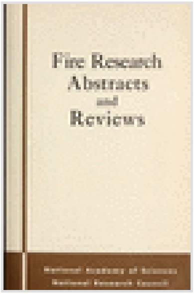

Fire Research
Abstracts
and
Reviews

Fire Research Abstracts and Reviews, Volume 9 (1967)

Pages
316

Size
6 x 9

ISBN
0309309409

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

Volume 9 1967 Number 1

Fire Research Abstracts and Reviews

National Academy of Sciences
National Research Council

FIRE RESEARCH ABSTRACTS AND REVIEWS

Robert M. Fristrom, Editor

The Committee on Fire Research

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 9 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.
1967

FIRE RESEARCH ABSTRACTS AND REVIEWS is published three times a year by the Committee on Fire Research of the National Academy of Sciences—National Research Council, 2101 Constitution Avenue, Washington D. C. It is supported by the Office of Civil Defense of the Department of the Army, the U. S. Department of Agriculture through the Forest Service, the National Science Foundation, and the National Bureau of Standards. The opinions expressed by contributors are their own and are not necessarily those of the Committee on Fire Research.

Library of Congress Catalog Card Number 58-60075 rev

Available without charge from the
Office of the Committee on Fire Research
National Academy of Sciences—National Research Council
Washington, D. C. 20418

FOREWORD

The tragic loss of three astronauts through an accidental fire has shocked the nation. In retrospect one might wish that there had been a more intensive study of fire dangers and problems, but this is neither profitable nor fair to the space agency whose safety record has generally been superb. The blame, if there is any, should fall on our society, which loses more through fire and spends less per capita on the study of fire problems than any other civilized nation.

What is important how is to encourage an intensified program for the understanding of the problems associated with unwanted fires, broadly based and scientifically oriented, so that society as a whole will be benefited. It is this broad approach which will forestall future problems. A crash program may lock the door while leaving the windows open. We in the fire research field have a special responsibility to press this broad viewpoint.

The inside cover of this issue records changes in the membership of the Committee on Fire Research. Dr. Walter T. Olson, Assistant Director, NASA Lewis Research Center, one of the founding members, has left the Committee because of other commitments. The loss of such an experienced member will be felt by the Committee. Your editor feels that he speaks for the fire research community as a whole in thanking Dr. Olson for his devotion and contribution to the cause of fire research, and in welcoming to the Committee a new member, Dr. Eric Wolman, operations research scientist of the Bell Telephone Laboratories, Inc., whose special knowledge should provide strength in a vital area of fire research. This marks the tenth year of the Committee on Fire Research. At this milestone it seems appropriate to reflect on the many positive achievements of the Committee in the difficult field of fire research, and to wish it a productive future.

In this issue, a number of items of special interest are presented in addition to the abstracts. First of these is a review, "General Programme for Scandinavian Long-Term Fire Research," by Ove Pettersson. This is a reprint of a pamphlet giving the views of our Scandinavian colleagues and it warrants careful consideration and comparison with our own effort. The second article is a very extensive review by I. K. Walker of the chemistry division of D.S.I.R., New Zealand, "The Role of Water in the Spontaneous Combustion of Solids." This is an area where Mr. Walker is eminently qualified to write, since his laboratory has been active in this field for a number of years.

The third item is a letter to the editor from Fire Chief (Ret.) C. V. Walsh of the New York Fire Department, outlining his views on the simulation of urban fires by woodland fires. This is a new feature for FRAR. Your editor feels that exchanges of opinion on important current questions in fire research should be encouraged and we plan to publish short items that appear to have general interest. The final item is a review of the revised "Directory of Fire Research in the United States" (1965), compiled by the Committee on Fire Research. This book is of particular interest because it represents the only assessment of the fire research effort in this country. Mr. D. W. Thornhill, Executive Secretary of the Committee on Fire Research, and his staff who prepared this book under the direction of Professor H. C. Hottel, Chairman of the Committee, are to be congratulated on a fine job.

Brief reports are given on the Eleventh International Symposium on Combustion and the evening session on fire research, sponsored by the Committee on Fire

Research. The week of the Symposium was concluded with a trip into the Southwest Pacific Forest Area, sponsored by the U. S. Forest Service. Demonstrations were given of new fire-fighting techniques and equipment, including the preparation and results of delivering chemical fire retardants by aircraft, and the use of helicopters in fighting forest fires. Work at the Forest Genetics Laboratory was inspected.

We note with regret the passing of one of our abstracters, Loren C. Bollinger. His death is a loss both to FRAR and the fire research field to which he dedicated his sceintific career.

R. M. Fristrom, Editor

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REVIEWS

General Programme for Scandinavian Long-Term Fire Engineering Research*

OVE PETTERSSON
National Swedish Institute for Materials Testing, Stockholm, Sweden

> "This publication presents a general programme for long-term fire engineering research at the inter-Scandinavian level. The object of this programme is twofold, viz., first, to facilitate the choice of research problems as outlined in the above, and second, to stimulate and to intensify joint inter-Scandinavian research in structural fire engineering. The programme in question was drawn up during Spring 1963 by Professor Ove Pettersson, Director, Fire Engineering Laboratory, National Swedish Institute for Materials Testing. The initiative in establishing this programme was taken by the Inter-Scandinavian Liaison Group (Nordiska Samarbetsgruppen, abbreviated NS) for Inter-Scandinavian Building Research Conferences (Nordiska Byggforskningsmoten, abbreviated NBM), cf. NBM XII 1963 General Programme for Inter-Scandinavian Building Research, by the Liaison Committee of Scandinavian Fire Engineering Laboratories (Nordiska Brandlaboratoriernas Samarbetskommitte, abbreviated NBS), and by the National Swedish Institute for Materials Testing, Stockholm."†

I. FIRE LOAD

For buildings of common types (domestic buildings, office buildings, schools› hospitals, etc.) it is required to carry out a survey on a statistical basis which is so broad as to enable the mean value of the fire load, the standard deviation in this load, and the type of the statistical distribution curve of fire loads to be calculated in a reliable manner. This survey must be reported so extensively as to make it possible to determine, for each individual enclosed space, the total heat value of the combustible material contained in the space, the corresponding rate of combustion, and—when the physical prerequisites to this determination will be known—the corresponding resultant emissivity. The most important parameters for these determinations are enumerated below, in Section II B.

II. PROCESS OF FIRE DEVELOPMENT

All phases of the process of fire development—ignition, flame stage, glow stage, and cooling-down phase—shall be explored by means of field tests as well as full-scale and model tests in the laboratory or by means of theoretical calculations, based on the heat and mass balance equations.

II A. Fires in Open Air

The rate of combustion, the rate of spread, the heat flow, the height of flames, the convection column, and the radiation characteristics (heat of radiation, emis-

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* National Swedish Institute for Materials Testing Proceeding No. 129 (1964) 13 pp., price 5 kroner.
† Selected quotations by permission of the Author.

sivity) shall be determined as functions of the following factors, among others, in so far as they are applicable.

1. Quantity of combustible material.
2. Type of combustible material.
3. Dispersion factor (hydraulic radius) of the combustible material.
4. Moisture content of the combustible material.
5. Wind velocity.
6. Temperature and relative humidity of the air.
7. Cloudiness.
8. Topography.

II B. Fires in Enclosed Spaces

The rate of combustion, the height of flames, the temperature, the enthalpy, and the composition of the combustion gases, the radiation characteristics, as well as the coefficients of heat transfer of the vertical and horizontal enclosing surfaces shall be determined as functions of the following factors, among others, in so far as they are applicable:

1. Quantity of combustible material.
2. Location of the combustible material in the enclosed space.
3. Type of combustible material.
4. Dispersion factor (hydraulic radius) of the combustible material.
5. Moisture content of the combustible material.
6. Quantity of air supplied per unit time (opening factor).
7. Temperature and relative humidity of the air supplied.
8. Horizontal and vertical co-ordinates of the enclosed space.
9. Thermal inertia and heat conduction characteristics of the enclosing structures, as well as those of the enclosed structures, if any.

II C. Questions Relating to Spread of Fire, etc.

The subjects to be studied under this heading comprise the spread of fire and the spread of gaseous combustion products (smoke, hot gases, combustible gases, poisonous gases, etc.) in an enclosed space, and from one story to another, e.g., through windows, ventilation ducts, or wall structures extending over several storeys. The effects of surface layers, surfacings, textiles, etc., shall also be examined in this connection. Important parameters in connection with these studies are most of the parameters enumerated in Sections II A and II B.

III. FIRE ENGINEERING QUESTIONS RELATING TO MATERIALS

The following subjects shall be investigated in the whole temperature range under consideration:

III A. Combustibility

III B. Strength and Deformation Properties (Including Residual Strength)

In the researches to be carried out in this section, it is essential to ensure that the tests shall cover all rates of increase and decrease in temperature which are met with in practice.

III C. Thermal Properties

The following coefficients shall be determined so as to take into account the rate of heating and the initial moisture content of, and the structural change (if any) in, the materials:

1. Coefficient of thermal conductivity.
2. Coefficient of specific heat.

III D. Risk of Vapour Blasting of Materials, e.g., Concrete

III E. Methods of Reconstructing Temperature Conditions in Actual Fires

These methods concern the study of colour changes, spectral analyses, colour indication, etc., of materials.

IV. FIRE RESISTANCE OF NON-LOAD-BEARING PARTS OF BUILDINGS

V. FIRE RESISTANCE OF LOAD-BEARING STRUCTURES

It is desirable that methods of calculation for dealing with this problem should soon be devised. Some of the essential aspects of the problem under consideration are enumerated in what follows.

V A. Temperature Field Calculations

Primarily, these calculations necessitate a solution—preferably by means of automatic electronic computers—of the equation of non-stationary heat conduction in the one-dimensional and two-dimensional cases for given processes of fire development. This solution shall take into account the variations in the coefficient of thermal conductivity, the specific heat, and in the coefficient of heat transfer with the temperature.

V B. Calculation of Load-Bearing Capacity of Statically Determinate Structures Exposed to Fire

In this calculation, the data obtained in Sections III B and V A shall be brought into relation with each other.

V C. Experimental Study of Load-Bearing Capacity of Statically Determinate Structures Exposed to Fire

V D. Load-Bearing Capacity of Statically Indeterminate Structures Exposed to Fire

This section shall comprise experimental and theoretical studies dealing with redistribution of stresses, membrane effects, and load-bearing capacity.

V E. Theoretical and Experimental Studies of Effects of Surfacings (Combustible and Incombustible) Used for Heat Insulation and for Increasing Thermal Inertia

V F. Residual Strength of Load-Bearing Structures

VI. FIRE ENGINEERING CHARACTERISTICS OF HEATING SYSTEMS AND APPLIANCES

This section shall deal with components of heating systems, such as fireplaces, stoves, furnaces, and chimneys, as well as with heating appliances and installations using oil, liquid gases, and other heat-generating agents.

VII. DESIGN AND DEVELOPMENT OF TESTING AND MEASURING DEVICES

A basic requirement in this connection is that the testing devices—especially those which are standardised—should be designed so as to be capable of simulating actual conditions in a range which is as wide as possible. For fire test furnaces, this requirement implies, among other things, that the flue gas temperature and the intensity of radiation (emissivity) should be controlled irrespective of each other.

VIII. INVESTIGATIONS OF FIRE EXTINCTION

Among the fundamental subjects to be treated in this section are fire-extinguishing agents (effects produced by the velocity of jet or spray, the throw, the degree of atomisation, the surface tension, etc.), fire extinguisher equipment, methods of fire extinction, as well as fire alarm devices and systems.

IX. APPLICATIONS OF STATISTICS AND OPERATION ANALYSIS TO FIRE ENGINEERING PROBLEMS

Many-sided and judicious statistical analyses of well-founded experiences relating to actual fires may be expected to furnish basic information which will help to treat fire engineering problems in conformity with the principle of minimum total cost, while giving due consideration to safety of human beings and to other relevant factors.

Some important questions to be dealt with under this heading are exemplified in what follows.

1. Causes of fires.
2. Extent of damage to buildings, machines, and human beings.
3. Relation between the frequency of damage and the extent of damage, on the one hand, and the extent of fire prevention and fire-fighting services, on the other hand.
4. Optimisation of fire alarm systems in individual buildings, industrial areas, forests, or communities.

Subject Headings: *Fire research, program, Scandinavia; Scandinavia, fire research program.*

The Role of Water in Spontaneous Combustion of Solids

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Introduction

Water is generally considered to be the enemy of fire, and yet most popular thinking about spontaneous combustion involves the concept of wet materials. Spontaneous fires in wet haystacks are so well authenticated that there is often a tendency to believe that the presence of water must accelerate the self-ignition of other materials such as coal, sawdust, cereal grains, fish-meal, city garbage, and so on.

Mechanism of Spontaneous Ignition

The present discussion is concerned with the ignition of porous solids by gaseous oxidation. This would also include circumstances where the actual material reacting to generate heat is a liquid, but is spread over the surface of a porous solid. The ultimate state of combustion is a state of inflammation or of glowing combustion, maintained by exothermic chemical reaction between atmospheric oxygen and the material under consideration (or its pyrolysis products). This state of combustion is preceded by an ignition mechanism, where exothermic processes raise the temperature to a point where combustion can begin. These exothermic processes may cover a wide range of chemical, biochemical, and physicochemical mechanisms.

It is not a simple matter to define ignition processes in solids, and these difficulties are well illustrated by the history of Committee D.5 of the American Society for Testing Materials. In 1937 a subcommittee was established[1] "to investigate methods for determination of ignition characteristics of solid fuels with a view of developing a standard method of test." Despite an attempt to define ignitibility,[2] and an investigation of a test method,[3] the subcommittee was discharged in 1950 with the pronouncement[4] that "further work . . . was not justified . . . until there may be developed a more consistent understanding of the meaning of the term 'ignitibility'."

During ignition of a solid, there is a thermal balance between heat generated by exothermic processes, and heat dissipated to the surroundings by thermal conductivity. This statement obviously involves a size effect, since generation of heat is related to the cube of dimension, but dissipation of heat is related to either dimension or the square of dimension. Van't Hoff[5] first showed that the sudden onset of thermal instability characterizing the phenomenon of ignition is a direct consequence of the increasing rise of reaction rate in a nonlinear manner with rise of temperature, in those cases where ignition is caused by a single chemical reaction. The term "thermal explosion" is commonly applied to a mechanism of this type. Semenov[6] proposed a mathematical treatment of the critical heat balance during thermal explosion for a mass of reacting material, uniform throughout in temperature, and with heat losses controlled by heat transfer at the surface. Frank-Kamenetskii[7,8] proposed a mathematical treatment of the critical heat balance during thermal explosion for a mass of reacting material with the surface cooled to ambient temperature, and with heat losses controlled by thermal conductivity within the material. And Thomas[9] later combined these two theories to deal with intermediate situations.

The fact that some of the key reactions in spontaneous ignition have negative temperature coefficients (e.g., bacterial metabolism, adsorption of water vapor) is not in conflict with the above theories. The ultimate thermal instability must arise from a reaction with a positive temperature coefficient, but this reaction may remain negligible in magnitude until some threshold temperature is reached.

