67-89, OCD Work Unit 2531C* (September 1967)

Untreated and 2% $(NH_4)H_2PO_4$ treated alpha cellulose samples were isothermally pyrolyzed in a fluidized bath in a nitrogen environment at 350°. The overall degradation pattern for the untreated samples seems to be similar to that which was observed between 275° and 300°C. The active pyrolysis of the retardant treated cellulose was completed in less than 1.0 minute, leaving a residual weight of 34%; whereas the active pyrolysis of the untreated samples was completed in 10 minutes, yielding a residual weight of 16%. A detailed examination of the initial period of the rapid volatilization and decomposition of the untreated samples at 288°C, indicated that the rate of volatilization and decomposition was at least four times as great as that portrayed by the region in which these parameters followed a zero-order rate.

Subject Headings: *Cellulose pyrolysis; Decomposition, thermal, of cellulose; Fire retardant cellulose, pyrolysis of; Pyrolysis, of fire retardant cellulose.*

Author's Summary

Miller, D. J. and Webb, C. W., Jr. (Freeport Sulphur Co., Belle Chasse, Louisiana) "Lower Flammability Limits of Hydrogen Sulfide and Carbon Disulfide Mixtures," *Journal of Chemical and Engineering Data* 12(4) 568–569 (1967)

The authors have measured the influence of H_2S on the lower flammability limit of carbon disulfide in air over a full range of constituent concentrations. They used a modified Bureau of Mines apparatus with upward propagation at atmospheric pressure in a borosilicate glass tube 122 cm long, 5.7 cm o.d. Carbon disulfide concentrations in the experimental mixtures were determined by infrared absorption in a 1 meter gas cell incorporated in the apparatus. The method was calibrated by using two standard gas mixtures to find the absorptivity coefficient of CS_2 at 2180 cm^{-1}. The H_2S concentration was determined using gas chromatography. Ignition was by a spark across a 2 mm gap initiated just as the stopper sealing the lower end of the tube fell away. A mixture was taken as flammable if the flame travelled uniformly up 80% of the tube length.

Le Chatelier's formula was used to estimate approximately the appropriate concentrations at the flammability limit for the various gas mixtures. Determinations of flammability limits for pure H_2S and pure CS_2 in air were also made. Good agreement was found with previously reported values.

The experimental results showed a considerable deviation from the predicted flammability limits. In the region of high CS_2 to H_2S ratios there are two lower limits; also in the range 3.35 to 3.42% of H_2S two lower limits were found. The results show clearly that even trace amounts of H_2S in CS_2–air mixtures substantially raise the lower flammability limit.

Subject Headings: *Flammability, limits of, in carbon disulfide and hydrogen sulfide; Carbon disulfide, flammability of, in hydrogen sulfide; Hydrogen sulfide, flammability of, in carbon disulfide.*

M. G. Perry

Mulcahy, M. F. R., Tucker, B. G., Williams, D. J.,* and Wilmshurst, J. R. (Coal Research Laboratories, CSIRO, Chatswood, N.S.W., Australia) "Reactions of Free Radicals with Aromatic Compounds in the Gaseous Phase. III. Kinetics of the Reaction of Methyl Radicals with Anisole (Metoxybenzene)," *Australian Journal of Chemistry* 20, 1155–1171 (1967)

The authors' previous work in this series on reactions of methyl radicals with toluene and phenol showed that the methyl radical attacked these molecules by abstracting a hydrogen atom from the methyl or hydroxyl group, and that the main products were formed by combination of the resulting conjugated radical with a second methyl radical. The present investigation aimed to see whether replacement of the hydroxylic hydrogen of phenol by a methyl group would revert the kinetics to the type found with toluene, and to determine the effect on the reactivity of the methyl group by interposing an oxygen atom between it and the ring.

The reactions were conducted in a stirred-flow reactor, described in earlier papers, under conditions at temperatures between 453° and 539°K, and total pressure between 10 and 30 torr. The concentrations of methyl radicals ranged from 2×10^{-12} to 5×10^{-11} mole cm^{-3} and those of anisole from 10^{-7} to 10^{-6} mole cm^{-3}.

The reaction was found to proceed mainly by the following mechanism

$$C_6H_5OCH_3+CH_3\cdot\rightarrow C_6H_5OCH_2\cdot+CH_4 \tag{1}$$

$$C_6H_5OCH_2\cdot+CH_3\cdot\rightarrow C_6H_5OC_2H_5 \tag{2}$$

$$C_6H_5OCH_2\cdot\rightarrow C_6H_5CHO+H\cdot \tag{8}$$

In this mechanism, the formation of methane and phenetole indicated that reactions (1) and (2) occurred. The fate of the important anisyl radical, $C_6H_5OCH_2\cdot$ was investigated and discussed in good detail and reaction (8) was postulated rather than the one

$$C_6H_5OCH_2\cdot\rightarrow C_6H_5\cdot+HCHO$$

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The Arrhenius parameters for reactions (1) and (8) were:

$$\log_{10}(A_1 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}) = 11.7 \pm 0.3,$$

$$E_1 = 10.5 \pm 0.8 \text{ Kcal mole}^{-1};$$

$$\log_{10}(A_8 \text{ sec}^{-1}) = 12.5,$$

$$E_8 = 21 \text{ Kcal mole}^{-1}.$$

The last two values were based on the assumption that the kinetics of reaction (2) were similar to those of the recombination of methyl radicals.

The paper gave an affirmative answer to the first objective and the required quantitative information to the second.

Subject Headings: *Aromatics, reactions of radicals with; Radicals, reactions with aromatics.*

A. S. C. Ma

Tsuchiya, Yoshio and Sumi, Kikuo (National Research Council of Canada, Ottawa, Canada) "Thermal Decomposition Products of Polyvinyl Chloride," *Journal of Applied Chemistry* **17**, 364–366 (1967)

When plastics are involved in a fire they may yield toxic decomposition products. Some quantitative data on the decomposition products of plastics are available in the literature, but it is difficult to assess the danger from the different amounts of various products because of the absence of a suitable method of evaluation. The authors have proposed a method of evaluation based on pyrolysis followed by gas chromatographic analysis and have used it to assess toxicity from various thermal decomposition products of polyvinyl chloride. Hydrogen chloride was found to be the main toxic decomposition product.

Subject Headings: *Polyvinyl chloride, decomposition of; Pyrolysis, of polyvinyl chloride.*

Authors' Abstract

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von Engel, A. (University of Oxford, Oxford, England) "Collisions in Gases and Flames Involving Excited Particles," *British Journal of Applied Physics* **18**(12) 1661–1677 (1967)

This paper comprises a semi-quantitative consideration of energy transfer processes in systems containing excited and/or charged species. It is divided into three sections: (1) a discussion entitled "Collisions of the Second Kind," which describes a number of systems in which such energy transfer has been observed and the cross sections for these processes, when they are known or can be inferred from theoretical considerations; (2) a discourse on how the phenomena described in the previous section are thought by Professor von Engel to pertain to the "Transfer of Potential Energy in Flames;" and (3) a discussion of the relationships known or postulated between "Excited Molecules and the Electric Strength of Gases." All three sections are primarily concerned with processes involving charged species, especially free electrons. In the latter case, a collision of the second kind may be represented by the equation

$$e+A^{\dagger}\rightarrow A+e^{*} \qquad (1)$$

in which the asterisk represents excess kinetic energy, the dagger represents higher potential energy states, and A may represent any atomic or molecular species.

Probably the most significant part of the paper for people working in combustion and related areas is the section concerned with excitation and ionization in flames. Von Engel and Cozens have been suggesting for some time that ions in flames may be the product of electron impact ionization—a collision of the first kind [the reverse of Reaction (1), in which $A^{\dagger}$ becomes sufficiently excited to ionize]. The hot electrons, according to their theory, are produced via collisions of the second kind, in which case $A^{\dagger}$ may be any of the excited species commonly observed in combustion. It should be noted that the theory requires an exceptionally high electron temperature. Available preliminary evidence, which lends some support to the thesis that the electron temperature in flames is well above equilibrium, has been cited in this paper. Evidence which points to electron temperatures equal to the bulk gas temperature also exists, however, and at present it is highly uncertain whether the electrons in any given flame are equilibrated with the other flame gases. This controversy has been overlooked by von Engel and remains one of several problems which must be resolved before his theory can be properly evaluated.

Subject Headings: ***Collisions and molecular excitation; Electrons, hot in flames; Flames, hot electrons in; Particles, excited in flames and gases.***

W. J. Miller

Vovelle, C., Delbourgo, R. and Laffitte, P. (Sorbonne, Laboratoire de Chimie générale, Paris, France) "Formation of Combustion Products from Air–Ether Mixtures as a Function of Variations in the Flame Obtained and the Inflammability Regions They Describe," *Comptes rendus* **265**(17), 899–902 (1967) (In French)

Combustion of premixed gaseous ether and air at sub-atmospheric pressures is characterized by regions of normal and cool flames as well as second-stage ignitions.[1] The authors of this communication report the detection of an additional transition region between normal and cool flames. The basis for their finding is the observation of variations in product gas species with changes in reactant mixture ratio.

The present experimental study was conducted in a closed tube at reactant pressures between 150 and 350 mm Hg, and ether ($C_4H_{10}O$)-air mixture ratios between one (1) and approximately eight (8) times stoichiometric; electrical ignition was employed. Infrared spectroscopy was used to measure the principal product gas component concentrations: CO; CO_2; the three hydrocarbons: acetylene, ethylene, and methane; methanol; acetaldehyde; and unreacted ether.

Near stoichiometric mixtures, the flames are found to produce mainly CO_2. As the proportion of reactant ether is increased, to approximately 2.5 times stoichiometric, the CO_2 concentration diminishes and the three hydrocarbons species and CO become increasingly larger fractions of the product gas. The authors identify these normal flame conditions as the first domain. The second domain, or transition zone, is considered to be heralded by the observation of unreacted ether and acetaldehyde in the combustion products. Coincidently, the three hydrocarbon products exhibit their maximum concentration under this condition. The rich mixture limit of the transition zone, and the change-over to cool flames, is considered to occur when the unburned ether, acetaldehyde and methanol product species become dominant; they are virtually unchanging in concentration with further increase in fuel richness. (In contrast, the normal flame products assume relatively small fractions in this regime.) Furthermore, at the highest reactant pressure tested (350 mm Hg), a second-stage combustion process can be distinguished from cool flames by a lower concentration of unburned ether and acetaldehyde products. Thus, the authors conclude that the different ether–air flame propagation limits can be differentiated by unique product species characteristics in addition to the conventional physical parameters criteria. Similarly, the newly identified transition zone can be defined by the nature of the reaction products. Finally, a study is suggested to see if selective reactant additives could influence the ether–air reaction.