The Effect of Water on the Heat Balance During Ignition

Ignition by thermal explosion can be evaluated by considering the heat balance for an assembly of material just insufficiently reactive to ignite. This represents a critical balance between processes generating heat and processes dissipating heat. Since inflammation (or glowing combustion) must be preceded by ignition, the role of water in initiating spontaneous combustion can be assessed by considering the effect of water on the various ignition processes. Unfortunately, knowledge is sadly lacking both of the processes involved, and of the influence of moisture on them. Much of the present mystery surrounding spontaneous combustion stems from this lack of basic knowledge of mechanisms.

(1) *Effect of Water on Surface Heat Transfer*

Dissipation of heat from a warm surface is normally controlled by the boundary layer of still air in immediate contact with the surface. Under dry conditions, conduction and radiation of heat are the only mechanisms operating across this layer. However, if moisture is present, the higher temperature of the surface may create a difference in water-vapor concentration across the boundary layer. Normal gaseous diffusion then results in mass transfer of water vapor, thus removing the latent heat of vaporization from the damp surface. A mechanism of thermal diffusion[10] can also operate, although this is generally of minor importance compared to gaseous diffusion.

(2) *Effect of Water on Internal Thermal Conductivity*

The presence of bound moisture in a hygroscopic material will raise the thermal conductivity by a direct effect on density (e.g., see Baxter,[11] Kumar[12]).

Internal transfer of heat within a dry porous solid will take place by a summation of thermal conductivity in the solid and gas phases, in combination with the effects of convection and diathermancy. If moisture is present, temperature differences within the bulk will cause differences in water-vapor concentration in the interstitial atmosphere, resulting in mass transfer of water vapor from hot zones to cooler, carrying with it the latent heat of vaporization. Although this heat-transfer mechanism is not large at room temperatures, at higher temperatures (e.g., 60°–100°C) it can rapidly rise to a magnitude many times the sum of all other mechanisms. The net effect is that wet porous solids have a very large temperature coefficient of effective thermal conductivity. Krischer and Esdorn[13] have shown how this mechanism would operate with porous materials such as wet lightweight concrete; and Nissan et al.[14] have described experiments demonstrating that the effect is a general one for a volatile liquid in association with a porous solid.

If the solid is hygroscopic, and there is insufficient water present to saturate it (i.e., if relative humidities are below 100%), a further mechanism also operates.

The mass transfer of water from the hot zone to colder zones (by a mechanism of gaseous diffusion, opposed to a minor extent by thermal diffusion[10]) will lower the relative humidity (RH) of the hot zone and raise that of the colder zones, finally creating a path of almost constant water-vapor concentration. Transport of water vapor by diffusion then ceases, and a balance results between the opposing forces of gaseous diffusion and thermal diffusion.[10] The mass transfer of water vapor will then cease altogether. The thermal conductivity then drops dramatically[15] at high temperatures (say, above 60°C), although not so drastically at lower temperatures.

(3) *Influence of Water on Thermal Diffusivity*

The role of water in altering the thermal conductivity of wet porous materials discussed under (2) above will affect thermal diffusivity directly. However, when hygroscopic materials self-heat, the presence of sorbed water can affect the diffusion of heat by another mechanism also. Heat can diffuse through hygroscopic materials both as sensible heat, and as latent heat contained in diffusing water vapor. Henry[16,17] has shown that these two diffusion processes are not independent, but can interact within the hygroscopic range to cause "waves" of simultaneous coupled diffusion of both temperature and water vapor. He showed[16] how diffusion coefficients may be calculated for these coupled waves.

The presence of water will affect thermal diffusivity by directly altering the specific heat. In addition, the presence of water will have a further effect on the effective specific heat of a porous material as the temperature changes. Redistribution of water between liquid and gas phases (i.e., in the interstitial atmosphere) can slightly alter the apparent specific heat, because of the large latent heat of vaporization of water. When the interstitial atmosphere is static, this effect is normally too small to be of significance in a spontaneous ignition mechanism, and it has been calculated,[18] for example, that it would change the specific heat of wet wool by less than 3% up to 90°C. Experiments carried out with sealed samples of wool in a calorimeter later demonstrated[19] that this estimate would be approximately correct.

(4) *Effect of Water in Ventilation*

If an aerial oxidation reaction is to continue for any length of time, fresh air must be brought into contact with the reacting material to replace the oxygen consumed. This air may arrive by diffusion, by convection, or by forced draught; or by any combination of these. The interstitial atmosphere displaced by this process will depart at a temperature close to that of the element of reacting material with which it has been in immediate contact, and thus carries with it a small amount of heat. If the material is wet, the departing air can carry a very large amount of heat as latent heat in the content of equilibrium water vapor. Effects of this type have been demonstrated[20–22] in the self-heating of coal in oxygen atmospheres.

(5) *Role of Water in Heat of Sorption*

Many materials suspected of spontaneous ignition are hygroscopic, and will generate large quantities of heat when wetted. When the water is adsorbed as vapor, the latent heat of vaporization is added to the heat of wetting, and this has been demonstrated to enhance oxidative temperature rises when dry coal is ventilated with moist oxygen.[20,22] When water vapor is adsorbed in hygroscopic textile fibers, large temperature rises can be produced[23,24]; and this has led many authors to suggest[25–28] that wetting might act as a trigger mechanism to raise temperatures to a point where other exothermic reactions could take place; or even to suggest[29,30] that heat of wetting might raise materials to full combustion temperatures.

(6) *Effect of Water on Oxygen Partial Pressure*

The partial pressure of oxygen in a dry normal atmosphere is 160 mm at all temperatures. If liquid water is in equilibrium with the atmosphere, the partial pressure of water vapor does not significantly affect the partial pressure of oxygen at room temperatures. At higher temperatures, the rising partial pressure of water vapor causes the partial pressure of oxygen to fall rapidly, and it becomes zero at 100°C.

If the relative humidity of an interstitial atmosphere is maintained at a figure below 100% (e.g., by admixture of a limited amount of water with a hygroscopic material) the partial pressure of oxygen will fall in a similar manner as the temperature rises, but not to so great an extent.

These changes in oxygen partial pressure will change the rate of any chemical reaction of order greater than zero (with respect to oxygen), in which the oxygen may participate. Since microbiological life is limited[31] to temperatures below 80°C, these changes in oxygen partial pressure are unlikely to alter bacterial or fungal metabolism to any great extent.

(7) *Role of Water in Microbiological Heating*

The metabolic processes of molds and bacteria can generate heat, and these organisms can both make use of a wide variety of foods. The various species have different optimum temperatures for growth, and different temperature limits[31] beyond which they cannot actively metabolize. It is most unlikely that any bacteria could generate heat at temperatures[18,32] above 80°C, nor any mold (fungus) at temperatures[33] above 60°C.

All molds and bacteria need water for their metabolic processes, and different varieties require different water activities. In general,[34] molds prefer relative humidities below 100%, while most bacteria need relative humidities above 90%. Molds can metabolize[35] at relative humidities down to 75%, and at even lower humidities after prolonged latent periods.[36] A recent account of the thermophilic fungi has been given by Cooney and Emerson,[33] and knowledge of the aerobic thermophilic bacteria has been reviewed by Allen.[37]

Not only does availability of water control the activity and variety of microbiological life, but the metabolism of micro-organisms in turn generates water from the substrate. Thus, damp or wet materials that are self-heating through microbial metabolism tend to steadily increase in water content. Concomitantly they often tend to increase in content of water-soluble materials. Milner and Geddes[38] and Rothbaum[39] have discussed how the interplay of these two circumstances can operate to change the RH, and thus to control the species of organism dominant both during a period of rising temperature, and during an extended period at a steady temperature.

(8) *Gaseous Oxidation in the Presence of Water*

The olefinic bonds of unsaturated lipids and rubbers can react exothermally with gaseous oxygen at room temperatures. It could also be said that all organic materials are undergoing a certain degree of aerial oxidation at room temperatures, although the rate of oxidation is usually greater in the case of unsaturated compounds.

Evidence is conflicting regarding the influence of moisture on gaseous oxidation of olefinic bonds. Thus, Thompson[40] studied atmospheric oxidation at 100°C of linseed oil spread on cotton waste, and stated that the presence of a limited amount of moisture actually increased the rate of heat production. Ellis[41] studied the absorption of oxygen by catalyzed elaidic acid dispersed on fine sand at temperatures between 50° and 80°C, and found that the presence of water vapor did not appreciably affect the rate of oxidation, even in atmospheres saturated at the temperature of the experiment. Walker and Harrison[42] studied the effect of using oxygen at various humidities on a standardized ignition test with unsaturated fat in pie wool at 100°C, and concluded that the presence of water definitely inhibited the oxidation reaction. Evidence is less conflicting regarding the influence of moisture on the low-temperature gaseous oxidation of common organic materials such as cellulose. Such evidence as exists is overwhelmingly in favor of a theory that materials such as degraded cellulose undergo exothermic reaction with oxygen more rapidly when wet than when dry. A similar mechanism is also known to occur with viscose rayon.[43] Examples of other materials that have been found to react more rapidly with oxygen when wet are coal,[44,45] charcoal,[46] hay,[15,45] wool,[39] glucose spread on asbestos fiber,[15] and sewage sludge.[47,48] Indeed, this principle of wet combustion[47] has long been applied in Scandinavia as a method of disposal for paper mill effluents, and has also been used for city-sewage sludges.[47,48] Although it is necessary to have the oxidizing material thoroughly wet to obtain a worthwhile speed-up of reaction rate from an engineering viewpoint,[48] it has been demonstrated in laboratory tests[43] that as little as 12% of water will significantly accelerate the rate of uptake of gaseous oxygen by viscose rayon.

There is a further factor that may be involved under industrial conditions. The catalytic influence of iron salts on the degradation of wet cellulose is well known,[49,50] and this is probably an oxidation mechanism. The presence of water is often necessary to bring catalytic metals commonly met with in normal engineering operations into a catalytically active state (e.g., tramp iron in sawdust heaps).

(9) *Water Formed by Oxidation Reactions*

Low-temperature chemical oxidation reactions usually have a respiration quotient well below unity,[51,52] and release a correspondingly small amount of water[51] in proportion to the oxygen consumed. Whether this water appears in the gas phase or adsorbed on the solid[44] depends on a number of factors, including the hygroscopicity of the solid, the temperature, the rate of generation of water, and the humidity and rate of ventilation of the interstitial atmosphere. The latent heat of vaporization of the water is often enhanced by an additional heat of sorption. It has been calculated[53] that if all the hydrogen in wool were oxidized to form water, and if this water were then to be adsorbed into undamaged wool (i.e., the most extreme conditions), then the heat represented by phase change of the water could amount to nearly 10% of the heat of total combustion. Because of the various factors discussed above, the effect is likely to be much smaller in any practical example.

(10) *Traces of Water as a Catalyst of Gaseous Oxidation*

The extreme view on the role of water as a catalyst of oxidation was advanced by Traube[54] who considered that no substance would be able to react with perfectly dry oxygen at normal temperatures. This view was later criticized,[55] although Smith[56] has listed a number of solids that are attacked by oxygen only when a trace of moisture is present. These appear to be all elemental solids, and would therefore not release water as a product of oxidation. It could thus be doubted that the presence of moisture is essential to the oxidation of natural products such as cellulose and olefinic lipids, since organic substances of this type release water as a product of gaseous oxidation (although in restricted amount[51]), and catalysis by water would thus merely render the reaction autocatalytic. Thus, Graham[44] demonstrated that extended drying in vacuum over sulfuric acid had only a minor effect on the rate of subsequent aerial oxidation of coal; and Walker and Harrison[42] failed to observe any difference in the rate of reaction with oxygen when pie wool had first been dried for 10 days at 100°C in a stream of carbon dioxide brought into equilibrium with magnesium perchlorate at room temperature. On the other hand, Jones and Townend[57] have suggested that a coal–water–oxygen "peroxygen" complex might play a significant role in the gaseous oxidation of coal. In any case, most of the materials that cause fires in commerce are so strongly hygroscopic, and the last traces of water are so difficult to remove from them, that the question of catalysis by traces of water could be of academic interest only, in a spontaneous ignition mechanism.

(11) *Effect of Prior Desorption of Water on Gaseous Oxidation*

Although no systematic investigation appears to have been made of the phenomenon, it is commonly believed among investigators of oxidation that prior desorption of water from wet porous materials will enhance the subsequent rate of gaseous oxidation of the dry material. A standardized ignition test applied to pie wool showed[42] that this material reacted a little more vigorously with oxygen at 100°C if it had first been immersed in water and dried in air at temperatures ranging between 15° and 35°C. The Lea peroxide value[58] of the fat was slightly lowered by this treatment.[42] Subsequent (unpublished) experiments in a calorimeter[59] have shown that if pie wool is wetted and then dried in an inert atmosphere immediately prior to calorimetric[59] experiments, the rate of subsequent heat generation in air is significantly higher than that of the same material dried from a lower moisture content. A theory is sometimes advanced that surfaces prone to react with oxygen can be protected by a film of adsorbed carbon dioxide, and that adsorption and subsequent desorption of water might displace this film. Thus, the Fire Protection Association has issued a warning[60] regarding the spontaneous heating hazard that may be caused by wetting and re-drying charcoal. Some support for this theory is provided by experiments[61] in which powdered graphite became pyrophoric after immersion in liquid argon, followed by desorption.

(12) *Role of Water in Hydrolysis Reactions*

Little is known about the part that hydrolysis reactions might play in ignition mechanisms. It is known, for example, that unsaturated fatty acids are more reactive than the corresponding glycerides,[62,63] so hydrolysis might act here to enhance reactivity slightly. It seems probable that the water causing this hydrolysis would need to be removed before self-heating proceeded very far, otherwise any increase in reactivity might be outweighed by thermal effects during ventilation (e.g., heat of vaporization).

Although it has been suggested[64] that hydrolysis might play a part in the pyrolysis of cellulose at temperatures up to 140°C, it seems unlikely that the heat generated directly by hydrolysis reactions would play a major role in any spontaneous ignition process. However, there is another way that hydrolysis could influence the heat balance, by controlling the mechanism described under (2) above. It has been shown[15] that the thermal conductivity of a wet porous material can vary widely with small variations in RH. If the hydrolysis products are water soluble, or if they are hygroscopic, production of a minor amount of hydrolysis product at an almost constant water content, can markedly affect the equilibrium RH of a material at high values of RH. This can in turn drastically influence thermal conductivity, and thus change the significance of a given exothermic reaction in controlling the heat balance.

(13) *Role of Water in Oxidation by Chemicals*

Oxidizing chemicals sometimes come into contact with oxidizable materials, and cause fires. Little is known about the role water might play in this type of reaction. However, it seems probable that the activity of many mild oxidizing reagents (e.g., sodium nitrate on sacking[65]) would be enhanced by the presence of limited amounts of water.

(14) *Direct Reaction of Chemicals with Water*

Some chemicals will inflame directly on contact with water at room temperature (e.g., metallic potassium), usually by generating combustible gaseous products. Chemicals of this type have been classified[66] into those producing hydrogen on contact with water and those producing gaseous hydrides; the latter are sometimes spontaneously inflammable.

The ignition hazards of chemicals of these types are obvious to a chemist, as also are the reactions causing ignition, and they will not be further discussed here.

Spontaneous Combustion of Wet Materials

The spontaneous combustion of wet materials has long presented a mystery. Belief in the spontaneous combustion of wet hay extends back to the ancient world, and it has been pointed out[67] that the ubiquitous Roman philosopher Pliny wrote in the first century A.D. "When the grass is cut it should be turned towards the sun and must never be stacked until it is quite dry. If this last precaution is not carefully taken, a kind of vapor will be seen arising from the rick in the morning, and as soon as the sun is up it will ignite to a certainty and so be consumed." While many other beliefs of ancient times have been disproved by modern science, the spontaneous ignition of wet haystacks has remained a well-authenticated but unexplained phenomenon until recent years. Scientific investigation of the circumstances was severely handicapped because no research worker had succeeded in reproducing the phenomenon at will,[68–70] but instead advantage had to be taken of accidentally discovered occurrences.[71–74] Because of the unexplained nature of spontaneous ignition in wet haystacks (both grass and alfalfa), many other wet materials came under suspicion of causing spontaneous ignition.

The first scientifically trained observer to describe a spontaneously igniting haystack was Ranke,[74] in 1873. Ranke was an agricultural chemist of private means, and the owner of an estate in Germany. On being informed that a barn of hay on his estate was in the course of igniting spontaneously, Ranke personally supervised dismantling of the mass, and has recorded an excellent description of the circumstances, together with an account[74] of experiments carried out with hay removed from the barn. No comparable description of a spontaneous hay fire became available[71] until 1935.

Ranke[74] described the burned material as an actual carbon, with sufficient retention of the original structure to enable the form of every blade of grass to be recognized. If this grass carbon was crushed on white paper it colored it black. Acting on a suggestion made by Professor Buchner, he postulated that the fire was caused by adsorption of oxygen on this hay charcoal, with consequent exothermic reaction. In laboratory experiments, he successfully carbonized hay at temperatures between 250° and 300°C, and obtained a product that would heat to redness on exposure to air. He found that if the hay were heated sufficiently to remove all volatile matter, it showed no pyrophoric properties. From this he concluded that the products of destructive distillation were also involved, perhaps playing a role similar to that of the oxidation of drying oils in the ignition of oily waste. To account for a temperature of around 300°C in the hay mow, he merely pointed to the thermal insulation of tightly packed hay, and referred vaguely to progressive chemical transformation of component parts of hay.

In the 50 years following Ranke's work, many Continental investigators became interested in the spontaneous combustion of wet hay, leading to a proliferation of improbable theories. It was known that bacterial growth would be limited to a temperature below the boiling point of water, and it was early recognized that Ranke's explanation based on thermal insulation could not explain the temperatures of over 250°C that he found necessary to make pyrophoric carbon in the laboratory. To overcome this difficulty, the German bacteriologist Miehe[75] postulated that hay might be carbonized by long continued heating at 70°–80°C. His theory was not supported by laboratory experiment. Truninger[68] measured the ignition temperature of hay and found it to be between 225° and 240°C. However, by heating a dish of finely ground hay in a drying oven at 163°C, he produced a light-brown material which began to smolder at one narrowly defined zone on its surface. When this thin smoldering layer was removed and the remaining material was mixed up, the latter began to carbonize and in a few minutes was in a full glow. Truninger[68] believed in the low-temperature-carbonization theory of Miehe[75] (which he nevertheless recognized as an unproved assumption); but his own experiments show that temperatures above 150°C are needed to carbonize hay.

Boekhout and De Vries[76] remarked on the striking similarities between the self-heating of tobacco and of hay, and suggested that enzymic reactions in these materials might be catalyzed by traces of iron (or manganese) in the sap of the plant. Direct enzymic reactions were also proposed[77,78] to account for the ignition of wet hay; but later experiments[79] failed to support these theories. Laupper[80] made an extensive study of the spontaneous combustion of hay, and decided that the substance responsible for the ignition reaction was not pyrophoric carbon, but pyrophoric iron (perhaps aided by pyrophoric manganese). He postulated reduction of the original iron salts to elemental iron, which is well known to have pyrophoric properties. Another theory is due to Dodd,[73] who examined many haystack fires in the role of insurance investigator. Dodd[73] inclined to the belief that enzymic attack on the phosphates (or phosphatides) present in the original hay would produce phosphoretted hydrogen, which is known to be spontaneously inflammable on contact with air. These theories are all plausible from a chemical viewpoint, but collapse under critical physicochemical examination. It is unlikely that reactions such as these could generate heat at a rate sufficient to ignite wet hay. A more probable explanation was proposed by Browne,[81] who suggested that the spontaneous combustion of hay is caused by microbial dehydration of sugars under almost anaerobic conditions to form highly unsaturated intermediates; and that these intermediates then oxidize with violent generation of heat when they gain access to air. Nelson and Browne[82] demonstrated an alkaline degradation of dextrose to unsaturated compounds of this type in the laboratory; but chemical examination[83] of self-heated haystacks did not yield any evidence in support of Browne's[81] theory.

Elucidation of the cause of fires in wet hay finally came[15] by considering together the facts in (2), (7), and (8) above. Thermophilic bacteria require a relative humidity above 90%, and are capable of raising the temperature a little above 70°C. At this temperature, the direct gaseous oxidation of hay will generate a significant amount of heat, undoubtedly accelerated by the presence of moisture. However, at relative humidities above 98%, the mass transport of water vapor (by diffusion) causes a high thermal conductivity, and the heat is dissipated. The temperature is thus unable to rise further. If the RH is below 98%, water can distil to create a path of constant water-vapor concentration along the thermal gradient, and the thermal conductivity will then drop dramatically. The heat generated by the relatively weak gaseous oxidation is thus able to raise the central temperature further. A rise in temperature above, say, 80°C accelerates the wet gaseous oxidation reaction, and completely inhibits the microbiological reaction. It will also raise the water-vapor concentration in the interstitial atmosphere, and diffusion then removes further moisture. Any diminution in the rate of gaseous oxidation caused by removal of water is presumably compensated by the further reduction of thermal conductivity, and by the temperature coefficient of the oxidation reaction. In this way, the hay at the center of the stack is gradually dried out and raised in temperature until it reaches a temperature of active combustion.

Rothbaum's theory [15] thus suggests that 96% RH would be a critical humidity for the spontaneous ignition of any wet organic material. He demonstrated the truth of this by laboratory experiments[15] with wet hay. The generalized application of the theory to other materials was supported by further experiments with wet esparto grass[84] and wet wool.[85] All of these materials were found to take fire in the narrow RH range between 94% and 98%—and in view of the postulates involved, it is doubtful if effects of size could significantly widen this range. Size is of course vital in determining whether the feeble gaseous oxidation of the wet organic material could generate sufficient heat to raise the temperature above the bacterial maximum. After the effect of size, the most critical factor is the equilibrium relationship between RH and moisture content characterizing the material. If the range of moisture contents corresponding to 94%–98% RH were very narrow, the material would be less likely to be brought to the critical RH in commerce. Moreover, if the range is very narrow, there is a chance of RH moving out of this range during the rise (at constant moisture content) from room temperature to, say, 70°–80°C. The width of the moisture content range will also depend on the amount of thermal and hydrolytic damage the material has suffered, because the presence of water-soluble degradation products must change the RH, and will probably widen the range of moisture content in equilibrium with RH's between 94% and 98%. The possibilities of the critical value of RH being attained are obviously increased if there are variations in moisture content throughout a stack. It may thus be significant that the igniting stack of chopped hay investigated by Musselman[71] was variable in water content, and that he remarks[71] "The fact that the heat varied at different points in this stack and was excessive at focal points, suggests that wet or green bunches of hay may have something to do with the dangerous rise in temperature."

Rothbaum's theory[15] thus proposes an explanation for the rise of damp hay from around 70°–75°C to generally recognized combustion temperatures, as due to straightforward sterile gaseous oxidation of wet hay. Firth and Stuckey[72] suggested that chemical reactions (catalytic decomposition of carbohydrates) are dominant at temperatures above 40°C; but Rothbaum's experiments[15] do not support this thesis, although he suggested that chemical heating reactions might be of greater significance above 40°C when unsaturated oils are involved, as with soya-beans.[86] Glathe[87] studied the spontaneous ignition of hay, and expressed his opinion that chemical heating would probably commence at 60°C, and that self-heating would change from a microbiological mechanism to a chemical one at temperatures between 60° and 75°C. He did not, however, discuss the nature of the chemical reaction. Rothbaum[15] has described experiments showing that "there is no essential difference in the way ignition temperature is reached by microbially heated hay and by hay that has been artificially heated to 90°C." In contrast with most previous theories, Rothbaum's[15] theory is supported by experimental evidence, and it is consistent with the known facts on haystack fires. It explains Firth and Stuckey's[72] remark (based on extensive practical experience) that "moisture content is a controlling factor in the spontaneous combustion of hay"; and Browne's[81] statement, "If the hay is too wet it will not ignite." (See also Truninger.[68]) It moreover offers an explanation of the reported failures of many investigators to set hay (or grass) on fire in laboratory experiments—in most cases their samples were too wet. This last comment cannot be made of failures to ignite hay in large-scale experiments; and Roethe,[70] for example, experimented with alfalfa hay ranging in moisture content from 10% to 60%, in piles of 14 to 48 tons. However, it is true to say that most experiments with haystacks have failed to pay sufficient attention to the need for employing a series of closely spaced moisture contents. When materials such as esparto grass are to be experimented with,[84,88] the gradations of moisture content would need to be very close indeed.[84]

Spontaneous fires in other wet materials are not so well authenticated as in hay. There appears to be evidence for the spontaneous ignition of wet stable manure,[89] wet sawdust,[90] and wet nutshells,[91] for example. Ignition has also been suspected in wet esparto grass,[88] wet fish meal,[92] wet wheat,[93] and wet sheepskins.[94] Although ignition has been demonstrated[85] under laboratory conditions in wet wool, there do not appear to be any well-authenticated cases of ignition of wet wool in commerce, and experiments[18,95–97] in which wool has deliberately been baled wet have not resulted in combustion. Other textile fibers have also failed to ignite when assembled wet in bales or large heaps (e.g., jute,[98,99] cotton[100,101]). However, it appears likely[84,85] that under sufficiently favorable conditions the mechanism proposed by Rothbaum[15] would be applicable to the spontaneous ignition of a wide range of wet organic materials.

Spontaneous Combustion of Air-Dry Materials

Many of the so-called "dry" materials that cause spontaneous combustion in commerce are hygroscopic, and contain appreciable quantities of bound water in an air-dry state. Thus, a material such as cellulose may contain 10% of bound water in equilibrium with common atmospheres; and wool can contain even more bound water under the same conditions. The types of coal that are prone to spontaneous heating generally contain appreciable amounts of water in an air-dry state. Hygroscopic materials such as these usually contain water in amounts depending on both temperature and humidity of the atmosphere with which they are in equilibrium.

When hygroscopic materials in an air-dry state ignite by self-heating, the bound water plays an important part in the heat balance, even if its presence does not modify directly the rate of reaction between the material and atmospheric oxygen. As the temperature rises by chemical reaction, the water-vapor partial pressure within the hot porous material rises above the partial pressure in the ambient atmosphere. The accompanying rise in water-vapor concentration means that water vapor will diffuse out from the interstitial atmosphere within the heated material to the ambient atmosphere, and will carry with it both the latent heat of vaporization and the differential heat of sorption. The migrating water vapor reacts with material in colder zones to liberate heat, and at the same time the normal diffusion of heat reacts with material in the colder zones to liberate water vapor. The diffusion of water vapor and diffusion of heat are thus interrelated, and Henry[16,17] has shown that these two processes are coupled together in a manner analogous to two coupled vibrations. Henry[16] derived the equations governing this situation for a zero rate of heat generation within the material, and showed how these equations could be modified to allow for heat generated by chemical reaction (or by microbial metabolism).

When a porous mass of oxidizable material is exposed to a higher temperature, the migration of bound water can have a further effect on the ignition process. Current mathematical treatments[102,103] that allow for the effect of reactant consumption during thermal explosion when the exothermic reaction has an order greater than zero, are limited to the assumption that temperature would be uniform throughout the reacting mass, and that consumption of reactant would also be uniform throughout the mass. However, for some time before ignition occurs, the consumption of reactant at the hot center will be greater than at the cool perimeter, leading to a lower concentration of reactant at the center; and this will act to diminish the tendency towards thermal explosion. If the air-dry solid contains adsorbed water, the raised temperature will cause an increased concentration of water vapor in the interstitial atmosphere, thus lowering the oxygen partial pressure. The increase in water-vapor concentration in the interstitial atmosphere (at constant absolute humidity in the ambient atmosphere) will further cause water vapor to diffuse outward, and air to diffuse inward. The course of this diffusion will be such that the material at the surface will be exposed to a higher partial pressure of oxygen than will the material at the center. This means that at a late stage in the process, when the material has almost dried out, the concentration of reactant at the hot center may be higher than at the perimeter. This would act to enhance the tendency towards thermal explosion. When materials are being tested for tendencies toward spontaneous combustion, a conventional approach is to expose the sample in a hot oven.[104–106] If the material is hygroscopic, this argument shows that the experimental results obtained may depend on the initial water content, even if allowance is made for the thermal effects of diffusing water vapor.

A special circumstance of the effect of water on thermal diffusivity operates in regard to materials that are stacked while still hot from a machine drier, and are then found to ignite. This behavior is not altogether unexpected in the case of materials that are known to be liable to self-heating and spontaneous ignition, and there are obvious hazards in assembling large masses of hot over-dried products such as textile fibers impregnated with linseed oil or with rubber compounds. However, it is often reported with surprise that materials commonly regarded as relatively free from hazards of spontaneous ignition at ordinary room temperatures, have yet been found to ignite when stored in large masses after machine drying—e.g., cardboard,[28] and wood fiberboard.[12,105,107] Henry's[16] theory suggests that the coefficient of thermal diffusivity operating in hot over-dried hygroscopic materials will be much lower than the diffusion coefficient conventionally calculated from the thermal conductivity, density, and specific heat; which means that these hot materials will cool much more slowly than would be expected from calculations based on conventional thermal theory. This phenomenon has been demonstrated by experiments[108] in which bales of hot over-dried wool were cooled both with and without enclosure in vapor-proof envelopes. The time for half the temperature change to take place in these experiments was shortened from 17 days to 3 days by enclosure in a vapor-proof envelope, demonstrating the increase in effective coefficient of thermal diffusivity caused by preventing exchange of moisture with room air.

The significance of this extended time of storage at a relatively high temperature can be realized, when considered in relation to the period of induction[109] that characterizes many oxidation reactions responsible for spontaneous ignition in commerce.[110,111] The consequent duration of high temperature storage is sometimes long enough to enable gaseous oxidation reactions to pass through a period of induction, and thus attain a rapid rate of chemical heating. Kumar[12] has discussed the importance of rapid cooling when wood-fiber insulating board is stacked after machine drying, and has shown that cooling by water spray does not increase the spontaneous ignition hazard, despite the influence of the heat of wetting.

When a hygroscopic solid naturally prone to exothermic oxidation is considered, local variations in water content throughout the material may render it liable to spontaneous ignition by self-heating mechanisms that would not operate if it were at a uniform water content. Thus, it has been found[91] that self-heating and charring in bins of soap chips (manufactured from oxidizable oils) can be caused by mixing two batches of soap chips of different water contents (see also Freitag[26]). Similarly, it is conceivable that pockets of wet material in which microbial heating is taking place could raise the temperature of nearby "air-dry" material sufficiently to cause oxidative heating to commence. In such a case, the normal transfer of heat would be enhanced by diffusion of water vapor from the wet to the dry zone. The water associated with sorption effects (3) and (5) and with ventilation effects (4) can also influence the course of self-heating in porous hygroscopic materials.