This disclosure should be evaluated as preliminary in nature. It is to be hoped and expected that a more comprehensive report supplying such desired details as reaction chamber characteristics, ignition energy, reaction temperatures, and spectroscopic technique and data analysis, will follow at an early date.

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Subject Headings: ***Combustion, products from ether-air mixtures; Ether–air, products of combustion; Products of combustion, from ether–air mixtures.***

K. M. Foreman

I. Physical Aspects of Fires

Atlas, R. A. (The Boeing Company, Seattle, Washington) "Frequency of Solar Radiation Transmission through the Atmosphere," *Report of The Boeing Company Code Identification No. 81205, Number D2-125625-1* (1968)

In order to provide a probabilistic basis for estimation of atmospheric transmission values, the cumulative frequency of hourly transmission of solar radiation has been tabulated as a function of solar elevation angle for 27 stations in the

United States. The data cover 11 years of Weather Bureau readings. Curves are provided for atmospheric transmission values that are 90, 80, 50 (median), and 20% of the average year versus solar elevation angle and for the mean or average transmission versus solar angle. The curves are for individual stations and for averages of the Southwest, Northeast, and the entire United States. Frequency distributions of the transmission are given for typical locations. The data apply to the estimation of the solar transmission associated with any assurance of occurrence at specific locations or areas of the United States.*

* See previous report by the same author. "Transmissivity of Solar Radiation through the Atmosphere,"

Subject Headings: *Solar radiation, transmission through atmosphere; Transmissivity, of solar radiation through the atmosphere.*

Author's Abstract

Bouvard, M. and Dumas, H. (Laboratories de Mécanique des Fluides, Université de Grenoble, Grenoble, France) "Study of Turbulence in a Confined Medium and the Diffusion of Solid Particles, *Comptes Rendus* 264(15) 709–711 (1967)

This note describes a method of generating and measuring turbulence in water (or liquid) in a closed container of relatively small dimensions. Suspension properties can also be measured but no results on these are reported in this note.

The container is a Plexiglass tank, approximating a cube 70 cm on a side and about half-full of water. In the bottom of the tank is a perforated plate capable of being moved up and down like a piston, with a stroke of 2 to 4 cm, a period of 6 strokes per sec, and driven by a constant speed motor through a crank. The perforations are 64 uniformly spaced holes 4.50 cm diam. This device generates the turbulence. The turbulent energy dissipated in the tank as heat is removed by a water-cooled coil in the bottom of the tank but controlled by regulators in such a way as to maintain both constant viscosity and a constant temperature in the middle of the tank, 19±0.1°C.

The turbulence characteristics are measured by a hot wire anemometer adapted for use in liquids; this was the reason for needing accurate control of temperature. Velocity fluctuations determining the turbulence are measured against a background velocity artificially created between the anemometer and liquid, since, by definition, this is zero for a stationary probe. The tip of the anemometer is rotated in a circle on a horizontal plane by fastening it to a radius arm attached to a vertical rotating spindle. The linear velocity of the probe tip can be held constant, but is adjustable in the range 70 to 150 cm/sec. The driving spindle can also be moved up and down in the vertical plane so that velocity fluctuations can be measured at various depths below the free surface of the liquid.

After perfection of the instrument by elimination of a number of (unspecified) problems, the turbulent velocity [RMS value, $(\bar{U}'^2)^{1/2}$ cm/sec] was measured at various depths below the liquid surface. It was found to vary from 6 cm/sec just below the surface rising with increasing depth on a smooth curve to 35 cm/sec near the top of the piston. The turbulent Re number was a little above 300. The results were virtually independent of the rotational speed of the probe, and of probe shape (two shapes tested).

In all, the equipment would seem to be a compact, versatile device for testing liquid anemometers and investigating certain aspects of turbulence in liquids.

Subject Headings: *Diffusion, of turbulent particles; Eddy diffusivity; Particle diffusion, turbulent; Turbulence, and particle diffusion.*

R. H. Essenhigh

Cheesewright R. (University of Michigan, Ann Arbor, Mich.), "Turbulent Natural Convection from a Vertical Plane Surface," *Journal of Heat Transfer, Transactions of the ASME* **90**(c), 1–8 (1968)

Experimental data for mean temperature and velocity profiles in a turbulent natural convection boundary layer are limited. It is surprising that such a fundamental phenomenon has not been explored in more detail. The majority of data previously available was obtained by Griffiths and Davis[1] in 1922.

The paper reports the measurement of mean temperature and velocity profiles and *local* heat transfer coefficients. A range of Grashof (Gr) numbers from 10^4 to 1.5×10^{11} was covered. Plate dimensions were 0.6×2.75 m. At the lower values of Gr the boundary layer is laminar. These measurements of the laminar case provide a check with other available experimental and theoretical results. The good agreement between the present laminar results and other measurements tends to establish confidence in the experimental technique. Both velocity and temperature were measured using fine wire platinum resistance thermometers. As the discussion at the end of the paper shows, there are subtleties involved in the measurements.

In the turbulent region the heat transfer rates agree well with existing data. Mean temperature and velocity profiles also agree reasonably well with those of other experimenters. Theoretical values of heat transfer rates predicted by Eckert and Jackson[2] tend to agree with the experimental results for $\mathrm{Gr} < 3\times10^{10}$. Below 3×10^{10} the data tend to follow the theoretical predictions of Bayley.[3] Neither of the theories provides a completely satisfactory description of observed results.

The theoretical prediction of mean temperature and velocity profiles fails to give correct maximum values. Shapes of the profiles are not satisfactory. The similarity variable $(y/x)\mathrm{Gr}^n$ is not adequate for correlating data.

Local heat transfer rates and mean temperature profiles are presented for the transitional region between laminar and turbulent boundary layers. Transition occurs in the range of Gr from 2×10^9 to 10^{10}. Prior to the present paper transitional profiles were not available.

This paper presents valuable data concerning turbulent natural convection boundary layers. It was found that the available theories are lacking in the ability to predict local heat transfer rates or the magnitude and shape of profiles. This paper forms the basis for additional theoretical work by providing detailed measurements.

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Subject Headings: ***Free convection; Heat transfer; Turbulent boundary layers.***

A. E. Fuhs

Davis, S. H.* and Segel, L. A. (The RAND Corporation, Santa Monica, California and Rensselaer Polytechnic Institute, Troy, New York) "Effects of Surface Curvature and Property Variation on Cellular Convection," *The Physics of Fluids* 11(3) 470–476 (1968)

In this paper the authors consider the stability of a motionless fluid layer of infinite horizontal extent, which is heated from below. In all previous nonlinear analyses, "free" surfaces have been idealized to be planar and stress-free. The authors take surface deflection into account and find an effect that is important when a correction to the Boussinesq approximation is necessary.

This paper shows how to take into account free surface deflection in a nonlinear stability analysis. For the problem considered, surface deflection is responsible for the appearance of a new term in the governing amplitude equations. Like the term arising from the non-Boussinesq effects considered by others this term is proportional to $\alpha_0 \Delta T_c$, where α_0 is the reference volume expansion coefficient and ΔT_c is the critical temperature difference. The effect of deflection is marked in very thin layers. In such layers, surface tension strongly influences nonlinear behavior.

The form of the amplitude equations is identical with those analyzed earlier by others. However, three new distinguished values of the Rayleigh number arise from this nonlinear stability analysis. The distinguished values of the Rayleigh number possess the following properties:

(a) For certain Rayleigh number values, although infinitesimal disturbances decay, disturbances of sufficient magnitude can grow to a steady final state consisting of hexagonal cells.
(b) For certain values of the Rayleigh number, only hexagonal cells are stable.
(c) For a certain range of Rayleigh values, rolls as well as hexagonal cells become a possible steady motion. As the Rayleigh number increases within this range, a decreasing perturbation amplitude is required to change hexagons into rolls.
(d) For Rayleigh number values greater than the range mentioned in (c) above, only rolls are stable.

Finally, the authors conclude sufficiently small perturbations must be assumed in order to guarantee validity of the theory. Quantitative experiments should reveal whether this assumption is so stringent that the theory deals only with

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very carefully controlled situations, or whether no precautions need be made to decrease the magnitude of natural perturbations inevitably present. The authors state that the relation between feasible experiments and theoretical results for an unbounded layer has received some attention by others but needs more.

Subject Headings: *Cellular convection and curvature; Convection, cellular and curvature; Curvature, and cellular convection.*

E. C. Woodward

Diamy, Anne-Marie, Ben-Aim, R., and Laffitte, P. (Laboratoire de Chimie Générale, Paris, France and Laboratoire de Chimie Physique, Parc Valrose, Nice, France) "Thermal Analysis of a Combustion Reaction," Bull. Soc. Chim. **1967**(4) 1281–1288 (1967) (In French)

The slow exothermic reaction preceeding cool flame combustion was studied on a rich mixture of *n*-pentane and oxygen ($n\text{-}C_5H_{12}+2O_2$) without and with addition of diluents (He, Ar, N_2, CO_2) in a spherical, 11 cm ∅, Pyrex reactor by means of a chromel-alumel thermocouple as time function of temperature and pressure under various initial conditions (P_0, T_0) ($275° < T_0 < 340°C.$).

It was proved that no catalytic effect resulted from the bare metal junction. Temperatures and pressures were registered with an electronic "M.E.C.I." recorder, the latter by means of mutual inductance variations of the manometer diaphragm.

Three types of curves were encountered:

(1) Slow reaction with a blunt maximum, T_m, of the order of 10°C.
(2) Cool flame with sharp maximum developing from a kink (ca. 15°C).
(3) Cool flame with sharp maximum, but without kink.

All curves show a sharp, but small, peak (ca. 5°C) corresponding to the filling of the evacuated reactor, thus marking the start of the reaction which was recorded over a period of ca. 500 sec. In all instances the decline from the main maximum is followed by a flat minimum and at least one more maximum before the initial temperature is reapproached. For the transition from type (1) to (2) a very small increase in the concentration of the reactants suffices, e.g., from 260 to 264 mm Hg, while type (3) invariably results from higher pressures. The kink is clearly the symptom of a critical condition, attained after an induction period of ca. 2 min.