Discussion

From the facts presented above, it can be seen that reactions such as hydrolysis, microbial metabolism, and heat of wetting, are not of themselves able to cause combustion. Combustion can be caused only by oxidation reactions, and these are of four basic types,

A. Oxidation of combustible materials by chemical oxidizers such as nitric acid, peroxides, or perchlorates.

B. Addition of gaseous oxygen to diene and triene bonds in organic compounds such as lipids and rubbers.

C. Direct reaction of gaseous oxygen with combustible materials at normal storage temperatures—e.g., phosphorus, pyrites, coal, and some forms of carbon.

D. Direct gaseous oxidation of most organic materials at higher temperatures (say above 80°C). At any given temperature, this reaction generally proceeds at a faster rate in wet materials than in dry materials.

Mechanisms A, B, and C, above, are sometimes able to generate heat at room temperature at a sufficient rate for piles of reacting material to rise right to combustion temperatures. For spontaneous combustion to occur by mechanism D in a pile of material initially at room temperature, normally it is necessary for some prior mechanism to raise the temperature to a point where D can be sufficiently active. Heat of wetting of a hygroscopic solid can sometimes achieve this, particularly when material is removed from a drier in an over-dried state, and is then assembled in large piles. Absorption of water vapor from the atmosphere can then maintain (or even create) a continuing high temperature in the material, thus enabling direct gaseous oxidation to proceed at a significant rate. The role of water in such a mechanism is obvious.

If the material is raised above room temperature by microbiological activity, this cannot of itself result in combustion. Fungi have an upper metabolic temperature limit of 55°–60°C, and thermophilic bacteria a limit of 75°–80°C. A link is required between these temperatures and temperatures around 150°C, where direct gaseous oxidation of common organic materials can often proceed at a significant rate. This link might be provided either by the oxidation of diene and triene bonds, or by the oxidation of wet organic materials under conditions such that oxidation of the dry material would proceed at a negligible rate. The relative roles of these two mechanisms will be different in different cases; but, in general, it is considered that for the successful continuation of self-heating to successively higher temperatures, oxidation of diene bonds is more likely than wet oxidation as a successor to fungal metabolism; and wet oxidation (8) is a more likely successor in the case of bacterial metabolism.

The proven spontaneous combustion of wet hay demonstrates that in a sufficiently large assembly of reacting material it is possible for a biological reaction to stimulate a relatively mild chemical oxidation, leading ultimately to ignition and combustion. From this it is sometimes argued that the much more violent exothermic reaction that occurs when gaseous oxygen attacks olefinic bonds should also be capable of being triggered by microbial heating. Although this is a plausible theory, the fact remains that operation of this postulated mechanism has not yet been demonstrated under laboratory conditions. For example, pie wool is known[97,112] to cause spontaneous fires under normal (air-dry) industrial conditions. However, experiments[18,95] have been carried out in which bales of pie wool were packed in a wet state, and none of these bales reached temperatures above the maximum[18,32] for bacterial metabolism (80°C). Moreover, two experiments[18] in which bales of wet pie wool self-heated to 72°C, resulted in the pie wool losing most of its tendency to react with oxygen when subsequently tested in a dry state. This loss in reactivity was greater than could be accounted for by direct gaseous oxidation, and it was concluded[18] that the olefinic bonds had been destroyed by bacterial attack. It has been speculated[18] that there might be a greater ignition hazard in bales of pie wool containing less water, and this view may be supported by an experiment with soybeans described by Milner and Geddes[86] (in which the temperature was still rising when the experiment was terminated at 101°C). However, Rothbaum and Dye[113] allowed fungi to attack damp wool under almost isothermal conditions, and found that pie wool showed little tendency to heat more rapidly or to reach higher temperatures than did other wools. The demonstration[113] that fungi metabolize fat in preference to wool must throw some doubt on whether the olefinic bonds in an unsaturated fat would survive an extended period of fungal metabolism (see also Dye and Rothbaum[85]). In the absence of a systematic investigation of the self-heating of olefinic materials containing a closely graded range of water contents, it must be concluded that there is as yet no definite demonstration of the temperature rise due to microbial metabolism being succeeded by gaseous oxidation of olefinic bonds, and thus causing spontaneous ignition. Further experiments may clarify this issue.

Summary

It can thus be seen that the spontaneous ignition of porous solids can take place by two essentially distinct mechanisms: thermal explosion caused by dry combustion, and thermal explosion caused by wet combustion.

In dry combustion, the presence of water plays only a minor part. Evidence is conflicting over whether moderate amounts of water would accelerate or inhibit the oxidation of olefinic bonds, and other oxidation reactions that are capable of generating heat rapidly at low temperatures. Probably, the major role that water can play in such reactions is by the heat of wetting of over-dried hygroscopic materials. This can provide a trigger mechanism to raise materials above room temperature so other reactions can begin. It can also act to delay the cooling of over-dried hygroscopic materials stacked hot from a drier, so that chemical oxidation reactions can proceed through a period of induction, and thus generate heat at a greater rate.

When thermal explosion is caused by wet combustion, water plays the key role. Materials such as cellulose will undergo gaseous oxidation more rapidly when liquid water is present, thus generating heat at lower temperatures than would the dry material. The heat balance is controlled by thermal conductivity, and the operative value of thermal conductivity is controlled by relative humidity. The relationship between water content and RH thus assumes an all important role.

This relationship is in turn controlled by the presence of water-soluble substances, which may be degradation products of the original material. Water also controls the microbiological growth that causes the initial heating of wet materials above room temperature; and one product of microbiological metabolism is water. In this complex interplay of relationships, and in view of the obvious effects of size, it is perhaps not surprising that authenticated spontaneous fires are relatively uncommon in wet materials (other than hay).

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Subject Headings: *Spontaneous ignition, effect of water on; Water, effect on spontaneous ignition.*

ABSTRACTS

I. Ignition Phenomena

Dudko, V. A. "Methods for the Detection and Prevention of Endogenous Fires in Polish Mines," *Bezop. Truda v Promyshl.* 9 (11), 59–60 (November 1965)*

A brief account of the methods and means employed in Poland for the detection of spontaneous heatings and the prevention of fires.

Subject Headings: ***Fire, detection; Fire, endogenous; Poland, mine fires; Combustion, spontaneous.***

Ivanov, V. A., Kulikova, E. N., and Serebryannaya, B. M. "Simplified Method for the Determination of the Explosibility of a Complex Gas Medium when Fighting Mine Fires," *Bezop. Truda v Promyshl.* 9 (10), 6–9 (October 1965)†

Presents a special Table for the rapid determination of the upper safe limits of the oxygen content in gas-air mixtures containing methane, hydrogen and carbon monoxide. The Table is based on the well-known fact that a limiting oxygen content corresponds to every explosive gas mixture, i.e., the limit at which the mixture will explode. Where the oxygen content is below this limit the mixture is safe. It is assumed that the proposed Table will prove useful in determining more rapidly than was possible hitherto whether or not a complex gas–air mixture is safe during the fighting of underground fires.

Subject Headings: ***Explosion, of mixtures; Explosion, gas, in mines; Fire, mine, explosion of gas.***

Kuchta, J. M., Martindill, G. H., and Spolan, I. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Fire and Explosion Hazards of Flight Vehicle Combustibles," *Aeronautical Systems Division, U.S. Air Force Contract 33(615)64–1007 Quarterly Progress Report June 1 to August 31, 1965*

Emphasis is being placed on evaluating various halogenated hydrocarbons as fire extinguishing agents. These compounds are in present use in aircraft fire protection systems. Some evidence has been obtained previously by other investigators that halogenated hydrocarbons (e.g., $CBrF_3$) may react with titanium and support its combustion.

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications* 14(6), 80. By Permission.

† Taken from *Safety in Mines Research Establishment Abstracts of Current Publications* 14(6), 12. By Permission.

A study was set up to determine the ignition and flammability characteristics of titanium and its alloys in air and with various halogenated hydrocarbon fire extinguishing agents (CH_2BrCl, CBr_2F_2, $CBrF_3$, $CF_3CHBrCl$, and $CCl_3CF_2CFCl_2$).

A literature search was made, apparatus was constructed, and ignition-temperature-type experiments were initiated with the fire-extinguishing vapors in contact with heated titanium in air, nitrogen, and argon atmospheres.

The results of the autoignition experiments in heated vessels are these. The minimum autoignition temperatures of bromochloromethane (840°F), dibromodifluoromethane (930°F), and 1–1–1-trifluorobromochloroethane (1165°F) in quiescent air were not influenced greatly by the addition of various quantities of titanium metal foil, turnings, or sponge. The autoignition temperatures of the other two halogenated hydrocarbons were above the maximum temperature (approx. 1200°F) possible in this equipment. In most of these experiments, the titanium appeared to display noticeable reaction with the vapors.

At 1020°F, additional tests were made. $CCl_3CF_2CFCl_2$, CBr_2F_2, and $CBrF_3$ reacted in air with the titanium specimens to produce a bright red glow or burning within 10 to 30 seconds. The other two agents reacted also, but to a lesser degree. The reactions with the titanium sponge and turnings were slightly greater than with metal foil. Glowing or burning was evident too when nitrogen or argon was substituted for air; the reaction, however, appeared to be less. Other tests, for comparison, were made with aluminum.

Other experiments were conducted with electrically heated wires. Minimum reaction temperatures were obtained for the five fire extinguishing agents with electrically heated titanium wires under static conditions. The wire diameters ranged from 0.021 to 0.062 inch. Larger wires tended to have higher minimum reaction temperatures.

The autoignition and wire-ignition experiments are being continued.

Subject Headings: ***Halogenated hydrocarbons, ignition temperature, in air; Ignition, temperature, halogenated hydrocarbons in air.***

L. E. Bollinger (Deceased)

Petrukhin, P. M. and Netseplyaev, M. I. "The Explosibility of Coal Dust with a Low Volatile Content," *Bezop. Truda v Promyshl.* **9** (11), 16–17 (November 1965)*

Russian experiments in recent years have established that dust from certain seams with a volatile content of 10% or less is still explosive. The authors stress that it is important to amend the safety regulations accordingly. Reference is made to investigations that show that coal dust with a 6–14% content of volatile matter was found to be explosive; in these tests 51.4% of the samples contained less than 10% volatiles. The causes for this were examined and are discussed in this article, as are the findings.

Subject Headings: ***Coal dust, explosion; Explosion, of coal dust; Coat dust, low volatility, explosion.***

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications* 14(6), 12. By Permission.

Schuster, F. (Essen, Germany) "The Effect on Ignition Limits of Various Combustible Gases and Inert Constituents," *Gas- und Wasserfach* **106**, 405–408 (1965)

This paper describes the application of a novel way[1] of plotting ignition limit data. (The data were originally obtained by Coward and Jones[2] for gases initially at room temperature and atmospheric pressure.) The plots are constructed with the vol. % $(G+I)$ in $(G+I+\text{Air})$ as abscissa and the vol. % (I) in $(G+I)$ as ordinate, where G is fuel and I (Inert) is noncombustible added to the fuel–air mixture. Such plots are said to show clearly the effects on ignition limits of either substituting fuels in a homologous series or admixing noncombustibles.

Limits of flammability in air diluted with N_2 are plotted for vapors of the following fuels: (1) *n*-alkanes—methane, ethane, propane, butane, pentane, and hexane; (2) olefins—ethylene, propylene, and butadiene; (3) benzene; (4) gasoline. Effects of substituting olefinic and/or aromatic fuels of the same carbon number on broadening the ignition limits of the *n*-alkanes are noted.

In the coordinates described, upper and lower limits merge at the tip of the flammability peninsula. The ordinate at this point represents the maximum for a flammable mixture and is an inverse measure of the flame-suppressant action of a particular noncombustible. The paper shows that flame-suppression exerted by noncombustibles added to mixtures of methane or gasoline vapor in air increases in the following order: argon, helium, nitrogen, "combustion gas" (15% CO_2+85% N_2), water vapor, carbon dioxide, dichloromonofluoromethane, dichlorodifluoromethane, trichloromonofluoromethane, and carbon tetrachloride.

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1. Schuster, F.: Gaswärme *13*, 175–178 (1964).
2. Coward, H. F. and Jones, G. W.: U.S. Bureau of Mines Bulletin No. 503, 1952.

Subject Headings: *Ignition, limits of; Fire, suppression of; Flammability, limits.*

S. C. Kurzius

Seki, K. et al. "Ignition of Methane–Air Mixtures by Feeble Electric Sparks," *Mining and Safety (Japan) 10* (11), 1–11 (1964)*

In this paper the authors described ignition phenomena in methane–air mixtures by feeble electric sparks. Many experiments were conducted with breaking wire electrodes and contacting wire electrodes, and characteristics of spark discharge were observed with synchroscope and theoretical consideration were conducted. Consequently, we have come to be able to analyze mathematically effects arising from variation in the circuit constant.

Subject Headings: *Electric sparks, ignition by; Ignition, by sparks, of methane–air; Methane–air, ignition by sparks.*

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications* 14(6), 77. By Permission.

Van Dolah, R. W., Zabetakis, M. G., Burgess, D. S., and Scott, G. S. (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "Ignition or the Flame-Initiating Process," *Fire Technology* **1**, 32–42 (1965)

This article is extracted from Information Circular 8137, "Review of Fire and Explosion Hazards of Flight Combustibles," issued by the Bureau of Mines in 1963. In very broad terms, it treats the process of ignition and considers the variations in the ignitabilities of combustible gas mixtures with different ignition sources. Included among the ignition sources discussed are electric sources, hot surfaces, heated gases, and hypergolic ignition.

The authors point out the apparent differences in the ways in which ignition sources act. For example, a spark is always not enough to create a flame kernel in the presence of a combustible mixture. The flame will fail to propagate only if the kernel is so small that it loses more heat than it generates, or if there are surfaces interposed to absorb sufficient heat to cool the flame kernel. Thus, the ignition by a spark can be considered energy-limited. On the other hand, ignition by a hot surface generally involves a much greater amount of energy but results in ignition only if a critical temperature, the "ignition temperature," is passed for a period of time in excess of the "ignition delay." Thus, ignition by a hot surface is more temperature- than energy-dependent. An understanding of the controlling factors in such ignition is invaluable in the development of safety equipment and procedures.

Electrostatic sparks are considered merely as point sources of energy. Curves are presented which show the critical spark energy for ignition of various fuels versus gap length, fuel–air ratio, and oxygen content of air. All of the data presented support the hypothesis of the minimum required size of the flame kernel.

The authors very interestingly point out that all of the spark ignition work done in their laboratory over many years resulted in minimum energies of between 0.001 and 10 millijoules. A man, they point out, with a capacitance of 300 micromicrofarads charged to 10,000 volts could initiate a spark equal to 15 millijoules. Thus, the problem of safety from electrostatic sparks is a serious one requiring careful consideration in hospital operating rooms in the presence of the anesthetic–oxygen mixtures, in oil tankers, in spray painting, and elsewhere.

Ignition by contact with hot surfaces is discussed briefly and compared with hot-gas ignition. A table is presented in which the hot-surface ignition temperatures are compared with the hot-gas ignition temperatures for various combustible gases. In all cases, the hot-gas-ignition temperatures are considerably higher and "approximate" the lower-limit flame temperatures. For example, for methane, the hot-surface ignition temperature is 537°C, the hot-gas ignition temperature is 1325°C, and the lower-limit flame temperature is 1518°C. The short contact times of the "hot-gas" ignition source is responsible for the high temperature required.

Ignition by compression, both simple adiabatic and also shock waves, is briefly mentioned. It is pointed out that at pressure ratios less than 10, fuel–air mixtures are unlikely to be ignited.

Hypergolic ignition, reserved here for spontaneous ignition occurring upon the mixing of a bi-propellant combination at ambient temperature, is also dealt with only briefly. It is pointed out that long ignition delays are often accompanied by destructive explosions, whereas short ignition delays lead typically to smooth ignition. The ignition delay can be expected to decrease with increases in temperature and pressure. It is fairly common for the minimum delay to occur with a slight excess of oxidant present.

The entire article is intended to direct the attention of the reader to those aspects of ignition which are understood well enough to provide guidance in techniques and procedures of safety. The authors succeed in alerting the nonspecialist to some of the considerations which could be crucial in fire prevention.

Subject Headings: *Ignition, combustible gas, in flight vehicles; Energy sources for ignition, gas mixtures in flight vehicles.*

F. Falk

III. Heat and Material Transfer

Fitzgerald, F. (The United Steel Cos., Ltd., Rotherham, England) **and Thring, M. W.** (University of London, London, England) "Heat Transfer from Flames in an Experimental Furnace," *Journal of the Institute of Fuel* **38,** 76–85 (1965)

The authors' stated purpose is to develop a method for calculating heat transfer to the stock in a gas-fired furnace, given the temperatures of the stock, the gas flame, and the refractory walls. In this they succeed. Their experimental vehicle is a instrumented laboratory furnace, $1\frac{1}{2}\times1\frac{1}{2}\times7\frac{1}{2}'$ long, fired at a constant rate of 450,000 Btu/hr. Three flames were used: long and short town gas and long calor gas. By subdivision of the furnace into 5 cubic regions, they calculate heat-transfer rates to a strip calorimeter from measured temperature profiles, using well-known, published correlations (i.e., those given in McAdams' 3rd edition). When these calculations are compared with the measured transfer rates to the calorimeter, the results are quite good ($\pm 15\%$).

To further demonstrate the applicability of this simplified calculation technique, they apply successively more complex, "exact" models to their data and show that the correlation is not materially improved.

This critical, self-evaluation of their results is perhaps the most significant contribution of this work. It clearly demonstrates that the nature of the data available for the estimation of furnace heat-transfer rates is usually so sparse, that the application of exact mathematical models often contributes nothing more than burdensome calculation complexity without any redeeming improvement in the prediction of performance.

The paper contains a completely worked out example of the authors' simplified technique, as well as various refined calculations. The graphical data presentations are somewhat confusing (Fig. 3 uses an inverted scale; Figs. 4, 5, 6 present similar data with different scales; and Figs. 9, 10, 11 use the same scale with different intervals). The random admixture of English engineering and metric units can be annoying.

Thus, to go from the graphical data presentation to the worked out example, one must transform from °C to °F to °R. Since the authors use English units in their correlations, the data should be presented in those units.

Subject Headings: *Heat transfer, from flames; Flame, heat transfer from, in furnaces.*

M. E. Gluckstein

IV. Diffusion Flames

Chung, P. M., Fendell, F. E., and Holt, J. F. (Aerospace Corporation, San Bernardino, California) "Nonequilibrium Anomalies in the Development of Diffusion Flames," *Report TDR–669(S6951–90)–1 under Contract AF 04(695)–669 Ballistic Systems Division, Air Force Systems Command, Norton Air Force Base, California* (September 1965)

The development of diffusion flames is analyzed for the stagnation mixing layer created by a jet of fuel injected into the oncoming stream of oxidant at the stagnation region of a blunt body. From the analysis, the conditions which distinguish the simple and multiple transitions from each other, between frozen and equilibrium chemical states, have been clarified. Though the actual numerical results were obtained for the stagnation mixing-layer geometry, the basic findings of the analysis should hold for other diffusion flames also.

Subject Headings: ***Diffusion flame, nonequilibrium in; Ignition, of diffusion flame; Extinction, of diffusion flame; Stagnation-mixing layer.***

Authors' Abstract

V. Combustion Principles

Bonne, U. and Wagner, H. Gg. (University of Göttingen, Göttingen, Germany)* "Untersuchung des Reaktionsablaufs in fetten Kohlenwasserstoff-Sauerstoff-Flamman III. Optische Untersuchunger an rubenden Flammen" ("Research on the Reaction Products of Rich Hydrocarbon-Oxygen Flames III. Optical Research on Conical Flames"), *Beriche der Bunsengssellschaft* **69**, 35–48 (1965)

Simultaneously with the mass-spectrometric measurements on soot formation in flat flames at low pressures, described in Part II (1), spectroscopic investigations of these flames have been carried out. The emission of the radicals C_2, CH, and OH, the temperature distribution of the OH radical concentration in the reaction zone were measured as a function of the composition of the gas supplied. In addition, the quantity of soot was determined, mainly through its absorption. The size distribution of soot particles could be derived optically from the difference between gas and particle temperatures. Furthermore, the influence of experimental conditions on the quantity of soot formed was investigated.

Subject Headings: ***Mass spectrometry, of flame; Free radicals, in flame; Emission spectroscopy, of flame; Soot, formation; Temperature, particles in flame.***

Authors' Abstract

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* U. Bonne's present address is Corporate Research Center, Honeywell, Inc., Hopkins, Minnesota.

Fristrom, R. M. (Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland) "Definition of Burning Velocity and a Geometric Interpretation of the Effects of Flame Curvature," *The Physics of Fluids* **8**, 274–280 (1965)

The burning velocity v_0 has been a subject of controversy for curved flames. This curvature is the macroscopic result of stream tube area variation. The flow cannot be one-dimensional, but for small curvatures it is quasi-one-dimensional. As usually defined, v_0 varies with curvature due to ducting. However, if the primary reaction zone is narrow, the velocity there, v_r, is approximately independent of curvature. v_r is a function of the reaction rate and is related to v_0 by the density ratio ρ_r/ρ_0 and the stream tube area ratio A_0, a geometric factor. Thus, the burning velocity in the absence of curvature, v_0^*, can be defined by $v_0^* = v_r\rho_r/\rho_0 = v_0 A_0$. It can be derived from measurements on flame tips or expanding flame kernels, and appears to be reproducible and independent of external variables such as geometry, inlet flow, and flame curvature. The concept was substantiated by measurements on the microstructure of matched flames of differing curvature and by quantitatively correlating the variation of v_0 with flame curvature in flame tips, expanding flame kernels, and turbulent flamelets.

Subject Headings: *Burning velocity; Flame, curvature effect geometrically interpreted.*

Author's Abstract

McAlevy, R. F., III, Magee, R. S., Wrubel, J. A., and Horowitz, F. A. (Stevens Institute of Technology, Hoboken, New Jersey) "Flame Spreading over the Surface of Igniting Solid Rocket Propellants and Propellant Ingredients," *Technical Report for National Aeronautics and Space Administration under Grant No. NGR–31–003–014* (January 1966)

The velocity at which flame spreads over the surface of igniting nitrate ester propellants, ammonium perchlorate, and thermoplastics has been measured as a function of pressure level and chemical nature of the surrounding, quiescent atmosphere as well as specimen-surface condition. Small test specimens, mounted horizontally, prepared surface upward, in a relatively large test chamber were ignited and the flame-spreading velocity obtained cinematographically. Flame-spreading velocity was found to vary: directly with pressure level (between 0.1 and 1.0 atmospheres); directly with oxygen fraction of environments composed of oxygen–nitrogen mixtures; and inversely with specimen-surface smoothness. For rough-surfaced specimens, photographic evidence of random ignition sites ahead of the spreading flame has been obtained, presumably a result of increased radiant heating. A gas-phase theory of flame spreading is presented; flame spreading is viewed as a continuous gas-phase ignition process. For smooth-surfaced specimens, an analytical prediction of flame-spreading velocity is supported by the data obtained.

Subject Headings: *Flame spread, velocity, solid surface; Flame velocity.*

Authors' Abstract

Meier zu Köcker, H. and Mülders, B. (Mitteilung aus dem Institut für Brennstoffchemie der Technischen Hochschule, Aachen, Germany) "Determination of the Ignition Lag and Combustion Rate of Free Falling Hydrocarbon Droplets," *Erdol und Kohle* **17**, 721–726 (1964)

The detailed investigations of the institute on the burning of liquid hydrocarbons in diffusion flames have now been completed by the development of a device for testing the ignition law and combustion rate of freely falling hydrocarbon droplets. Within certain limits, an optimal approximation to the conditions of technical combustion can be obtained from experiments of this kind. The operation of the metering device has been checked by the use of different hydrocarbons. Determinations of the ignition lag and combustion rate were made in pure oxygen between 600° and 850°C. Some organic compounds have been examined with regard to their effectiveness as ignition accelerators or inhibitors.

Subject Headings: *Droplets, combustion, rate of; Droplets, combustion, ignition lag Hydrocarbons, droplet combustion rate (ignition lag).*

Authors' Abstract

Parandjuk, S. (Aerospace Technology Division, Library of Congress, Washington, D.C.) "The Theory of Detonation, the Combustion Mechanism, and the Properties of Explosives: Compilation of Abstracts," *Surveys of Soviet Scientific and Technical Literature ATD Report 65–111* (Report No. 3 in a series) (December 1965)*

This report is based on Soviet open literature available at the Aerospace Technology Division of the Library of Congress. It consists of abstracts of articles dealing with the theory of detonation, the combustion mechanism, and the properties of explosions. Full translations of some of the source material may be available through agencies and commercial sources. Information can be obtained from the Aerospace Technology Division.

Subject Headings: *Combustion, theory and mechanisms; Explosives, properties of.*

Author's Foreword

Takeyama, T. and Miyama, H. (Toyo Rayon Institute, Japan) "The Radiation of Excited OH Radicals Formed in Ammonia Oxidation," *Paper presented at Third Symposium on Combustion in Japan, December 11, 1965*

The ultraviolet radiation of OH ($^2\Sigma^+$) at 3067 Å was studied, by shock-heating mixtures of ammonia and oxygen in argon, 6% NH_3, 4% O_2, 90% Ar and 4%

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* Processed for Defense Documentation Center Defense Supply Agency. Available at Clearinghouse for Federal Scientific and Technical Information, U.S. Department of Commerce, Springfield, Virginia, 22151, $2.00.

NH_3, 6% O_2, 90% Ar, with a monochromator and photomultiplier in the range of conditions $1600 \leq T \leq 2100°K$ and $3.5 \leq P \leq 4.5$ atm. The radiation profiles obtained showed two types of radiation; a strong spike which appears immediately after an induction period and a weak and constant-level emission, which follows the spike and persists for up to 500 μsec.

The former emission was observed also in the oxidation of hydrogen, methane, and acetylene, but the latter emission only in the oxidation of methane and acetylene.

For the oxidation of ammonia, the temperature coefficients of intensities of the latter emission divided by the sum of spectral emissivities were found to be not large enough to be explained by the thermal excitation of the ground-state OH ($^2\pi$) to the $^2\Sigma^+$ state. Thus, this emission was attributed to chemiluminescence.

The resonance energy transfer mechanism, i.e., $NH + NH \rightarrow N_2^* + H_2$, $N_2^* + OH \rightarrow OH^* + N_2$, was suggested as a possible reaction process.

Subject Headings: ***Oxidation, ammonia, OH radical radiation; Radical, OH, in ammonia oxidation.***

T. Kinbara

Tsuji, H. and Hirano, T. (University of Tokyo, Tokyo, Japan) "Some Observations on the Ion-Concentration Distributions in a Two-Dimensional Nozzle Burner Flame at Atmospheric Pressure," *Paper presented at Third Symposium on Combustion in Japan, December 11, 1965*

Experiments were carried out for studying the electrical properties of a burner flame at an atmospheric pressure with or without seeding materials. The distributions of positive ion concentration and of temperature, as well as isotherms and equi-ion-concentration lines, were observed for each of the two-dimensional nozzle burner flames of propane–air mixtures (gas velocity at the burner port, 1.3 m/sec; equivalence ratios of mixtures, 0.9, 1.0, 1.1, 1.2 and 1.3). The temperature and ion concentration along some stream lines were observed. The breakdown voltage between two small electrodes inserted in the mantle of the burner flame was also measured and its correlation with the ion concentration was studied.

A rectangular converging nozzle burner 8×50 mm at the port was used. The aqueous solution of K_2CO_3 was fed into the combustible mixtures through an atomizer in the air-feed line. The Langmuir probe for the measurement of the ion concentration was a Pt-Rh wire 0.3 mm in diameter and 12 mm long, and the probe current was obtained through the medium of a synchroscope.

With pure flames, the maximum of the ion concentration along any stream line appeared just behind the luminous zone and a little before the point of maximum temperature, as in the case of a flat flame. Chemi-ionization is considered to disappear in about 3 msec after the fuel gas has passed through the luminous zone, and after that the ion concentration decreases to the value showing the thermal ionization of the combustion gas. This maximum concentration (due to chemi-ionization) was found to be related with temperature in Arrhenius' type.

With seeded flames, equi-ion-concentration lines were very similar to isotherms, though the maximum of ion concentration appeared behind the maximum of temperature. For a given amount of seeding additives, the ion concentration depended not only on the gas temperature but on the equivalence ratio of the mixture.

The correlation between the breakdown potential and the ion concentration was confirmed, and the authors suggested the breakdown potential be used as a measure to show the extent the gas is ionized.

Subject Headings: *Ions, distribution in flame; Flame, ion distribution in.*

T. Kinbara

Zeegers, P. J. T. (Physics Laboratory, State University, Utrecht, The Netherlands) "Recombination of Radicals and Related Effects in Flames," *Thesis* (*1966*) Sponsor: C. Th. J. Alkemade

The investigations reported in this thesis are concerned with chemical equilibration of flame gas constituents after primary combustion of premixed hydrogen, carbon monoxide, or acetylene as fuel gas with air has taken place at 1 atm. In these flames, we studied the occurrence and decay of excess concentrations of H, OH, and O radicals above the primary reaction zone, and their influence upon the local flame temperature, upon the emission of the blue K doublet, of the u.v. OH bands and of the visible and u.v. quasi-continuous background.

In Chapter I we describe, in general terms, the properties of premixed flames, the kinetics of recombination reactions and radical equilibria, and some applications of flames in chemistry and physics. After this general introduction, we summarized the objects of our investigation and the methods of measurement employed.

Chapter II deals, in some detail, with the equipment to obtain premixed flames surrounded by a cold, streaming nitrogen sheath, the purity and purification of the unburned gases, the optics, and the detection device. In particular, attention is given to the experimental set-up for the determination of ground-state OH concentrations by u.v. OH-band absorption. Here, advantage is taken of an auxiliary acetylene flame emitting the same u.v. OH bands, as a specific background source. The calibration of the OH absorption in terms of relative OH concentrations is carried out by a variable multiple-pass arrangement.