The main objective of the present investigation was the critical temperature elevation, Δ, in dependence on the parameters P_0, T_0, λ (=thermal conductivity) and C_v (=heat capacity) as compared to the "preheat" of the thermal theory of explosions[1] expressed by T_0 and the energy of activation, E.

The direct determination of Δ by the kink measurement is unfortunately restricted to a small domain of T_0-P_0 curves. However, an indirect method was based on the ground that ΔT_m values of slow reaction type (1) records converge with increasing T_0 toward the limit Δ. Thus Δ is obtained by extrapolation of observed ΔT_m values as function of P_0. Both methods, where applicable, check very well. Experimental Δ-values measured in the center of the reactor are listed in Table 1. As can be seen there is an uncertainty of about ±5%. On increasing

TABLE 1

Diluent	1–2–0	1–2–3	1–2–6	1–2–12	1–2–24
He	7.5–8.5	10–11	13–14	15–16	18.5–19.5
N_2		7.5–8.5	8–9	7.5–8.5	6.5–7.5
Ar		6.25–6.75	6.25–6.75	6–6.5	5.5–6
CO_2		6.5–7.5	6.5–7.5	6.25–6.75	5.75–6.25

the diluent concentration. Δ rises strongly with He—, i.e., from 10° to 20°C. Δ passes through a flat maximum with N_2 dilution. Δ decreases slightly with Ar, and a little more with CO_2. The authors also report that the effect of diluents on Δ is opposite to that on ΔT_m, except for CO_2.

For comparison of the experimental values with predictions from the theory of thermal explosions[1] the authors utilize the equation:

$$\Delta = fRT^2_{0k}/E \qquad (T_{0k} = {}^\circ\mathrm{K}) \tag{1}$$

where $f=1$ or 1.61 for convective or conductive heat transfer, respectively, and where $E=40$ kcal is taken from the work of Lucquin.[2] The values listed in Table 1 are reported to be invariably and distinctly smaller than calculated with $f=1.61$. Surprisingly better agreement is obtained with $f=1$, although the possibility of convective heat exchange is excluded by the existence of a temperature gradient, as ascertained by temperature measurements half-way between wall and center of the reactor.

The most probable cause of deviations is the contribution to heat generation by wall reactions. This possibility is certainly not excluded. For temperature measurements inside, the reactor very close to the wall revealed excess temperatures of 1° to 2.5°C.

On the basis of Table 1, and presumably guided by the described considerations the authors arrive at the conclusion: "Since Δ varies with nature and concentration of the diluent it depends on thermal properties of the reactant medium in a way not foreseen by the thermal theory."

However this statement cannot be unreservedly accepted. For if

$$T_{0k} = (\Delta E/Rf)^{1/2} \tag{2}$$

is substituted in Frank-Kamenetzki's[3] critical condition one obtains:

$$\frac{fr^2Qka\exp-(fE/R\Delta)^{1/2}}{\Delta N\lambda} = \delta_{cr} \tag{3}$$

Hence, it becomes clearly evident that the thermal theory predicts an increase of the preheat with increase of thermal conductivity. Nevertheless, in view of the fact that the pyrolysis of n-pentane represents one of the classical examples of chain reactions[4] there can be little doubt that the partial oxidation of this hydrocarbon involves similar characteristics. In other words, the simple thermal theory is not applicable. The authors deserve credit for having pointed to the need of a more comprehensive theory.

References

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Subject Headings: ***Combustion, thermal analysis of, Thermal analysis, of combustion.***

H. M. Cassel

Fohl, T. (Mt. Auburn Research Associates, Inc., Cambridge, Massachusetts) "Turbulent Effects in the Formation of Buoyant Vortex Rings," *Journal of Applied Physics* **38**(10) 4097–1098 (1967)

The author discusses the process in which a mass of buoyant fluid released from rest forms a buoyant vortex ring. Literature cited by the author pertains to the motion of a fully formed buoyant vortex ring. He discusses the factors which relate the parameters of such literature to the initial size and buoyancy of a mass of fluid released from rest.

If the deformation of a spherical mass of buoyant fluid into a vortex ring proceeded in a regular and reproducible way, the parameters of the vortex ring could be readily predicted from the initial conditions. However, turbulent eddies occurring during ring formation introduce a random factor in the ratio R_1/R_0 which is difficult to predict. Here, R_0 is the radius of the original buoyant sphere and R_1 is the radius of the vortex ring at the end of the formation phase. The effect of eddies is to increase the radius of the vortex ring over the radius which it would have if the formation took place with no random eddies present.

The random factor which causes the variations of vortex ring characteristics from release to release is contained in L. The length L is a length characteristic of size of the eddies which protrude from the envelope of the evolving vortex ring. The length L is roughly the size of the larger eddies although no well-defined relationship exists which connects L with measurements of eddy size. The eddy size depends sensitively on the size of irregular motions of the buoyant fluid at the moment of release as well as on the densities of the buoyant fluid and the surrounding fluid. The uncertain nature of the occurrence and growth of these eddies results in large variations in the characteristics of vortex rings formed by the release of buoyant fluid, even when the original conditions of density and size are kept constant. Since there is no relation which connects a measurement of eddy size to a value of L, the author is limited to the qualitative statement that the larger the eddies, the larger L, and hence the spreading coefficient will be. Because eddies occur in a random way, a series of releases in which larger eddies occur will show larger variation in the spreading coefficient from release to release as well as a larger average value of the spreading coefficient.

In order to test these ideas the author carried out a series of model experiments. A mass of light gas mixed with smoke was released and its motion recorded by photographing it against a grid with periodic light flashes and an open shutter camera. Measurements of size and position as a function of time were made from the resulting photographs. The buoyant gas was released by bursting a soap bubble containing the mixture. The author used a very light gas consisting of a helium-air mixture in the hope that the motion would be stable against Rayleigh-Taylor instabilities when circulating, and that a smoother flow would result. This stabilization apparently was effective in that the very light rings proved less turbulent than those formed of a heavy gas released by a bubble and allowed to drop.

Without an independent measure of the size of the eddies, the author concluded it is not possible to test the theory of buoyant vortex ring production rigorously. However, he concludes the qualitative results of experiments tend to follow the theoretical predictions.

Subject Headings: *Buoyant vortex rings and turbulence; Turbulence, effect on vortex rings; Vortex rings, and turbulence.*

E. C. Woodward, Jr

Law, Margaret (Joint Fire Research Organization, Boreham Wood, England) "Radiation from Fires in a Compartment," *Joint Fire Research Organization Technical Paper No. 20* (1968)

Intensities of radiation from fires in a compartment have been measured, both from the windows and from the emerging flames. The emitted intensity depends on the fire load in the compartment and on the ventilation area. The flame radiation is in general small compared with the window radiation and although for the highest fire load and the smaller window area used in the experiments the flames have a significant increase in radiation, this was not large enough to warrant recommending any increase in separation distances between buildings, which have been based on window radiation only.

When the intensity reaches its maximum value the compartment can be assumed to be a black body. The average intensity of radiation shows the same relationship with rate or burning per unit window area as found in other experiments. Thus, intensity of radiation and compartment temperature can be predicted for other compartments.

Subject Headings: *Compartment fires, radiation from; Fire radiation, from compartments.*

Author's Summary

Melvin, A. (Gas Council Basic Research Group, Fulham Works, London, England) "Transient Convective Heat Transfer from Gaseous Explosions," *British Journal of Applied Physics* **18**, 1783–1786 (1967)

In this paper the rate of cooling of an explosive gas mass is studied, starting from the time that the explosion process has been completed.

The process was first investigated experimentally in the following manner. A hydrogen-air mixture contained in a Pyrex vessel of 2.4 cm diameter and 33.25 cm length was ignited by an axially located hot wire. The subsequent temperature distribution was determined by means of an interferometer. A helium-neon laser was used as a light source and the light beam was directed through the gas mixture in a direction parallel to the axis. Readings were obtained at time intervals of about 1/250 sec. The interferometric figures were clear and undistorted, indicating good radial symmetry as well as the absence of turbulence. The experimental results are represented in the form of the temperature ratio $(T-T_0)/(T_1-T_0)$ as a function of r^2/a^2 (T_1=axial temperature at time $t=0$; T_0 is the temperature to which the gas will cool asymptotically; r=radial position; a=tube radius). For these coordinates the experimental results at each given time form a fairly straight line. At $t=0.036$ sec the temperature ratio at the center is about 0.92 and decreases to 0.78 at $r^2/a^2=1.0$. At $t=0.384$ the corresponding numbers are about 0.35 and 0.30.

To aid in the interpretation of the results a simple analytical approach was undertaken in which the cooling process was assumed to take place by conduction only, and any contributions by convection were taken into account by defining an "effective" conductivity, which in addition was assumed to be constant throughout the volume.

By comparing the results of the analysis to the experimental data it may be concluded that the analytical model represents the actual cooling process fairly adequately. The "effective" thermal diffusivity was 4 to 5 times that of the "true" diffusivity. Also for the problem under investigation, the boundary conditions rather than the diffusivity itself were the governing factor in determining the cooling rate.

Subject Headings: ***Explosions, transient heat from; Heat transfer, transient, from explosions; Transient heat transfer, from explosions.***

R. H. Sabersky

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van Tiggelen, P. J. and Duval, A. (University of Louvain, Louvain, Belgium) "The Concept of a Mean Temperature in the Flame Reaction Zone," *Bulletin de l'Académie r. de Belgique, Classe de Sciences* **53**(4) 326–365 (1967)

This paper presents a theoretical study of the concept of mean temperature in the flame reaction zone. The theory is based on the kinetic theory of gases. A homogeneous reactor model is used for representing the flame front. The mean temperature T_m in the reaction zone is obtained from the assumed form

$$T_m=T_i+\sigma_m(T_f-T_i)$$

where σ_m is the mean temperature coefficient, T_i and T_f represent respectively the temperature of initial and burned gases. The mean temperature coefficient is determined from the following equation by taking the average of a function which describes the combustion process.

$$[T_i+\sigma_m(T_f-T_i)](1-\sigma_m)^n \exp(-E/\{R[T_i+\sigma_m(T_f-T_i)]\})$$
$$=(1-\sigma_{\text{inf}})^{-1}\int_{\sigma_{\text{inf}}}^{1}[T_i+\sigma(T_f-T_i)](1-\sigma)^n \exp(-E/\{R[T_i+\sigma(T_f-T_i)]\})$$

where E is the over-all activation energy, n the over-all reaction order, σ_{inf} the inflection point of the curve $f(\sigma)$ which represents the integrand in the above equation. The values of σ_{inf} and σ_m are computed and tabulated for different values of E, n, T_f and T_i with $n=1$ and 2, E varied from 10 to 60 kcal/mole over steps of 5 kcal/mole, T_f from 1800° to 2700°K over steps of 100°K and T_i from 300° to 650°K over steps of 50°K.