Chapter III is mainly concerned with the homogeneity of flame-gas composition and metal content, with the measurement and calculation of rise velocity of the burned gases, and with the measurement of local flame temperature. The rise velocity ranged from 4 to 10 m/sec. The maximum temperature in hydrogen and carbon monoxide flames ranged from 1900° to 2060°K, and in acetylene flames from 2300° to 2400°K. In the latter flames, the fuel-to-oxidant gas ratio was chosen such that no C_2, CH, CN, and NH radicals could be detected in emission. The cold nitrogen sheath was tested for its effectiveness to prevent secondary combustion at the flame border which would disturb the flame homogeneity. In this chapter, also, a brief survey is given of our method for calculating the equilibrium flame-gas composition at the known local flame temperature.

In Chapter IV, the decay of excess H, OH, and O radicals is theoretically described on the basis of a mechanism involving slow nonequilibrated termolecular recombination reactions as well as fast binary equilibrated reactions between radicals and stable molecules. We derived a mathematical expression for this decay, which takes into account the effect of the varying temperature with height upon the state of the partial equilibria, the varying concentration of the stable species, and the dissociation of stable molecules into radicals. This general expression is valid shortly above the reaction zone, where the radical concentrations may largely exceed their equilibrium value, as well as at larger heights in the flame, where the radical equilibria are nearly established. The measured dependence of the H and OH concentration on height was found to be consistent with this theory.

From the experiments in H_2 flames we derived values of the specific rate constants k_2^M for the recombination reaction $H+OH+M \rightarrow H_2O+M$, where M is a third body that stabilizes the association complex $(H \cdot OH)^*$. We found for these specific ternary rate constants in the temperature range from 1900° to 2050°K:

$$k_2^{H_2}=(9\pm3)\times10^{-31}\text{cm}^6\text{sec}^{-1} \text{ and } 2k_2^{N_2}+k_2^{H_2O}=(1.5\pm0.3)\times10^{-31}\text{cm}^6\text{sec}^{-1}.$$

Our measurements in C_2H_2 flames yielded only a value of the effective over-all binary rate constant of the above reaction at about 2350°K: $k_2^M[M]=(1.1\pm0.3)\times 10^{-13}\text{cm}^3\text{sec}^{-1}$, with M as yet unspecified. As a side result, we obtained a new value of the reaction enthalpy of the reaction $Li+H_2O \rightleftarrows LiOH+H$; i.e., $\Delta W^*=+14\pm2$ kcal/mole (cf. Appendix 3). The decay of excess O radicals in the recombination zone of carbon monoxide flame could be related to the initial rise in temperature with height. From our investigations and Hollander's in CO flames, we derived for the reaction $CO+O+M \rightarrow CO_2+M$ specific ternary rate constants at about 2050°K: $k_3^{O_2}=(1.2\pm0.3)\times10^{-31}\text{cm}^6\text{sec}^{-1}$, and $k_3^{CO_2}=(2.4+0.3)\times10^{-33}\text{cm}^6\text{sec}^{-1}$. The specific rate constants for this reaction with CO or N_2 as third body appeared to be smaller than $k_3^{O_2}$ by an order of magnitude, and could not be determined.

In Chapter V, we investigate the effects of radical recombination reactions upon the local flame temperature, and upon the emission of the blue K doublet at 4044/47 A and of the OH band at 3064 Å. The initial rise in temperature with height could be associated quantitatively with the corresponding decrease in radical concentrations. The population of OH in the vibrational level $v'=0$ of the $^2\Sigma$ state as well as that of K in the 5^2P state was found to be suprathermal under conditions where the radical concentrations are in excess of their equilibrium values. From the dependence of the suprathermal population of these states on excess radical concentrations in the temperature range of 1900° to 2020°K, we derived rate constants for the following chemiluminescent reactions:

$$H+OH+OH(^2\Sigma) \rightarrow H_2O+OH^*(^2\Sigma;\ v'=0) \quad \text{with } k_2^{*OH}=(7\pm1)\times10^{-33}\text{cm}^6\text{sec}^{-1},$$

$$H+OH+K(4^2S) \rightarrow H_2O+K^*(5^2P) \quad \text{with } k_2^{*K}=(3.5\pm0.3)\times10^{-30}\text{cm}^6\text{sec}^{-1}.$$

As a side result, we found that at 2000°K the ratio of the dissociative quenching by H_2O to inelastic collisional quenching by H_2O of excited OH* and K* amounted to 0.2 and 1.5, respectively. Moreover, from the comparison of experimental results in a H_2–O_2–Ar and a H_2–O_2–N_2 flame, we could rule out the possibility of excitation of OH and K by multi-step processes including vibrationally excited N_2 as an intermediate carrier of chemical recombination energy.

Chapter VI inquires into the (quasi-) continuous background emission in the visible and u.v. part of the spectrum of several types of flames. No background emission could be detected at all in H_2–air flames (except, of course, for OH-band emission), when extreme precautions were taken against stray light and impurity radiation. The background emission of CO and nonincandescent C_2H_2–air flames was analyzed with moderate spectral resolving power in the wavelength interval from 2200 to 6000 A. It appeared to be composed of two parts; one part which is induced by thermal inelastic collisions of CO_2 molecules with flame particles showing an activation energy about equal to the photon energy $h\nu$, and another, chemiluminescent part which is strictly proportional to the product $[CO][O]$. The reaction rate constant of this chemiluminescent part appeared to be not appreciably dependent on temperature.

From these investigations, we arrived at empirical parameters from which the spectral intensity of the background emission may be predicted in absolute measure as a function of wavelength, once the flame-gas composition, temperature, and flame thickness are specified. In a separate section (cf. Appendix 5), an interpretation is presented of the experimental results described in Chapter VI, in terms of chemiluminescent reaction kinetics. In this interpretation, the background emission is thought to arise from excited CO_2 states which may be depopulated by radiative transitions to (low-lying vibrational levels of) the electronic ground state, as well as by inelastic collisions.

Subject Headings: *Radical, recombination in flame; Flame, radical recombination in.*

Author's Abstract

VI. Radiation

Parker, W. J. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Thermal Hardening Considerations Pertaining to Residential Areas," *USNRDL–TR–984 under Office of Civil Defense Work Unit No. 2541B* (February 1966)

The incendiary effects of thermal radiation from nuclear weapons on residential areas is considered. It is concluded that a hazard does exist and that the most desirable means of protection is to make the exposed materials ignition-resistant. This has the benefit of providing fire protection in peacetime as well as in war, and has a better chance of public acceptance. While some fireproof fabrics and flame-retardant treatments for cotton and other materials are now available, there are drawbacks which hinder their universal acceptance. The development of new and improved methods of treatment depend upon an improved knowledge of the mechanism of pyrolysis and ignition and a more fundamental understanding of the action of effective retardants.

A discussion of some of the features of the pyrolysis, and ignition of cellulose and the action of flame retardants that are of importance in the thermal hardening problem is presented. Some experiments which may help to elucidate these processes are suggested. It is recommended that various fire-retardant treatments including presently used chemical flame retardants, halogen flame inhibitors, preheating treatments, and exposure to ionizing radiation, be evaluated in terms of the protection that they might provide against the thermal radiation from nuclear weapons.

Subject Headings: *Cellulose, ignition of; Fire resistance, coatings; Flammability, pyrolysis; Pyrophoric materials; Thermal hardening; Radiation, thermal.*

Author's Abstract

Sachs, A. and Harris, D. (Institute for Defense Analyses, Washington, D. C.) "Thermal Effects of Nuclear Weapons," *Research Paper P–221 under Office of Civil Defense Contract OCD–OS–63–134* (January 1966)

Literature reviewed in the course of developing a model of the thermal effects of nuclear weapons is abstracted and summarized under twelve headings:

Ignition of Materials
Ignition Points
Atmospheric Effects
Thermal Effects of Nuclear Detonation
Fire Susceptibility Factors
Thermal Damage Assessment Models
Fire Development
Mass Fires
Fire Spread Models
Countermeasures
Fire Protection
Miscellaneous

Subject Headings: *Conflagration; Flammability; Ignition; Nuclear weapons, thermal effects of; Radiation, thermal.*

Authors' Abstract

VII. Suppression of Combustion

Sumi, K. (National Research Council, Ottawa, Canada) "A Small-Scale Fire Extinguishment Test for Mechanical Foam," *Fire International* **1**, 56–65 (1965)

A fire test, using a 2-ft-by-2-ft tank, has been developed for assessing the potential extinguishing effectiveness of foam. This performance-type test is believed to fulfill the features that were considered to be important.

The test developed represents conditions often encountered in the extinguishment by foam of a flammable liquid fire. The adjustable foam generator permits study of the foam parameters on extinguishing effectiveness. The radiometer used for determining control time reduces inconsistencies resulting from visual observation and observer's judgment. The use of a small tank permits tests to be conducted indoors on a year-round basis and relatively inexpensively.

The 2-ft-by-2-ft test appears to be as adequate as a 10-ft-by-10-ft test as a means for assessing the effectiveness of foam. The reproductibility of results was slightly better for the 2-ft-by-2-ft test than for the 10-ft-by-10-ft test.

Subject Headings: *Extinguishment, test of foam; Foam, tests.*

Author's Conclusions

VIII. Model Studies and Scaling Laws

Kennedy, M. and Roberts, F. "Modelling Fires in Mine Roadways," *2nd International Fire Protection Seminar, Karlsruhe, Germany, September 30–October 2, 1964* (Reprint)*

The paper discusses a theoretical and experimental study of a fire propagating along a wooden lining in a ventilated and thermally insulated duct, on a reduced scale. The fire is described in terms of a model consisting of four contiguous longitudinal zones; the form of various models and their instrumentation are explained, some results are given and are analyzed in terms of the proposed scaling laws.

Subject Headings: *Fire, in mine roadways; Modeling, mine roadway fires; Mines, fire in roadways of.*

IX. Atomization of Liquids

Bellavin, P. N. and Wright, E. R. (U.S. Naval Air Engineering Center, Philadelphia, Pennsylvania) "Improved Techniques for Determining Foam Compatibility and Particle Size Distribution in Multipurpose Phosphate Dry Chemical Fire Extinguishing Agent," *Report No. NAECOAML–2273 under Bureau of Naval Weapons Weptask SEQ 012 001/200 1/F012 05 04* (November 1965)

An improved technique for determining the compatibility of multi-purpose phosphate dry-chemical fire-extinguishing agent with mechanically produced foam in the presence of a standard hydrocarbon fuel is described.

A method for the determination of sub-screen particle size is also described and is recommended for adoption because of its applicability to this type of material.

Subject Headings: *Fire extinguishment, by powders; Foam, and powders, compatibility of; Powders, and foam, compatibility of; Fire extinguishment, by phosphate.*

Authors' Abstract

X. Meteorological Interactions

Hull, M. K. (Pacific Southwest Forest and Range Experiment Station, U.S. Forest Service, Berkeley, California), **O'Dell, C. A. and Schroeder, M. J.** (U.S. Weather Bureau, Berkeley, California) "Critical Fire Weather Patterns—Their Frequency and Levels of Fire Danger," *Report under Office of Civil Defense Contract OCD–PS–65–27* (1966)†

Weather is one of the dominant factors responsible for uncontrollable spread of mass fires in both urban and rural areas. Identification of the weather types caus-

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ing critical burning conditions in 14 contiguous regions of the United States was the subject of the previous report.[1] However, to be of much practical value, knowing what the critical weather types are and where they influence burning conditions adversely, is not enough. We must also know when they will occur and the type of weather and burning conditions that can be expected. This study is a step in that direction.

Ten years of synoptic weather maps (1951–1960) were studied to determine the frequency of occurrence of each of 21 critical fire-weather types, by months, on a year-round basis. Next, various statistics were computed showing mean values and variations of weather parameters and fire danger indexes, by type and month, at each of a network of 89 representative cities. Using these data as a climatology reference, fire-weather forecasters should be able to make a first approximation probability statement about the occurrence of a particular weather event.

Conclusions

1. Fire danger is not always high when one of the critical fire-weather types occurs; therefore, the forecaster must still assess the weather situation for precipitation, temperature, and past weather, since these factors cannot be readily interpreted from the synoptic charts themselves.
2. If applied intelligently, the statistics can be used effectively as an aid in forecasting specific values of several weather parameters.
3. Fire control planners should find the statistics helpful in developing long range fire plans.

Reference

1. SCHROEDER, MARK J., ET AL.: Synoptic weather types associated with critical fire weather. U.S. Forest Service, Pacific Southwest Forest and Range Experiment Station, Berkeley, California. 492 pp., illus., 1964.

Subject Headings: ***Fire weather, patterns.***

Authors' Summary

Welker, J. R. and Sliepcevich, C. M. (University of Oklahoma, Norman, Oklahoma) "The Effect of Wind on Flames," *Technical Report No. 2 through National Bureau of Standards for Office of Civil Defense under Contract OCD–OS–62–89* (November 15, 1965)

This report presents the results of a systematic investigation of the effect of wind on liquid pool fires. The primary result of the investigation was the measurement and correlation of flame angles of tilt. In addition, data were obtained for fuel-burning rates, flame size, flame radiation, and wake-gas temperatures. The unexpected phenomenon of flame trailing was measured and correlated.

Analysis of the flame-bending data was facilitated by assuming a model of the wind-blown flame and using a momentum balance equation to express the flame bending mathematically. Dimensional analysis was used to determine the relevant parameters for the data correlations. The extent of flame bending was found to depend primarily on the Reynolds number, the Froude number, and the ratio of fuel vapor density to ambient air density.

In addition to the studies on wind-blown flames, an investigation was started into the behavior of interacting liquid-fueled fires. A strong interaction effect was found, with the flame size, fuel-burning rate, and flame radiation increasing as the separation distance of the fires decreased.

A basic study into radiation heat transfer was started in an attempt to provide a sound theoretical basis for calculating heat transfer from flames. In this study, the spectral nature of radiation from flames is considered.

Subject Headings: *Fire, pool (liquid), effect of wind on; Wind, effect on fires, of liquid pools*

Authors' Abstract

Rios, J. (University of Oklahoma, Norman, Oklahoma) "Interaction Effects of Wind-Blown Proximate Flames from Burning Wood Cribs," *Dissertation Flame Dynamics Laboratory, University of Oklahoma, Norman, Oklahoma* (1966)

Research on characteristics of free-burning fires has been increasing during recent years. Most of the studies have utilized single flames from solid, liquid, or gaseous fuels. However, the largest amount of destruction and loss of life is usually caused by mass fires, i.e., fires made up of several separate units of fuel burning simultaneously. Some studies have been carried out to gain an insight of the phenomena occurring during the mass fires.

The present lack of basic information hinders the study of the effects of mass fires. The object of this study was to contribute such information. The case of two proximate fires burning under the action of wind was considered. Single fires were also burned under windy conditions to relate their behavior with that of the proximate fires. Wood cribs were utilized as the fuel. A weighing system was designed and built into the test section of a wind tunnel to use in recording burning rates. Essentially, the spacing between the two fires and the wind speed were varied. The size and arrangement of the fuel in the crib, its moisture content and the type of wood (yellow pine) were the same for all experiments.

As a result of these studies, it was concluded that: (1) the burning rate per unit area of the single fire as well as for each of two proximate fires can be correlated in terms of the depth of flaming zone only, irrespective of wind velocity and spacing between the fires; (2) total burning rate, flame length, and propagation rates for single fires or each flame of proximate fires can also be correlated in terms of the depth of the flaming zone; (3) the rate of propagation can be predicted satisfactorily from burning rate and depth of flaming zone data for either single or proximate fires; (4) the burning-rate correlation of this study is in reasonable agreement with a previous correlation for wood cribs burning in still air after correcting for differences in initially exposed surface area of the fuel and the fuel loading between the studies; (5) the burning-rate correlation for wood cribs is approximately the same as for liquid fires reported by others, except that the latter has a larger exponent; (6) the mathematical model for flame bending of wind-blown fires can be applied to single fires and the upstream flame of proximate fires by using the coefficients derived experimentally in this study; (7) the data on temperatures in the wake of the gases indicated that the wind tunnel walls, and particularly the ceiling, exerted a pronounced effect on the temperature profiles; and (8) steady state was not achieved with respect to radiation from the fires, even after steady state was reached in burning rate, temperature of the wake gases, and rate of fire spread, in that order.

Subject Headings: ***Fire, interaction between fires: Fires, wind-blown, interaction between fires; Fire, crib.***

Author's Summary

XI. Operational Research Principles Applied to Fire Research

Central Mining Research Station (Dhanbad, India) "Scientific Study of Fire in an Indian Coal Mine," *Central Mining Research Station Research Paper No. 11* February 1964)*

The paper presents details and typical results of the scientific investigation undertaken by the Central Mining Research Station during August 1961 to May 1962 on the fire which broke out in the Kurasia Colliery, a public sector mine in Madhya Pradesh producing about 3000 tons of coal per day. In all, 1750 samples of mine air were analyzed, over 2000 temperature measurements were made, and about 100 pressure readings were recorded. The data and their interpretation directly contributed to understanding the nature and extent of the fire, and to formulate steps for controlling and eventually quenching the fire. As a result, it was possible to reopen the mine for production in the relatively short time of less than a year from the start of the fire. There are four appendices to the report.

Subject Headings: ***Coal, mine fire in India; Fire, coal mine in India; India, coal mine fire.***

XII. Instrumentation

Abraham, J. and Gumnick, J. L. (ITT Industrial Laboratories, Fort Wayne, Indiana) "Fire and Explosion Detection for Advanced Flight Vehicles," *Technical Report AFAPL–TR–66–19*, *Air Force Aero Propulsion Laboratory*, *Wright Patterson Air Force Base*, *Ohio* (May 1966)

The objective of this program was to develop a method of detecting fires and explosions using radiation in the ultraviolet below 2900 A. Experiments were carried out to determine the best metal photocathode to be used in a biplanar structure of quartz construction to produce amplification by electron multiplication in a hydrogen-gas discharge. Experiments leading to a choice of molybdenum are described and the operation characteristics of test vehicles and final devices both evacuated and gas filled are described.

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Experimental demonstration of the feasibility of the technique used are also discussed. The device was found to operate successfully at temperatures up to 590°C.

Subject Headings: *Explosion, detection of; Fire, detection; Detection, of explosions; Detection, of fire; Detection, ultraviolet fire; Aircraft, fire detection in.*

Authors' Abstract

XIII. Fire-Fighting Techniques, Equipment

2nd International Fire Protection Seminar. Volume I. "Plastics under Fire Treatment," Karlsruhe, Germany (30 September–2 October 1964)

Following the 2nd International Fire Protection Seminar held at the Karlsruhe Institute of Technology from September 30 to October 2, 1964, the "Verinigung zur Forderung des deutschen Brandschutzes" decided to publish in two volumes the relevant papers and the contributions to the discussions.

Volume I comprises subjects dealing with: "Plastics under Fire Treatment."
Volume II contains collectively the subjects: "Models in Fire Research" and "Fire Fighting Methods."

The large number of participants among the parties at home and abroad interested in fire safety, as well as the usually lively discussions have proved once again that there exists the sincere desire for an exchange of ideas and cooperation on an international basis.

The wealth of subjects dealt with did not permit a clarification of all issues in the course of the discussions, and to harmonize the differing views held. Therefore, by publishing collectively all contributions and discussions, the possibility presents itself for conveying an impression of the manifold unsolved problems to not only those who participated but also to all parties professionally interested in fire safety—and to incite them to continued cooperation.

Subject Headings: *Plastics, fire behavior; Fire, behavior, of plastics; Model, in fire research; Fire-fighting, methods.*

Publisher's Preface

Miller, C. F. (Stanford Research Institute, Menlo Park, California) **and Kerr, J. W.** (Office of Civil Defense, Washington, D.C.) "Field Notes on World War II German Fire Experience," *SRI Project No. MU–5070 under Office of Civil Defense Contract N228–(62479)65419* (October 1965)

To obtain and preserve available basic data on World War II fires in Germany, the authors visited (under the United States Office of Civil Defense sponsorship) key locations and authorities in Germany and the United Kingdom in February and March 1965. This report describes the locations and authorities visited, and summarizes the types of recorded data that were found, as well as the results of conversations during the visit. Data gathered remain the property of the United States; they will be collated at Stanford Research Institute and will serve as input to future analytical studies by the Office of Civil Defense and its contractors.

Subject Headings: ***Fire fighting, German, World War II; Fire storm, in Germany; Hamburg fire.***

Authors' Abstract

Ödeen, K. (Royal Institute of Technology, Stockholm, Sweden) "Theoretical Determination of Temperature Development in a Number of Constructions Subjected to Fire," *Division of Building Construction*, *Royal Institute of Technology*, *Stockholm Sweden Bulletin 9* (1963) In Swedish.

The temperature distribution caused by the Swedish standard fire test for varying time has been calculated and the results can be used for determining when the temperature has reached a critical level for the strength of the material. In particular, the yield for hot-rolled reinforcement steel is reduced by increased temperature and has reached design stress at about 550°C. Thus, the concrete coverage can be ascertained. Such a method has been tried for slabs and has shown good agreement with experimental Swedish Codes of practice.

Characteristic for the standard fire-temperature–time curves is the fact that the stress is laid on the ascending part of the curve, whereas the descending part is treated summarily. (In principle, Swedish regulations assume an irregular stopping of the test after a certain time.) Since the temperature increase in parts of the construction can be considerable, even after heating has been stopped, it is obvious that the entire temperature development should be determined as accurately as possible. In order to carry out this, it is necessary that all the factors which determine this—such as fuel supply (fire load), type of fuel and grade of fineness, air supply, and the heat characteristics of the heating cell's surrounding walls—are taken into account. At the division of building construction at the Royal Institute of Technology in Stockholm, a test building has been built for this purpose. The building is in the form of a long concrete tunnel with an approximately semi-circular cross section. In the building, different amounts and types of conbustible matter are allowed to burn out. The combustion air is measured and supplied with the aid of fans, and the temperature distribution in the room and the surrounding walls is measured using thermo-elements and radiation gauges. The temperature development was registered during an experiment (fig. 15). This experiment was carried out with a fire load of 25 kg/m² and an air supply of $\mathcal{Q}=1.0$ m^3/s. The fuel used was 1″ × 4″ planks. The series of experiments in the fire room which have been described are being carried out and will include about 20 tests.

When determining the fire-resisting quality of a structural member, both from the point of view of resistance to fire spread or its supporting capacity, it is necessary to know the temperature variations in different parts of the construction. Determination of the variation by means of full-scale tests with samples can only be carried out to a restricted extent. This accentuates the need for a method of calculating the chart of the temperature–time development in a construction with a chosen temperature variation in the surrounding air. The solution of this problem represents, in principle, the solution of the equation for heat conductivity, but even if the heat flow is assumed to go in only one direction, in other words, that it is restricted to application to walls or slabs of considerable extent in their own plane, such a solution is complicated by the normal assumptions that significant factors are independent of temperature generally do not apply even approximately in the temperature regions where fire is concerned. This is true especially of the heat-conductivity coefficient λ and the heat surface transmission coefficients a_i and a_u on the fire side and the free-air side of the wall. This means, among other things, that an analytical treatment of the problem becomes extremely complicated and in practice impossible to carry out with reasonable amounts of work. In the literature there are given methods for numerical treatment which have become fairly easy to carry out with the use of electronic computers. The article describes the theory for numerical treatment and gives a collection of the measurements described in the literature for the dependence of heat characteristics on temperature. In addition, calculated temperature distribution charts in various structures caused by a standard fire test are given. Finally, the temperature–time development in the fire chamber according to the standard fire test is discussed and compared with the fire temperature development in a test carried out by the author.

Subject Headings: ***Building design, temperature development during fire; Temperature, development in buildings during fire; Fire tests, for buildings.***

Author's English Summary

Pettersson, O. (National Swedish Institute for Materials Testing, Stockholm, Sweden) "Structural Fire Engineering Research Today and Tomorrow," *Acta Polytechnica Scandinavica Civil Engineering and Building Construction Series No. 33* (1965) Price 10 kroner

Fire engineering design of buildings and parts of buildings is at present characterized by procedures which are nonfunctional and undifferentiated from the viewpoint of structural design, and which are to a great extent based on regulations and recommendations. For instance, load-bearing structures are now conventionally designed in a comparatively judicious fashion so as to take account of static and dynamic loads, whereas the state of fire engineering design gives rise to an undesirable lack of balance between these two fundamental and equivalent phases of structural design work.

The object of this publication is to evolve a theoretical procedure of structural fire-engineering design which is intended to be qualitatively equivalent to the present-day methods of design for static and dynamic loads. The various steps of the design procedure in question are dealt with in detail, and are illustrated by examples which spotlight the scope of knowledge that is available in this field today. In this connection, mention is also made of the most important research problems which must be solved in order that the proposed procedure may be applied as generally as possible in the future.

The publication is to be regarded as a complement to the "General Programme for Scandinavian Long-Term Fire Engineering Research," which has been drawn up by the Author in the spring of 1963 at the request of the Inter-Scandinavian Building Research Conferences, of the Liaison Committee of Scandinavian Fire Prevention Laboratories, and of the National Swedish Institute for Materials Testing, Stockholm.

Subject Headings: ***Building design, and fire; Fire, engineering and structural design; Structural fire engineering.***

Author's Abstract

XIV. Miscellaneous

Handbuch der Raumexplosionen (Handbook of Explosions in Restricted Spaces) (H. H. Freytag, Editor), Weinheim: Verlag Chemie GmbH, 1965.* (German)

A number of authors contribute sections on the combustion process in the gas phase, spherical detonations, the properties of combustible dusts and vapors in air, electrical installations as ignition sources, the ignition hazard of electrostatic charging, frictional and impact sparks, spontaneously combustible materials, light and heat radiation, how operational planning can prevent explosions in restricted spaces, explosion pressure venting, and fire control.

G. Leuschke, "Light and heat radiation," Chap. 3g, pp. 423–442.

The aspects covered by the author are photochemical and photothermal radiation, ignition sources, results of experiments on ignition due to radiation (explosives, foils, dusts, gases, and vapors), the risk of explosion in the presence of solid particles, the hazard of dust explosions (deposited dust, dust/air mixtures).

H. H. Freytag, "How operational planning can be used to avoid explosions in restricted spaces," Chap. 4a, pp. 471–616.

This section contains chapters on the theory of explosion hazards, explosive materials, dangerous concentrations (assessment, measurement of gas and dust in air), pressure venting, safety equipment, faulty apparatus and processes as a cause of explosion, maintenance, and the combination of different safety measures.

W. Wegener, "Systems producing the hazard of explosions in restricted spaces: How the properties of these systems can be altered by increasing or reducing the oxygen concentration in the air," Chap. 2c, pp. 187–202.

The author discusses the relationship between oxygen concentration and safety factors, and between oxygen concentration and explosion effect and describes how a protective gas may be used to suppress explosibility.

Subject Headings: ***Combustion, processes; Detonation; Explosion; Flammability, explosion limits; Ignition; Operations research, in explosion prevention; Spontaneous combustion.***

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications* 15(2), pp. 24, 26, 27. By Permission.

Lommasson, T. E. (The Dikewood Corporation, Albuquerque, New Mexico) "Preliminary Investigation of Firestorm Start-Criteria," *Report DC–TN–1050–1 under Office of Civil Defense Contract OCD–PS–65–53* (June 1965)

A quantitative hypothesis is developed that relates inrush wind velocity at the edge of a potential firestorm area to the release rate of fires within the area and to the size of the area itself. The effects of spread from initial fires are considered and criteria are derived to estimate the way in which the fires are likely to develop with time. The hypothesis was applied to German World War II firestorm and group fire situations, and appears to yield reasonable results in predicting the occurrences of each. The hypothesis may be applied to nuclear attacks against urban target areas.

Subject Headings: *Convection column, fire induced; Fire, development and spread; Nuclear weapons; Radiation, thermal; Fire storm, criterion for.*

Author's Abstract

McAuliffe, J. and Moll, K. (Stanford Research Institute, Menlo Park, California) "Secondary Ignitions in Nuclear Attack," *Final Report through U.S. Naval Radiological Defense Laboratory for Office of Civil Defense under Contract N228 (62479) 65701* (July 1965)

This civil defense study analyzes secondary fires (i.e., fires caused by blast and other nonthermal effects) and other fires caused by disruptions to normal activities because of attack.

Secondary ignition frequencies are estimated at 0.006 per 1000 sq ft of total floor area damaged by at least 2 psi blast pressure. This estimate is consistent with available data from atomic and conventional bombings, explosive disasters, and earthquake and tornado experiences. The estimate implies that secondary ignitions can be the major cause of nuclear fires.

The study resolves existing contradictory conclusions from Hiroshima and Nagasaki on the basis of known physical effects. It shows from statistical analyses that the most hazardous structures are wooden ones; the most hazardous fire sources are electrical and heating equipment; and the most hazardous occupancies are storage of high-energy materials such as oil and chemicals. It attributed secondary ignitions mainly to the rupture of fuel lines and containers by flying debris and collapsing structures.

The study also concludes that fires during warning and postattack recovery periods are not potentially critical civil defense problems. However, hazards from such fires, as well as from nuclear- and disaster-caused fires, can be greatly reduced by cutting off electricity and other energy supplies.

Subject Headings: *Ignition, secondary, during nuclear attack; Nuclear attack, secondary ignition during.*

Authors' Abstract

List of Bureau of Mines Publications and Articles. January 1, 1960 to December 31, 1964, with Subject and Author Index, by R. D. Sylvester. 297 pp.

Supplements the 50-year list of Bureau publications issued from July 1, 1910, to January 1, 1960, and the 50-year list of articles by Bureau authors published outside the Bureau during the same period. Lists more than 3,000 major reports by Bureau authors which were published during the 5 years in regular Bureau of Mines series, in scientific, technical, or trade journals, or in other media, and tells how these may be obtained by the public. Summarizes the vast majority of these reports. Lists the libraries which maintain files of Bureau publications. Summarizes unpublished reports that are available for consultation at certain Bureau offices and libraries, and lists these places. Describes cooperative publications which were issued by organizations with which the Bureau of Mines cooperated on research. Patents issued to Bureau personnel are also listed, as well as instructions on how to apply for permission to use them. One of the outstanding features of this Special Publication is an exhaustive subject and author index. $1.75 (paper cover). (A hard-cover volume will also be available later.) Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.