To determine the over-all activation energy E from the experimental data of T_f, T_i, burning velocity v_0 and flame front thickness e_s, two methods were proposed.

1. In the preheating method, let flames propagate in an identical mixture with different initial temperature. E is estimated from the following equation

$$\log v_0+\tfrac{1}{2}\log T_m-\tfrac{1}{2}n\log(1-\sigma_m)=k'-(0.4343E/2RT_m)$$

where k' is a function of the mole fractions of reactants.

2. In the dilution method, let flames propagate in a mixture with the same fuel-oxidizer ratio but different amounts of inert diluent. E is obtained from

$$\log v_0+\tfrac{1}{2}\log T_m-\tfrac{1}{2}n[\log x_0+\log(1-\sigma_m)]=k''-(0.4343E/2RT_m)$$

where x_0 is the total mole fraction of the reactants, k'' function of the mole fractions of reactants.

Subject Headings: *Deflagration flame, mean temperature; Flame reaction zone, mean temperature; Flame temperature, kinetic theory.*

S. J. Ying

Willis, G. E. and **Deardorff, J. W.** (National Center for Atmospheric Research, Boulder, Colorado) "Development of Short-Period Temperature Fluctuations in Thermal Convection," *The Physics of Fluids* **10**(1) 931–937 (1967)

This paper describes an experimental investigation of the temperature fluctuations which occur when horizontal plates are maintained at a fixed temperature difference.

The investigation was carried out using four substances whose Prandtl Numbers varied over a significant range: air (0,71), water (6,8), two grades of Dow Corning 200 (18 and 57). The temperature fluctuations were determined by a single thermocouple located midway between the plates.

The temperature fluctuations measured fall into there categories: no fluctuations, intermittent fluctuations, and irregular fluctuations. The transition point in going from one regime to another was determined as a function of the Rayleigh number for the four different fluids. Both transition points were found to be a strong function of Prandtl number. The first transition point, Rayleigh number, Ra′, which marks the outset of intermittent turbulence, is increased from 5.5×10^4 to 1.5×10^5 when the Prandtl number is increased from 0.71 to 57. The second transition point Rayleigh number, Ra″, which marks the outset of irregular turbulence increased from 1.1×10^4 to 1.4×10^6 for the same change in Prandtl number.

The spectra of the temperature fluctuations were determined from a direct Fourier analysis for each case. The analyses show that low frequency fluctuations occur at lower Rayleigh numbers, but that the high frequency fluctuations suddenly appear at the transition points given above.

Since it was found that the first super-critical heat-flux transition of Malkus, which occurs at a Rayleigh number of approximately 8200, is independent of Prandtl number it can be concluded that the two phenomena are not directly related.

Subject Headings: *Fluctuation in temperature, in thermal convection; Temperature, fluctuations in thermal convection; Thermal convection, temperature fluctuation in.*

F. R. Steward

Woodruff, L. W. (Lockheed Missiles and Space Company, Sunnyvale, California) **and Giedt, W. H.** (University of California, Davis, California) "Heat Transfer from a Partially Dissociated Gas with High Lewis Number," *Journal of Heat Transfer* 88(4) 415–420 (1966)

Although a number of heat transfer measurements have been performed for dissociated gases, the gas mixtures were usually such that the Lewis number was close to unity. The working fluid in the present case consisted of the products of combustion of a 1:1 mixture of oxygen and acetylene. For this working fluid atomic hydrogen is the principal component which, by diffusion, influences the total heat transfer. Based on this diffusional process the Lewis number (defined here as $D\rho c_p/k$) is approximately equal to three.

In order to aid in the interpretation of the test results an approximate analysis of the problem was performed. An effective Prandtl number was defined as

$$P_r' = P_r\{1+(L_e-1)[(h_{D_e}-h_{D_w})/(h_e-h_w)]\}^{-1}$$

where L_e is the Lewis number corresponding to the diffusion of atomic hydrogen, h_D is the enthalpy change due to dissociation, and h is the absolute enthalpy. The subscripts e and w refer to the free stream and the wall, respectively. It is then shown that the ratio of the heat transfer rate for $L_e=1$ ($q_{L_e=1}$) to that at an arbitrary value of $L_e(q_{L_e\neq1})$ is given by

$$q_{L_e\neq1}/q_{L_e=1} = (P_r/P_r')^{2/3}$$

The experiments were conducted by letting the combustion gases flow over a molybdenum plate. Thermocouples were installed in the center of the plate. The free stream temperature was obtained by the sodium line reversal method and the enthalpies were calculated from this information. Experiments were conducted for plate temperatures from 2000° to 3500°R. The free stream temperature was between 5200° and 5800°R.

The results are presented in a graph of $Nu'/(P_r')^{1/3}$ vs x/δ, where δ is the dynamic boundary layer thickness and Nu' is defined as $q \times P_r'/\mu(h_w - h_e)$. The experimental points lie within a few per cent of the analytically predicted line which starts at the origin and goes through a point given by $Nu'/(P_r')^{1/3} = 60$ and $x/\delta = 30$. A graph of $q_{L_e \neq 1}/q_{L_e=1}$ vs $(h_{D_e} - h_{D_w})/(h_e - h_w)$ shows the experimental point grouping around the curve for $L_e = 3.0$, with a scatter of about $\pm 7\%$. The graph also shows that an increased heat transfer rate has to be expected for the higher Lewis numbers. At an enthalpy ratio of 0.4, for example, the heat transfer rate for $L_e = 3.0$ is about 50% above that expected for $L_e = 1.0$.

Subject Headings: *Dissociation of gases, with high Lewis number; Gases, dissociated, with high Lewis number; Lewis number, in dissociated gases.*

R. H. Sabersky

J. Meteorological Aspects of Fires

Colón, José A. (U.S. Weather Bureau, ESSA—Environmental Science Services Administration) "Air Pollution Meteorology and Transport of Pollutants," *Discussion Presented at Community Air Pollution Seminar, Hotel San Cerónimo Hilton, San Juan, P.R.* (February 7, 1966)

José Colón developed this discussion for a seminar on air pollution at San Juan, Puerto Rico. The paper is basically in two parts. The author presents general principles that are important in the diffusion and transport of pollutants and then discusses meteorological factors of Puerto Rico which would influence the diffusion and transport of pollutants generated in their atmosphere. He limits his discussion to the characteristics of transport and diffusion of pollutants once they enter the atmosphere and deliberately avoids the mathematics of diffusion and transport.

The factors generally characterizing the atmosphere and producing what we know as weather conditions are temperature, pressure, humidity, visibility, wind direction and speed, types and amounts of clouds, and various forms of precipitation. The main concern in pollution problems is the diffusion of materials produced because of man's activities. The degree of the pollution problem is dependent upon the amount and the properties of the pollutants and the existing weather conditions.

The author indicates that wind is the main element in diffusion and transport so the basic problem to be considered is wind or the lack of it. Atmospheric elements like humidity, sunlight, or temperature are important because of their possible effect on the properties of the pollutants by chemical reactions as well as their influence on air motion.

The main area of concern is in the immediate vicinity of the earth's surface; therefore, it is important to study the structure and behavior of air motion in the layer near the surface. One of the most important physical factors at the surface is friction and because we are generally not dealing with a flat surface it is difficult to treat this problem mathematically.

The atmosphere has a great facility for dissipating pollutants because air is always in motion. Air motion can be considered by scales such as hemispheric systems, cyclonic systems, and also in a smaller scale of several kilometers on down to the scale of molecular activity. Air motions in the larger wind scales are responsible for the transport of properties. Air motion near the surface, because of friction, is generally turbulent flow. Turbulence enhances diffusion. Man-made and topographic obstacles generate mechanical turbulence, which also influences diffusion.

Pollution is most dangerous when it is concentrated near the living zone surface. Ideal conditions allow the pollutants to spread out and upward to diffuse into larger scale and to be transported away from the origin.

Vertical motions are generated by thermal gradients, generally thought of as stability of the atmosphere. Atmospheric stability will control the vertical dispersion of pollutants and therefore is a prime factor in diffusion of pollutants.

The author discusses the development of inversion layers and why they are important as a weather system inhibiting diffusion. Inversions occur mostly at night and in winter when the overlying surface is cooled by radiation. Weather conditions conducive to severe air pollution are characterized by calm or very light wind or stable air near the surface or at some distance above the surface. Clear air at night tends to increase the chance of inversion while a cloud deck may inhibit the formation of inversions.

In Part 2 of his paper, the author discusses the weather patterns of Puerto Rico. Puerto Rico is situated in the region of the trade winds. It experiences a steady and persistent wind system blowing from an easterly direction. A most important factor of the surface winds of Puerto Rico is the sea breeze. This system is strictly thermal and is produced by differences between radiative properties of a land and a sea surface. Tables and figures which describe typical Puerto Rican weather are presented.

The author summarizes that in approaching the problem of air pollution at a given locality one needs to examine the prevailing wind flow over the whole region; then a study of day-to-day variations which are likely to occur must be considered. The characteristics of the flow in the immediate vicinity of concern should be carefully examined. Topographic features and physical obstructions as well as bodies of water are factors to be taken into consideration.

Subject Headings: *Meteorology, and transportation of pollutants; Pollutant transportation.*

A. P. Brackebusch

Fuquay, D. M., Baughman, R. G., Taylor, A. R., and Hawe, R. G. (Northern Forest Fire Laboratory, Intermountain Forest and Range Experiment Station, U.S. Forest Service, Missoula, Montana) "Characteristics of Seven Lightning Discharges That Caused Forest Fires," *Journal of Geographical Research* **72**(24) 6371–6373 (1967) (Letters)

This paper reports on the characteristics of fire setting lightning discharges. The evidence from seven carefully documented cases supports the hypothesis that lightning fires are caused by discharges with long-continuing currents.

The only previous documentation of this kind was in 1958, when both the discharge and its ignition effects were recorded for two discharges, both of which were long-continuing currents.

Definitive field study of lightning discharges has been limited in the past. This is not surprising, when the well-known uncertainty of time and location of discharges, and the difficulty of obtaining significant measurements, is taken into account.

The authors describe the techniques used. An aerial observer in a small plane flew a short distance ahead of the storm and undertook to identify the location of the tree or other ground terminal of each cloud to ground discharge. He was able to do so in seven cases out of thirty observed discharges. Data on each discharge were recorded by lightning sensors at a nearby recording station. These consisted of fast and slow field change meters and a nondirectional luminosity device. In addition each lightning discharge was photographed by a 35 mm camera operated by an electrostatic triggering device.

The fast and slow field change sensors differ only in the grid resistor which establishes a time constant of 5 msec for the fast antenna and 5 sec for the slow antenna. The output of the sensors was recorded on a 7-channel tape recorder.

Data obtained in this way for the seven fire setting discharges showed at least one long-continuing current phase exceeding 40 msec duration in each case, with a maximum of 282 msec. The amperage was quite variable ranging from 25–298. The average value of the continuing current was 158 amps over an average interval of 203 msec. Although this is a small sample, the fact that all seven cases are consistent in showing a persistent current, gives strong support to the thesis that lightning fires *are* caused by a special type of lightning discharge.

Subject Headings: *Fires, forest and lightning; Forest fires, and lightning; Lightning, and forest fires.*

A. A. Brown

Loeb, L. B. (University of California, Berkeley, California) "The Mechanisms of Stepped and Dart Leaders in Cloud-to-Ground Lightning Strokes," *Journal of Geophysical Research* **71**(20) 4711–4721 (1966)

The basic mechanism of the cloud-to-ground stroke has never been clearly delineated. The tendency to compare the usual stroke to the common spark between metal electrodes is illusory. The usual cloud-to-ground stroke originates within the cloud. It lowers a negative charge from a cell of some square kilometers in area and of the order of 4 km or more high, over a path from cloud base to ground that is frequently more than 3 km long. As far as the author knows, the precise problems concerning formation of this channel, drainage of the cloud mass, and maintenance of channel conductivity have not been previously formulated. He lists them in the form of seven questions with answers from hypotheses which utilize the recent observations of several investigators.

(1) How does the charge stored on raindrops in cubic kilometers of cloud funnel down to the stepped leader channel of at most a meter or so in diameter, in order to discharge from 0.3 km to perhaps 1.3 km height of charge in the negative cell per stroke?

(2) How is the discharge which appears to start upward from the small + charge in the convective base of the cloud, able to forge into rain-free, clear air below the cloud base and continue as a stepped leader stroke with nearly constant diameter to the ground?

(3) What causes stepping?

(4) How is conductivity maintained in the channel forged by the stepped leader over the tens-of-milliseconds progress of the leader to the ground? To sustain a conducting channel requires a ratio of field strength to pressure of 30 volts/(cm× torr) to sustain a conducting channel. Such a ratio entails a potential of 7×10^9 volts for a 3-km-long channel if one treats the channel as a continuous gaseous conductor? Such potentials do not occur in nature, the observed limit being at most an order of magnitude less.

(5) How is it that the stepped leader stroke shows a channel diameter of some 1 to 3 m photographically and yet the intense core at some 30,000°K of the channel illuminated by the return stroke is but some millimeters, and the larger conducting mantle of the return stroke is of the order of some 3 to 4 cm in diameter as indicated by fulgarites and bonnets?

(6) Why is the stepped leader channel zigzagged in its path to the ground?

(7) What starts the dart leader and how is a low-conductivity channel maintained for the tenths of seconds between return strokes?

Subject Headings: *Clouds, and lightning; Dart leaders, in lightning; Lightning, mechanism of.*

W. G. Morris

Warner, J. and Twomey, S. (Radiophysics Laboratory, CSIRO, Sydney, Australia) "The Production of Cloud Nuclei by Cane Fires and the Effect on Cloud Droplet Concentration," *Journal of the Atmospheric Sciences* **24**, 704–706 (1967)

The authors report that droplet concentration measurements made in warm cumuli near Bundaberg, Queensland, in November 1964 contained concentrations some 5 to 10 times higher than previously observed in the same area in maritime air. At the time, they considered it reasonable to attribute the high concentration to the presence of cane fire smoke over the area. This was the first time that cloud studies coincided with cane surgar harvesting season.

In November 1966 the second series of observations were made to test the hypothesis that cane fires contributed the higher number of nuclei for the formation of droplets in warm cumuli. Measurements were made on 5 days, both offshore and inland, when the wind at sub-cloud layer was between northeast and southeast. This was planned so that the seaward observation area was not contaminated directly by smoke from the cane fires. Landward observations were some kilometers downwind when cane fires were present but never directly within a visible smoke plume. The smoke was judged to be uniformly distributed up to cloud base levels over many tens of kilometers in the observation region. Clouds were normally less than 2 km deep and on only one day exceeded 3 km. They were always wholly warmer than zero degrees centigrade.

Air samples were collected below cloud base or when a selected cloud dissipated and samples were collected from a nearby similar cloud. Three liters of air were collected and stored, and then later subjected to various supersaturations in a thermal diffusion chamber. From determinations of active nuclei vs supersaturation the droplet concentration which would occur in a given updraft was computed.

Cloud droplet concentration varied greatly even at the same level within the cloud but the mean droplet diameter stayed quite constant. In spite of wide variations from slide to slide, the landward and seaward samples were quite different.

The lowest daily concentration found in the landward area was higher than the highest daily average found in the seaward area. The authors plot the means of observed droplet concentration in a table.

Next, the authors attempted to determine if burning cane sugar could account for the concentration of nuclei apparently present in the atmosphere downwind of the canebrake. Small samples of dry sugarcane were burned in a silica crucible in a laboratory room. Based on the tonnage of sugarcane available for burning and the laboratory results, the authors concluded that there was no real difficulty in accounting for the high concentration of nuclei observed over the land.

They concluded that smoke from cane fires contaminated areas of many tens of thousands of square kilometers and indicated that one might anticipate that production of rain might be retarded by the coalescent processes. They indicated that a later paper will examine that possibility.

Subject Headings: *Cane fires, cloud nuclei from; Droplets, in clouds from fire nuclei; Nuclei, of clouds, from fires.*

A. P. Brackebusch

Wright, J. G. and Beall, H. W. (Forest Fire Research Institute, Ottawa, Canada) "The Application of Meteorology to Forest Fire Protection," *Technical Communication No. 4, Imperial Forestry Bureau, Oxford* (1965) *Reprinted ODC 431.1:431.5, Information Report FF-X-11* (February 1968)

This is a reprint of an excellent review article. The material is somewhat dated since original publication was in 1945. It is still worthwhile reading for the non-specialist.

Subject Headings: *Forest fires, and meteorology; Meteorology, and forest fires.*

R. M. Fristrom

K. Physiological and Psychological Problems from Fires

Pryor, A. J., Fear, F. A., and Wheeler, R. J. (Southwest Research Institute, San Antonio, Texas) "Mass Fire Life Hazard," *Final Report under Contract No. NOO228-67-CO-838, OCD Work Unit 2537A* and *NRDL-TRC-68-23* (March 1968)

An experiment program was conducted to determine the significance of human exposure to combinations of four variables found within a mass fire environment. The four variables of temperature, oxygen, carbon monoxide, and carbon dioxide were studied, individually and in combinations of two and three variables.

In this initial effort to further define the significance of human exposure to combustion products, a series of animal exposures was conducted. Adult Swiss albino mice in groups of ten were used in each exposure test, and each test was limited to a maximum of 4 hours. The number of mice fatalities and the time of their death were recorded during a 4 hour (maximum) exposure period study. The animals that died in each test were grossly examined, and tissues were shaved from the first and last to die in each individual exposure. These tissues were then preserved in paraffin with a percentage of the tissue used in the preparation of microscopic slides for detailed study.

Analysis of the data indicates the significance of four variables when encountered in combination of two or three at a time as compared to exposures of one or two at a time. These exposures to combined variables indicated that levels which were not lethal during the 4 hour exposure period in uncombined form became lethal when combined. A further reduction was noted when three variables were combined in such a manner that any two variables from a minimum lethal combination of three variables would not produce death. In general, these results were consistent throughout the report, except for some carbon monoxide data that did not follow a general pattern.

Gross examination of the animals killed did not reveal lesions; however, generalized congestion was present. Histopathological examination of the slides prepared from the tissue taken from a cross section of the tests revealed these conclusions: The degree of congestion was found to be similar, irrespective of the time of death. And this finding suggests that the end result of all tests was a disruption of the thermoregulatory center in the brain. This was probably due to an anoxic effect which caused all the animals to have an elevated temperature and circulatory collapse at the time of death.

Subject Headings: *Combustion products, fire hazards; Life hazard, mass fires; Toxicity of fire, survival criteria.*

Authors' Summary

Thorne, P. F. (Joint Fire Research Organization, Boreham Wood, England) "A Review of the Toxic Properties of Some Vaporizing Liquid Fire Extinguishing Agents," *Joint Fire Research Organization Fire Research Note No. 659* (April 1967)

The toxic properties of six well-known vaporizing liquids have been compared with those of carbon dioxide and nitrogen, having regard to their relative extinguishing properties. Criteria for the choice of vaporizing liquids have been suggested.

Subject Headings: *Fire extinguishing toxicity. Toxicity, of fire extinguisher.*

Author's Summary

Williams-Leir, G. (National Research Council of Canada, Ottawa, Canada) "Multiple Regression Analysis of Fire Deaths from Burns," *National Research Council of Canada Building Research Note No. 58* (March 1967)

A multiple regression procedure for investigating relations between associated variables is described. Besides statistical criteria, prior knowledge and the simplicity and usefulness of the result are taken into account. The procedure is illustrated by an analysis of survival of burn victims in Ontario.

Subject Headings: *Burns, deaths from, in Ottawa; Deaths, from burns, in Ottawa.*

Author's Abstract

L. Operations Research, Mathematical Methods, and Statistics

Crowley, J. W., Smith, B. R., Avise, H. J., and Whitney, N. G. (System Sciences, Inc., Bethesda, Maryland) "Firefly—A Computer Model to Assess the Extent of Nuclear Fire Damage in Urbanized Areas," *OCD Contract DAHC-67-C-0147, Work Unit No. 1614B* (May 22, 1968)

A computer model called *Firefly* has been developed and written in FORTRAN IV for the CDC 3600. This model may be applied to obtain statistical data on the expected numbers of buildings destroyed by fire from the thermal pulse of a hypothetical nuclear weapon and from any subsequent urban fire spread. Many variables concerning numbers and sizes of buildings, their construction, and separation distances may be evaluated.

Subject Headings: *Computer model, urban fire spread; Firefly, model for fire damage; Urban fires; Fire models; Fire spread, in urban fires.*

Authors' Abstract

Fry, J. F. (Joint Fire Research Organization, Boreham Wood, England) "Fires in Post-War Multi-Storey Flats in London, 1965," *Joint Fire Research Organization Fire Research Note No. 674* (March 1968)

Records of fires in post-war multi-storey flats attended by the fire brigades in London are examined from time to time to see whether these buildings present exceptional fire risks.

Apart from fires in dust chutes the rate of incidence of fire in the flats is lower than that in dwellings as a whole.

There is no evidence that the fires experienced in the flats are more dangerous than those in other dwellings and the building standards appear to be satisfactory in preventing the spread of fire.

Subject Headings: *Apartment fires, London 1965; Multi-storey flats (see Apartment); Statistics, apartment fires in London 1965.*

Author's Summary

Hogg, Jane M. (Joint Fire Research Organization, Boreham Wood, England) "The Relative Fire Frequency of Different Industries in Great Britain," *Joint Fire Research Organization Fire Research Note No. 681* (1968) *Revision of Fire Research Note No. 558* (1967)

This is a statistical study of fire frequency as related to industrial techniques.

Subject Headings: *British industry, fire frequency ranking; Fire, frequency in British industry; Industrial fire frequencies, in Britain.*

R. M. Fristrom

Labes, W. G. (IIT Research Institute, Chicago, Illinois) "Fire Department Operations Analysis," *Final Report under Contract No. NOO22867CO701, OCD Work Unit 2522F* (January 1968)

Studies of fire department operations were conducted as part of Contract OCD-OS-62-210, "An Approach to Trans-Attack Fire Suppression in Urban Areas." Twenty-seven fires were investigated.

Fire department operational research studies were conducted and an interim technical report was issued on Contract No. N228(62479)69031, OCD Work Unit 2522F, "Fire Department Operations Analysis".* The interim report covered the first year of a two-year study; analysis of the results and conclusions were drawn from the data on 73 fires.

This present work is an extension of the previously conducted fire department operational studies. Sixty-one fire reports have been compiled and analyzed during the present study, including the collection of more complete information on the use of manpower during fire fighting operations. This report includes the data on 61 fires from this work, as well as the data on 73 fires from the previous studies; analysis of the results and conclusions are drawn from the entire body of data on 134 fires. This final report covers the results of a two year study; the work included in the interim report has been refined and extended.

Data taken from the fire reports permits an evaluation of fire fighting operations as carried-on in the field under a variety of conditions. This body of data, together with its various trends and correlations, has been studied with a view toward developing greater efficiency in the use of water for fire control and extinguishment, and in the use of manpower and equipment at the time of a nuclear emergency.

The report submitted on each fire included in this analysis provides a relatively complete time history of the fire from ignition (where possible to estimate) to the beginning of fire fighting operations, through control to final extinguishment and overhaul. Individual fire reports were prepared by two professional fire department chief officers, and one fire protection engineer who gathered information through actual observations at the fire scene, and subsequent interviews with the fire department officers involved in suppressing the fires. An attempt was made to obtain a good cross-section of fire operations by choosing various types of occupancy, sizes of city, types of construction and magnitude of the fires.

For the purpose of analysis and correlation, the primary body of data has been divided into two groups. One group consists of 64 fires which occurred in buildings with residential occupancies, including four of the five hotels. The other group consists of 63 fires which occurred in buildings housing other than residential occupancies, and is referred to as nonresidential fires. Seven fires were excluded because their fire areas were too large to be classified within their respective groups.

Within each group of fires, correlations of essential variables with respect to fire area were obtained. Postulating certain fire brigade teams operating during the post attack period of a nuclear emergency, the number of such teams required to "knockdown" fires of various sizes was estimated. As a function of the time after the initial flashover area, a method of estimating the fire area in buildings was presented.

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* *Fire Research Abstracts and Reviews* 7, 119 (1965).

TABLE 1
Residential building fires

Fire area A_2 ft²	Water app. rate Q GPM	Control time T_c min.	Quantity of water W gallons	Man hours for control MH	Manhours for final ext. and overhaul MH	Number of brigade teams for knockdown			
						Type A 60 GPM/Team	Type B 80 GPM/Team	Type C 150 GPM/Team	Type D 500 GPM/Team
100	49	15	400	8	8	1	1	—	—
200	96	15	760	8	9	2	2	—	—
300	142	16	1060	9	10	3	2	1	—
400	186	16	1360	9	11	3	3	2	—
500	227	17	1660	10	13	4	3	2	1
750	324	18	2410	12	15	6	4	3	1
1000	410	19	3160	13	19	7	5	3	1
1250	485	20	3910	15	21	8	6	4	1
1500	550	22	4660	16	24	9	7	4	2
1750	600	23	5410	18	26	10	8	4	2
2000	640	24	6160	19	29	11	8	5	2
2250	670	25	6910	21	32	11	9	5	2
2500	690	27	7660	22	35	12	9	5	2

TABLE 2

Non-residential building fires

Fire area A_2 ft²	Water app. rate Q GPM	Control time T_c min.	Quantity of water W gallons	Man hours for control MH	Man hours for final ext. and overhaul MH	Number of brigade teams for knockdown			
						Type A 60 GPM/Team	Type B 80 GPM/Team	Type C 150 GPM/Team	Type D 500 GPM/Team
500 or less	207 or less	44 or less	35,500 or less	49 or less	29	4 or less	3 or less	2 or less	1
1000	410	51	43,000	50	31	7	5	3	1
2000	790	56	58,000	54	36	13	10	5	2
3000	1140	61	73,000	58	41	—	14	8	3
4000	1470	66	88,000	62	46	—	—	10	3
5000	1780	71	103,000	66	51	—	—	12	4
6000	2050	76	118,000	70	56	—	—	14	4
7000	2300	81	133,000	74	61	—	—	—	5
8000	2530	86	148,000	78	66	—	—	—	5
9000	2730	91	163,000	82	71	—	—	—	6
10000	2900	96	178,000	86	76	—	—	—	6

Significant Findings

1. Within each category, residential and non-residential, it is possible to represent the frequency of occurrence versus fire area in terms of statistical parameters. However, the sampling procedure used eliminated both very large and very small fires from consideration, and any conclusions drawn from statistical analysis would not necessarily be valid for the overall situation. (See Tables 1 and 2).

2. Correlations have been obtained between the maximum floor area involved by fire and the following variables

Water application rate density for fire control
Water application rate for fire control
Quantity of water used for control
Fire control time
Man-hours expended for rescue through extinguishment
Man-hours expended for salvage and overhaul

3. Water application rate densities used by fire departments to control real fires are about twice those reported by various investigators for control of experimental fires.

4. Fire brigade teams with selected water application rate capabilities are postulated and designated as Types A, B, C and D. The number of these types of brigade teams required for "knockdown" of fires of various sizes is indicated in the accompanying tables. For these fire sizes, values of other essential variables also are included in the tables.

Application of the accompanying table requires prediction of fire area ($A2$) in order that the number of brigade teams needed to suppress a given fire can be estimated. Based upon limited fire spread data in residential buildings, the accompanying fire growth curves were developed. These curves represent the building area subject to flashover as a function of time after flashover in the room of origin (A_0); values of (A_0) were assumed to be 100, 200, 300, 400 and 500 square feet. The application of this method presently is limited to a residential building divided into various interconnecting spaces. For buildings with large undivided areas, the space time relationship of fire spread has not been determined.

Subject Headings: *Fire department operations; Fire fighting, manpower, Fire fighting, equipment; Fire fighting, water usage; Fire fighting, time; Fire control; Fire extinguishment.*

Author's Summary

Martin, S. B., Staackmann, M., and Ramstad, R. W. (URS Corporation, Burlingame, California) "Fire-Service Capabilities for Damage Control and Rescue," *Final Report under Contract NOO228-67-C-694, OCD Work Unit 2512A* (March 1968)

This study examines the capabilities for fire control and rescue activities by the fire services following nuclear attack on urban areas. The subjects treated include: (1) feasibility of various strategies and tactics; (2) guidelines for tactical decisions for limited information cases; (3) resource and manpower requirements for typical operations; (4) rationale for allocation of services to demands; and (5) basic concepts of a method for evaluating performance. The research reported accomplished the following: (1) development of analytical methods and preliminary performance models; and (2) studies of specific cases to test the analytical methods and to provide a preliminary evaluation of some operational concepts. A follow-on study is recommended to bring the research to a conclusive stage.

Subject Headings: *Fire services, capabilities in nuclear attack; Rescue and damage control, by fire services; Urban areas, damage control and rescue.*

Authors' Abstract

M. Model Studies and Scaling Laws

Martin, S. B., Renner, R. H., and Jones, R. E. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Application of Fire Fundamentals to Models of Macroscale Phenomena from Nuclear Weapon Bursts," *Report under Contract USNRDL-TR-67-114, OCD Work Unit 2532A* (October 1967)

The application of fire fundamentals to macroscale fire phenomena is reviewed to date as part of the OCD program for assessing urban vulnerability to fire caused by nuclear weapon bursts. Sufficient background information is provided for use in future fire damage assessment and fire protection procedures. Included are the characteristics of fires in enclosures, characteristics of fires in the open (basic processes, techniques for estimating fire spread, and role in fire spread models) and the interaction (coalescence) of small- and large-scale, free burning fires. The technical material presented will be useful for determining the importance of each parameter governing macroscale fire phenomena, the synergistic effects of interacting parameters, and what additional information is needed on the sensitive parameters and their interrelations.

Subject Headings: *Fire research; Models, of fires; Nuclear weapons bursts, fire from.*

Authors' Abstract

Parker, W. J. (U.S. Radiological Defense Laboratory, San Francisco, California) "Urban Mass Fire Scaling Considerations," *Report under Contract USNRDL-TR-67-150* (October 19, 1967)

The results of summer studies by four professors on the scaling of mass fires and the burning rates of materials in large fires are presented as appendices of this report. These results are summarized and analyzed in terms of their application to the civil defense mass fire problem. Overall mass fire scaling alone cannot determine the street environment which is required for civil defense planning. This information may, however, be obtainable from overall mass fire scaling in conjunction with local mass fire scaling and some flame interaction experiments. More research is needed on the internal and external heat transfer characteristics of flames from pyrolyzing organic solids.

The mass fire scaling schemes discussed fall into three categories: (1) the surface heat flux or surface temperature is specified. The model fire must be large enough to allow neglect of viscous effects and to develop full-scale turbulence. Geometric detail, temperature lapse rate, ambient atmospheric vorticity, and wind velocity are modeled. (2) The rate of fuel gas evaluation at the surface instead of the heat flux or temperature is specified. (3) The Reynolds number and the Grashof number along with two radiation parameters, a fuel gasification parameter, and a gas phase heat release parameter are held fixed by operating the model with a modified atmospheric composition and gravitational acceleration constant using a pressure chamber and a centrifuge. Surface boundary conditions are taken care of automatically and to not have to be specified as in the previous cases. No minimum fire size is required. However, a maximum of two orders of magnitude of scaling can be achieved by this technique.

The first category appears to be the most practical at the present time.

Subject Headings: *Mass fire scaling; Scaling, of urban fires; Urban fires, scaling of.*

Author's Summary

Thomas, P. H., Baldwin, R., and Theobald, C. R. (Joint Fire Research Organization, Boreham Wood, England) "Some Model-Scale Experiments with Multiple Fires," *Joint Fire Research Organization Fire Research Note No. 700* (February 1968)

The paper describes some experiments undertaken to test the feasibility of designing a small-scale model that may be used in the laboratory for the study of multiple fires. The results are discussed in terms of a geometric scaling law, relating the inflow velocities to the square root of the flame height, and compared with some observations on large-scale fires conducted under the auspices of Project Flambeau.

The behavior of the array of fires was influenced by the separation between the fuel beds and the type of fuel. In some of the fires persistent fire whirls were observed.

Subject Headings: *Modeling, of multiple fires; Multiple fires, scaling of; Scaling, of multiple fires.*

Authors' Summary

N. Instrumentation and Fire Equipment

Bartkowiak, A. and Kuchta, J. M. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "A Large Spherical Vessel for Combustion Research," *I&EC Process Design and Development* 5(4) 436–439 (1966)

Available data on the limits of flammability and detonatability for many combustion gases and vapors are not in agreement on account of size differences among the vessels used in the tests. The variation in the results is more pronounced at reduced pressures. However, if the vessel diameter is sufficiently large, the lower and upper limits of hydrocarbon–oxygen–nitrogen mixtures do not vary greatly with decreasing pressure.

The importance of vessel diameter in the propagation of a flame front or a detonation wave may be explained by the loss of heat to the vessel walls. The burning velocity should then decrease with decreasing vessel diameter until enough heat has been lost to quench the flame. Thus the quenching diameter is dependent on the given mixture and environmental conditions. In order to prescribe adequate safety standards a large vessel should be used, and the U.S. Bureau of Mines has installed a 12 ft diameter sphere for combustion studies of gases, vapors and small quantities of solid explosives.

The spherical shell is made up from 6 steel plates of ASTM Type A-212B, 0.68 in. thick, welded together, and is designed to withstand 300 psig. Seven access ports, ranging from 1 in. to 12 in. diameter are located at strategic points around the surface. Two elliptical access doors of 0.56 in. thickness are fitted to one of the 4 side plates to create an inner door for studies at ambient or higher pressures and an outer door which is used for reduced pressure experiments. The doors are sealed by an O-ring. All welds were completely X-rayed and the vessel subjected to both a pressure and vacuum test. It has been calculated that the maximum permissible charge weight is approximately 5 lb of TNT and 7 lb of PETN.

The sphere may be used for the determination of the flammability and ignitability of gaseous mixtures, observations on flame propagation over large distances, and the behavior of small flames in different atmospheres and pressures. In connection with explosion phenomena, the effects of venting stratification and turbulence can be examined together with the extent of damage to surrounding materials.

Subject Headings: *Combustion, research vessel for; Vessel, for combustion research.*

P. L. Start

Becker, H. A. (Queen's University, Kingston, Canada) **and Hottel, H. C. and Williams, G. C.** (Massachusetts Institute of Technology, Cambridge, Massachusetts) "On the Light-Scatter Technique for the Study of Turbulence and Mixing," *Journal of Fluid Mechanics* **30,** 259–284 (1967)

The light-scattering property of colloidal dispersions can be utilized for the detection of concentration fluctuations accompanying turbulent mixing. This technique was first applied to investigate the isothermal, air, free jet mixing in which the nozzle fluid was an oil/air smoke. Subsequent work has included free and confined jet mixing; turbulent dispersion in a pipe flow; mixing in a well stirred reactor and temperature-induced concentration fluctuations in a turbulent flame. Since the technique provides a powerful tool for investigating turbulence and mixing, this paper presents the theory and measurements required to indicate its capabilities and limitations.

The principle of the technique may be briefly summarized. One of the streams entering a mixing field is marked with a sol (in gases, a smoke or fog). Light scattered by the sol from a beam projected into the field is intercepted by an optical system at one side and focused onto a slitted diaphragm. The slit allows the light scattered from a short segment of the incident beam to fall on a phototube. The electrical signal produced by the phototube is ideally proportional to the amount of sol in the defined control volume, and when that volume is small enough, to the point concentration. The response of the phototube is linear in light flux in the normal range of loading and up to 10^8 c/s. Thus the problems of nonlinearity, which complicate most methods of turbulence study, are absent.

However, the technique has other difficulties and limitations, the description and mathematical analysis of which provide the basis of the paper. The measuring techniques which receive special attention are: (1) The phototube response to scattered light. (2) The scattered-light technique may be used directly to study the concentration field of the marked material, and indirectly to study the concentration field of the material of the marked stream. In either case the required information is partly obscured by superimposed noise which may take the form of optical attenuation noise; optical background noise; source fluctuation noise; dark noise; marker shot noise; electronic shot noise. Consideration of the summation of these sources of noise leads to an assessment of the total phototube response. (3) The colloidal particles used as markers must have small inertia as measured by their ability to follow the stream motion through sinusoidal velocity fluctuations of any frequency. The size of particle and the frequency to which it is able to respond is calculated. The particle must not evaporate, sublime, coagulate or react chemically. (4) Consideration is given to the effect of the marker on the mixing media and it is justifiably assumed that at low concentrations the effect is negligible.

The theory of the resolution of the point concentration is presented in detail to obtain expressions for the mean marker concentration, the total mean-square concentration fluctuation and for fluctuations in the marked material. Experiments have been carried out to demonstrate the theoretical relations obtained in the detailed analysis and to establish completely quantitative correction procedures for the treatment of data.

It is evident that the scattered-light technique as so far developed is essentially a tool for investigating the convection ranges of the concentration fluctuation spectrum. It cannot give information about the mixing of gases in the spectral region where molecular diffusion is important because sol particles do not portray gas behavior at this level. However, the Schmidt numbers of sol particles in gases are similar to those of liquid pairs in important cases of liquid mixing, and hence the marker sol behavior in gas mixing may portray reasonably well certain cases of liquid mixing.

Subject Headings: *Mixing, optical studies of; Optical studies, of turbulence and mixing; Turbulence, optical studies of.*

G. L. Isles

Heselden, A. J. M. and Woolliscroft, M. J. (Joint Fire Research Organization, Boreham Wood, England) "Wood Block and Other Measurements at *Flambeau Test Fire* 760–12," *Joint Fire Research Organization Fire Research Note No. 698* (February 1968)

Detailed results of the measurements made by the United Kingdom team at the Project Flambeau test fire 760–12–67 are presented and discussed. The damage to standardized wood blocks increased from the edges of the array to a maximum about midway between the center and the northeast corner, broadly the region where fire whirls were observed. This increase may well be due to changes in convective heat transfer over the array. Systematic differences in the damage sustained were found between blocks exposed at various positions, facing in various directions; these largely corresponded to differences in the configuration factor of the fuel pile with respect to the block. Peak wind speeds of more than 60 ft/s were registered at ground level within the array by simple "turn-over" wind gauges. Peak temperatures in the streets exceeded 200°C.

Subject Headings: *Flambeau, tests for; Wood block tests, for Flambeau.*

Authors' Summary

Lawson, D. I. (Joint Fire Research Organization, Boreham Wood, England) "Fire Detection Systems Using Laser Beams," *Joint Fire Research Organization Fire Research Note No. 673* (August 1967)

An analytical treatment is given of the sensitivity of an interferometric fire detector using laser beams. It is shown that the system would probably give false alarms due to building distortions.

An alternative system is discussed, depending on the bending of laser beams in the space above a fire due to changes in the refractive index of the atmosphere.

Subject Headings: *Detection of fires, by laser beams; Fire detection, by laser beams; Laser beams, and fire detection.*

Author's Summary

MacPherson, J. I. (National Research Council, Canada) "Ground Distribution Contour Measurements for Five Fire-Bombers Currently Used in Canada," *National Research Council Report LR-493* (November 1967)

This report presents the results of the fire-bomber ground distribution tests made at Uplands Airport during the spring, summer, and fall of 1967. A total of 37 contour patterns are presented for five of the major existing fire-bombers currently used in Canada; the Turbo-Beaver, the Otter, the Twin Otter, the TBM Avenger, and the Canso. Pertinent meteorological data, speeds, altitudes, and recovery percentages are included with each contour pattern, and contour lengths and enclosed areas are calculated for each drop distribution. The effects on the ground distribution of using long-term retardant and a water-thickening additive are also discussed.

A total of 37 drops were made and analyzed for five of the major fire-bombing aircraft currently used in Canada. The small grid spacing, large number of collection units, and careful data reduction and analysis, all contributed to the production of very representative contour pattern diagrams for each of the drops. In addition, the following more specific conclusions can be made.

(1) The 15×7.5 ft basic cup spacing was found to be a most satisfactory compromise, producing a grid system capable of capturing the fine detail in the contours, but still employing a manageable number of cups.

(2) Conducting the drop tests in the early morning with low temperatures and light winds gave the most consistent contour patterns and greatest recoveries. Evaporation of water from the cups after the drop becomes a more serious source of error at temperatures above 60°F.

(3) Evaporation from the falling cloud of water appears to be the major cause of reduced recovery. The percentage recovery seems to be related more to temperature than to any other meteorological variable.

(4) The effect of wind is to steepen the water density gradient on the upwind side of the contour pattern and, in some cases, to produce a tail that stretches the contour pattern along the wind direction rather than the aircraft's flight direction.

(5) The Canso produced the most consistent set of contours in these tests. The Twin Otter releases its water the fastest, producing an unusual ball-shaped cloud of water with greater penetration and a more concentrated ground distribution.

(6) Float tanks discharging inward towards the aircraft centreline are very effective in producing a single concentrated peak in the wetted area. The ground distributions produced by aircraft with twin fuselage tanks sometimes exhibited two areas of peak concentration.

(7) The long-term retardant produced a smaller, more dense pattern, less influenced by evaporation and wind drift, than did water when tested from the same aircraft. In preliminary Otter tests with a coarser grid spacing, the water-thickening additive did not appear to produce a noticeable change in the contour patterns or in evaporation.

(8) A total of approximately 985 man-hours of labor were required to conduct the drop tests, analyze the data, and produce the contour patterns.

Subject Headings: *Aerial spraying, forest fire fighting; Aeronautics, in forestry.*

Author's Abstract

O'Dogherty, M. J. (Joint Fire Research Organization, Boreham Wood, England) "International Standards for Fire Extinguisher Construction and Performance," *Joint Fire Research Organization Fire Research Note No. 682* (September 1967)

The following note compares the existing requirements of the French, German, and British Standards for hand fire extinguishers, and makes suggestions for the requirements of a proposed set of International Standards to replace the equivalent National Standards.

Subject Headings: *Fire extinguishers, standards for; Standards, for fire extinguishers.*

Author's Summary

O'Dogherty, M. J., Nash, P., and Young, R. A. (Joint Fire Research Organization, Boreham Wood, England) "A Study of the Performance of Automatic Sprinkler Systems," *Joint Fire Research Organization Fire Research Technical Paper No. 17* (1967)

This paper describes experiments to provide data to assist in the design of automatic sprinkler systems for the fire protection of buildings. Consideration has been given to the size of fire required to operate a sprinkler and to the water requirements to control a fire once the system has been operated. The size to which a fire grows before a sprinkler actuates has been determined for different rates of growth, for a range of ceiling heights, horizontal distance of the sprinkler from the fire, and depths of the sprinkler below the ceiling. The extinction of different wood crib fires by water spray has been studied at various stages in their growth, using a range of rates of water application per unit plan area. The extinction of fires in different types of combustible material is discussed in relation to the water requirements per unit plan area to achieve effective control, in terms of rate application total quantity.

Subject Headings: *Automatic sprinkler performance; Sprinkler behavior.*

Authors' Summary

Vandersall, H. L. (Monsanto Company, St. Louis, Missouri) "The Use of a Small Flame Tunnel for Evaluating Fire Hazard," *Journal of Paint Technology* **39**, 494–500 (1967)

The 25 ft flame tunnel test of ASTM Method E84-61 is the standard for fire resistance accepted by most building codes but it is too cumbersome and expensive for daily use in a research laboratory. An inexpensive, convenient 2 ft tunnel is described, the findings of which can be correlated closely with those of the standard 25 ft tunnel.

Test specimens are flat sheets of wood or other material $3\frac{7}{8} \times 23\frac{7}{8}$ in. in size, equilibrated at 75°F and 50% relative humidity, or fire retardant paints, or intumescent coatings on such flat supports. Shorter pieces may be butted to make the $23\frac{7}{8}$ in. length. The specimen is mounted on an angle-iron frame inclined 28° from the horizontal, supported on a Transite housing that rests on a steel base plate so that the lower end (fire end) of the frame is $7\frac{3}{8}$ in. and the upper end (flue end) $18\frac{7}{8}$ in. above the base. A Fisher Scientific No. 3–900 gas burner is placed $2\frac{1}{4}$ in. from the fire end and $1\frac{1}{8}$ in. from the bottom of the sample. The open flue end and cut-off bottoms of the sides of the housing permit natural draft. A transparent Vycor window in one side of the housing, calibrated at 1-in. intervals, together with notches spaced 1 in. apart on both sides of the angle-iron frame, permits observation and measurement of the advancing flame front. The burner is ignited by an electric spark device. Natural gas of 1055 Btu/ft^3 at 3 oz/in^2 and 4.82 ft^3/hr is supplied to the burner. A timer sounding every 15 sec is used. A thermocouple and potentiometer record the temperature on the back of the specimen at a point over the flame. Consumption of the specimen can be measured by weighing it before test, then equilibrating and weighing again after test. The specimen is exposed to flame for 5 min, position of the flame front is observed every 15 sec during the first 4 min, afterburning and afterglow may be observed after the flame is extinguished at the end of 5 min.

The tunnel is calibrated daily with preconditioned 1 in. thick red oak plank and $\frac{1}{2}$ in. thick asbestos millboard. The average of the highest three consecutive values is taken as the flame length, L. The flame length on asbestos, L_a, is subtracted from the flame length on red oak, L_0, to give the flame spread, s. A flame spread constant, k, is defined as $k=100/(L_0-L_a)$.

The panel to be tested is weighed, inserted on the tunnel, the thermocouple put in position, the panel covered with a $3\frac{7}{8} \times 23\frac{7}{8} \times \frac{1}{2}$ in. piece of asbestos millboard, and finally weighed down to prevent warping with a $\frac{1}{2}$ in. thick steel backing plate. The burning test is then started. The average of the highest three consecutive values is taken as L_s. Then the flame spread, FS, is calculated as $FS=k(L_s-L_a)$. Correlation with the ASTM standard method as run by Underwriters' Laboratories is according to $y=4.8+0.92x$ in which x is the result by the 2 ft tunnel and y that predicted for ASTM Method E84-61.

Other possible observations are panel consumption, time of afterflaming, time of afterglow, degree of intumescence of intumescent coatings, insulation value, and char depth and volume.

Subject Headings: *Fire hazard testing, with flame tunnel; Flame tunnel, for fire hazard testing; Tunnel, flame, for fire hazard testing.*

F. L. Browne

O. Miscellaneous

Anderson, W. and Shitman, R. (Disaster Research Center, Ohio State University, Columbus, Ohio) "A Few Preliminary Observations on 'Black Tuesday'—The February 7, 1967 Fires in Tasmania, Australia," *Report of Department of Sociology* (March 9, 1957 and Revised October 20, 1967)

Description of Tasmanian fire with comments on problems of combatting fires with unorganized volunteers.

Subject Headings: *Mass fires, in Tasmania; Tasmanian mass fires.*

R. M. Fristrom

Ödeen, K. (Royal Institute of Technology, Stockholm, Sweden) "Fire Resistance of Prestressed Concrete Double T Units," *Royal Institute of Technology, Civil Engineering and Building Construction Series No. 48* (1968)

An account is given of a method for determining by means of calculations the fire endurance of reinforced or prestressed concrete beams, and this method is specially applied to the fire grading of a certain definite type of prestressed concrete members, viz., double *T* units. The method in question is based on the calculation of temperature fields which are produced in the structure under exposure to fire. If the strength and deformation characteristics of the constituent materials at the temperatures under consideration are known, then the load-carrying capacity of the structure can be determined, from these temperature fields. A survey is made of the present state of knowledge of the above-mentioned characteristics of materials, and it is shown that this knowledge is inadequate in some essential respects. In view of this fact, and taking into account some critical considerations concerning the standard fire endurance test procedures which serve as a basis for fire grading at the present time, only the principles of calculation of the load-carrying capacity under fire exposure are outlined, and the numerical evaluation is limited to a few characteristic examples.

Subject Headings: *Fire resistors, of prestressed concrete; Prestressed concrete; Fire resistance, of concrete; Prestressed fire resistance.*

Author's Abstract

Packham, D. R. (Commonwealth Scientific and Industrial Research Organization, Melbourne, Victoria, Australia) **and Peet, G. B.** (Western Australian Forest Department, Manjimup, Australia) "Developments in Controlled Burning from Aircraft," *Report of Commonwealth Scientific and Industrial Research Organization* (October 1967)

Controlled burning from aircraft was first tested operationally in Western Australia during November 1965. As the results were encouraging, an expanded program was undertaken during 1966. The aim of this program was to treat 188,000 acres from the air in 18 days of suitable weather.

The original method of marking flight paths with hydrogen-filled balloons was changed and a new ground-making system used. This technique permitted cross-wind dropping runs which greatly reduced visibility problems caused by smoke. In addition, a semi-automatic incendiary priming and dropping machine made possible the ejection of incendiaries at shorter intervals than previously.

The results of the controlled burning program using the improved methods surpassed expectations. Scorch exceeded acceptable limits in only four of 24 separate areas of high-quality jarrah forest and this degree of scorch was associated with the burning of dense inflammable scrub in low-quality forest or on flats.

Subject Headings: *Aircraft ignition, of controlled burns; Controlled burns, ignited from aircraft.*

Authors' Summary

MEETINGS

Symposium No. 2: **Behavior of Structural Steel in Fire.** Proceedings of the Symposium held at the Fire Research Station, Boreham Wood, England, on 24 January 1967. Price $10.80. Available in the United States through the British Information Service, 845 Third Avenue, New York, New York 10022. The Content is indicated by the titles of papers given below.

Further Experiments on Temperatures Reached by Steel in Building Fires—E. G. Butcher, G. K. Bedford, and P. J. Fardell (Fire Research Station)
Parameters Determining the Severity of Fire—A. J. M. Heselden (Fire Research Station)
Analysis of Some Results of Experimental Fires—Margaret Law (Fire Research Station)
Comparison between Furnace Tests and Experimental Fires—E. G. Butcher and Margaret Law (Fire Research Station)
The Severity of Fires in Steel-Framed Buildings—L. G. Seigel (United States Steel Corporation, Monroeville, Pennsylvania)
Some Aspects with Regard to the Behavior and the Calculation of Steel Structures in Fires—J. Witteveen (Instituut T.N.O. voor Bouwmaterialen en Bouwconstructies, Delft)
Fire Resistance of Steel Deck Floor Assemblies—H. Shoub and S. H. Ingberg (National Bureau of Standards, Washington)
Temperature of Protected Steel in Fire—T. T. Lie (Instituut T.N.O. voor Bouwmaterialen en Bouwconstructies, Delft)
Furnace Tests and Fire Resistance—D. Sfintesco (Centre Technique Industriel de la Construction Metallique, Puteaus, France)
Fire Tests on Protected Steel-girders—C. Meyer-Ottens (Institut fur Baustoffkunde und Stahlbetonbau der Technischen Hochschule, Braunschweig, W. Germany)
Behavior of Structural Steel in Fire—O. Piermarini (Finsider S.p.A., Roma)

Subject Headings: ***Steel, behavior in fires; Fire behavior, of steel.***

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ABSTRACTS AND REVIEWS