Subject Headings: ***Publications, Bureau of Mines.***

BOOKS AND PAMPHLETS, MEETINGS

Books and Pamphlets

Committee on Fire Research, "Directory of Fire Research in the United States," *National Academy of Sciences—National Research Council Publication 1409 Third Revised Edition* (1965) $4.00

The material in the Directory is published as submitted by the laboratories at which the research has been performed. This material has been arranged by individual laboratory; first recorded is the laboratory's research supported by out-of-house funds, hereafter called sponsored research; then its work supported primarily by its own funds, hereafter called in-house research. Research that the laboratory sponsors is reported under the research group that does the work.

The categories used to describe the scientific nature of the research are those used in the Committee on Fire Research journal, *Fire Research Abstracts and Reviews*. Categories are at best only a guide, and the large number of entries under "Miscellaneous" indicates that the list sent out was not adaptable in some cases.

The following indexes are included:

1. An alphabetically arranged Institutional Index gives the name, address, and head of each laboratory.
2. An Index of Sponsors lists titles of projects supported by each sponsor and indicates the laboratory that did the research.
3. An Index of In-House Projects lists the in-house projects under the name of the laboratory.
4. A Subject Index lists the names of projects according to thirteen categories and a miscellaneous section, and indicates the name of the laboratory for each project.

Unquestionably, but unintentionally, some laboratories and some research have been omitted from this Directory. Since there is no central office in the United States concerned with fire problems, part-knowledge and hearsay are a part of the initiating process of collection of material on any subject in the broad field of fire. Classified material is ruled out; and there are laboratories that do not wish to publish.

This is the third revision of the Committee on Fire Research's survey of Fire Research in the United States. As with previous surveys it represents a census of those laboratories who by their own definition do fire research in some form. As a result, a number of the 250-odd research projects are only periferally connected with fire studies. In addition, almost half of the projects listed termination dates prior to 1966. Despite these reservations, this represents a substantial effort. Most of the work reported is applied rather than basic research. This imbalance seems likely to be continued in the immediate future since there appears to be no major change in the composition or support of the groups in the fire research field.

The three most popular areas of research were Ignition, Suppression of Combustion, and Fire-Fighting Equipment and Techniques, each with over 80 projects.

The two areas of least interest were Atomization and Modeling Studies, with 7 and 12 projects, respectively. The remaining nine categories included from 25–70 projects apiece.

Subject Headings: ***Fire research, in United States; United States, fire research directory.***

R. M. Fristrom

National Fire Protection Association, "Tentative Basic Definitions for Use in Fire Reporting and Tentative Method for Property Classification" *NFPA Report 901–T and 902–TR* (1965)

This booklet describes the classification procedure under consideration by the NFPA for adoption as a standard.

Subject Headings: ***Property, classification; Classification, of property.***

Editor

Meetings

Eleventh International Symposium on Combustion, University of California, Berkeley, California (August 14–20, 1966)

As is usual at this biennial meeting, a number of papers of interest in the fire research field were presented. A list of the titles is given below. Most of them will be reviewed in subsequent issues of FRAR. Of particular interest were the sessions on fire research which included discussions on fire aerodynamics, fire models, and related combustion problems. An evening discussion on fire research was sponsored by the Committee on Fire Research, National Academy of Sciences—National Research Council is reported elsewhere in this section.

In addition to the technical sessions, several events of interest occurred. Dr. John Longwell of Esso Research and Engineering Co. was elected President of The Combustion Institute. He takes over direction of the Institute affairs from the founding President, Dr. Bernard Lewis (Combustion Research Associates), who has held the presidency for the past 12 years. The Twelfth Symposium is scheduled for 1968 at the University of Poitiers, France. Dr. Marjory Evans of Stanford Research Institute will be the Papers Subcommittee Chairman. It is hoped that Fire Research will be a prominent topic in this forthcoming Symposium.

Symposium Papers of Interest in Fire Research

Howard, J. B. (Massachusetts Institute of Technology, Cambridge, Massachusetts), **and Essenhigh, R. H.** (The Pennsylvania State University, University Park, Pennsylvania) "Mechanisms of Combustion of Devolatilizing Coal Particles in Pulverized Fuel Flames," Paper No. 38, page 28.

Subject Headings: ***Coal particles, combustion mechanism of, in pulverized fuel flames.***

Emmons, H. W. and Ying, S. J. (Harvard University, Cambridge, Massachusetts) "The Fire Whirl," Paper No. 46, page 38.

Subject Headings: *Fire whirl, bouyancy and vorticity; Bouyancy and vorticity, of fire whirl.*

Chigier, N. A. and Charvinsky, A. (Israel Institute of Technology, Haifa, Israel) "Aerodynamic Study of Turbulent Burning Free Jets with Swirl," Paper No. 47, page 39.

Subject Headings: *Jets, turbulent burning, aerodynamics of; Aerodynamics, of turbulent jets.*

Lee, S. (State University of New York, Stony Brook, New York) **and Ling, C.** (Christian Brothers College, Memphis, Tennessee) "Natural Convection Plume above a Circular Ring Fire," Paper No. 48, page 41.

Subject Headings: *Plume, convective, above ring fire; Model, study, convective plume above ring fire.*

Smith, R. K. (University of Manchester, Manchester, England) "Radiation Effects on Large Fire Plumes," Paper No. 49, page 42.

Subject Headings: *Plumes, fire, radiation effects on; Radiation, effects in fire plume.*

Murty, K. A. and Blackshear, P. (University of Minnesota, Minneapolis, Minnesota) "Pyrolysis Effects in the Transfer of Heat and Mass in Thermally Decomposing Organic Solids," Paper No. 50, page 44.

Subject Headings: *Pyrolysis, of cellulose, heat and mass transfer; Heat transfer, and mass transfer, in cellulose pyrolysis.*

Kinbara, T. (Sophia University, Tokyo, Japan), **Endo, H.** (University Electro-Communication, Tokyo, Japan), **and Sega, S.** (Toho University, Chiba, Japan) "Downward Propagation of Smouldering Combustion through Solid Materials," Paper No. 51, page 44.

Subject Headings: *Combustion, smoldering, through solid materials; Solid materials, propagation of combustion.*

Tarifa, C. S. and Torralbo, A. Am. (Instituto Nacional de Tecnica Aerospacial "Esteban Terradas," Spain) "Flame Propagation along the Interface between a Gas and a Reacting Medium," Paper No. 52, page 45.

Subject Headings: *Propagation, of flame, at fuel surface; Radiation, effects on flame propagation; Convection, effects on flame propagation.*

Murty, K. A. and Blackshear, P. (University of Minnesota, Minneapolis, Minnesota) "Some Effects of Size, Orientation and Fuel Molecular Weight on Fuel Surfaces Burning in Stationary Air," Paper No. 53, page 45.

Subject Headings: *Burning rate, of fuel surface, effect of convection and radiation; Convection, effect on burning rate; Radiation, effect on burning rate.*

Albini, F. A. (Institute for Defense Analyses, Arlington, Virginia) "A Physical Model for Fire Spread in Brush," Paper No. 54, page 46.

Subject Headings: *Fire spread, in brush, model for.*

Roberts, A. F. (Safety in Mines Research Establishment, Buxton, England) "An Analogue Method of Estimating Wood Pyrolysis Rates," Paper No. 55, page 48.

Subject Headings: *Pyrolysis, of wood, rate of; Pyrolysis rate, of wood.*

Hamilton, C. W. and Schott, G. L. (Los Alamos Scientific Laboratory, New Mexico) "Post Induction Kinetics in Shock Initiated H_2—O_2 Reactions," Paper No. 63, page 55.

Subject Headings: *Kinetics, post-induction, of H_2—O_2 reaction; H_2—O_2 reaction, kinetics of.*

Jenkins, D. R. and Yumlu, V. S. (Shell Research, Ltd., Thornton, England) **and Spalding, D. B.** (Imperial College, London, England) "The Combustion of Hydrogen and Oxygen in a Steady Flow Adiabatic Stirred Reactor," Paper No. 80, page 74.

Subject Headings: *Combustion, hydrogen-oxygen, mechanism of.*

Mayer, S. W. and Schieler, L. (Aerospace Corporation, Los Angeles, California) **and Johnston, H. S.** (University of California, Berkeley, California) "Computation of High Temperature Rate Constants for Bimolecular Reactions of Combustion Products," Paper No. 87, page 82.

Subject Headings: *Kinetic constants, calculation of, in bimolecular reactions.*

Dixon-Lewis, G., Williams, A., and Pye, J. W. (The University, Leeds, England) "Some Observations on the Combustion of Methane in Premixed Flames," Paper No. 102, page 103.

Subject Headings: *Methane, combustion of, in premixed flames; Premixed flames, methane combustion.*

Tsuji, H. and Yamaoka, I. (University of Tokyo, Japan) "The Counter-Flow Diffusion Flame in the Forward Stagnation Region of a Porous Cylinder," Paper No. 105, page 107.

Subject Headings: *Diffusion flame, aerodynamics of, chemical parameters of; Chemical parameters, of diffusion flame; Aerodynamics, of diffusion flame.*

Zimpel, C. F. and Graiff, L. B. (Shell Oil Company, Wood River, Illinois) "An Electron Microscope Study of Tetraethyllead Decomposition in an Internal Combustion Engine," Paper No. 109, page 113.

Subject Headings: *Tetraethyllead, anti-knock mechanism, in engines.*

Howson, A. C. (I.C.I., Runcorn, Cheshire, England) **and Simmons, R. F.** (Manchester College of Science and Technology, Manchester, England) "The Kinetics of the Thermal Reaction between Hydrogen and Oxygen in $BaBr_2$ Coated Reaction Vessels," Paper No. 118, page 124.

Subject Headings: *Explosion limit, hydrogen-oxygen, in presence* $BaBr_2$.

Gray, P. and Lee, P. R. (The University, Leeds, England) "Studies on Criticality: Temperature Profiles in Explosive Systems and Criteria for Criticality in Thermal Explosions," Paper No. 123, page 132.

Subject Headings: *Explosion, thermal, critical parameters in methyl nitrate; Critical parameters, in thermal explosions, of methyl nitrate.*

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," Paper No. 126, page 137.

Subject Headings: ***Hydroxyl radical, reaction with methane.***

R. M. Fristrom

Informal Specialists Meeting at Eleventh International Symposium on Combustion: "Free Burning Fires." Sponsored by Committee on Fire Research (E. E. Zukoski, Chairman) August 17, 1966

An informal conference entitled "Free Burning Fires" was held during the Eleventh International Symposium on Combustion at the University of California, Berkeley, the evening of August 17. It was sponsored by the Committee on Fire Research and chaired by Professor E. E. Zukoski of the California Institute of Technology.

The meeting was opened by Professor E. E. Zukoski, who outlined the statistics and significance of fires in the United States.

Professor H. Emmons of Harvard University spoke on the aerodynamics of fire in enclosed spaces. Dr. M. Gerstein of Dynamic Science Corporation discussed the significance of fundamental fire research data and its use by the practitioner, using room fires as an example. Professor H. C. Hottel of Massachusetts Institute of Technology spoke on fire research practices. Professor C. Tarifa of the Instituto Nacional de Tecnica Aerospacial, Madrid, Spain, discussed their program of fire research on fire brands and flame propagation.

There was a floor discussion of the possible utility to fire research of blowoff and flash-back measurements on porous cylinder diffusion flames.

The meeting was concluded by a discussion of the present and future prospects of fire research.

Subject Headings: ***Conference, on free burning fire; Fire, free burning; Fire, conference on.***

Editor

LETTERS TO THE EDITOR

"A Fire-Service Viewpoint of Woodland and Urban (Building) Fire Situations"

Fire situations resemble other situations in that they consist of conditions, circumstances, or elements that become the pertinent factors in determining solutions to the problems presented. Such factors clarify the objective, dictate the selection of activities to achieve the objective, and influence all decisions.

Pertinent factors, by nature, are noncontrollable, semicontrollable, or controllable, but are referred to here as primary and secondary to indicate a time sequence in origin and not necessarily a degree of importance. Primary factors should be recognized and evaluated on arrival at the fire, in making initial and subsequent decisions; secondary factors appear as soon as work is started, due to the inevitable, reciprocal effects of one activity on another. Activities may be complicated or even simplified by factors individually as well as by the result of the relationships between said factors.

Primary factors at serious structural fires may include: endangered occupants; buildings of many different types of construction, heights, ages, and areas; structural collapse; various kinds of occupancies and industries with their inherent hazards; unique fire spread; back-draft explosions; vehicular traffic; the presence of fixed systems (standpipe, sprinkler, and other). By contrast, woodland fires, except where they threaten populated areas, feature none of the foregoing factors and hence are not truly representative of urban, and especially, city fire conditions. Structural fire spread is unique because the fire can travel through interior and exterior vertical and horizontal channels, thereby presenting difficult and extremely important problems impossible to simulate at woodland fires.

Consideration of some secondary factors increases doubts that woodland fires can completely or accurately simulate urban (building) or city fire conditions. For example, ventilation, a very essential activity at structural fires for relieving smoke and heat conditions, locating the fire, and controlling its direction, is not essential at woodland fires. On the other hand, some major activities at woodland fires, such as establishing firebreaks and applying special extinguishing agents from planes, are inappropriate for fires in buildings.

For more rewarding research results, the situations in question could be more realistic.

Charles V. Walsh
Deputy Chief (Ret.)
New York City Fire Department

Subject Headings: *Fire, woodland, simulating urban fire; Fire, urban, simulated by woodland fire.*

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Volume 9 Number 2

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.
1967

FIRE RESEARCH ABSTRACTS AND REVIEWS is published three times a year by the Committee on Fire Research of the Division of Engineering—National Research Council, 2101 Constitution Avenue, Washington D. C. It is supported by the Office of Civil Defense of the Department of the Army, the U. S. Department of Agriculture through the Forest Service, the National Science Foundation, and the National Bureau of Standards. The opinions expressed by contributors are their own and are not necessarily those of the Committee on Fire Research.

Library of Congress Catalog Card Number 58-60075 rev

Available without charge from the
Office of the Committee on Fire Research
National Academy of Sciences—National Research Council
Washington, D. C. 20418

FOREWORD

We regret to report the retirement of Professor Hoyt C. Hottel of the Massachusetts Institute of Technology as chairman of the Committee on Fire Research. Your editor believes he is joined by the entire fire research community in thanking Professor Hottel for his many contributions during the decade in which he formed the Committee and so ably led it. It is reassuring that leadership has been transferred to the experienced hands of Professor Howard W. Emmons of Harvard University, and that Professor Hottel has consented to remain as a member of the Committee. We welcome Professor Emmons and wish him every success in the task of building an even more effective Committee on the base that Professor Hottel has laid.

Other changes have occurred in the Committee membership. The terms of two members have expired. Professor Perry L. Blackshear, Jr. of the University of Minnesota and Mr. John Rhodes of the Factory Mutual Engineering Corporation have served the Committee with distinction and deserve a "well-done" from the fire research community. To compensate for this loss we welcome three new members of experience and ability. Dr. Carl W. Walter, Clinical Professor of Surgery at Harvard University, will broaden the area of competence of the Committee with his experience in the medical field. Dr. John A. Rockett, Director of Basic Research of the Factory Mutual Engineering Corporation, will strengthen the Committee with his experience in the physics of combustion and practical knowledge of fire problems. Mr. Raymond M. Hill, Chief Engineer and General Manager of the Department of Fire, City of Los Angeles, brings to the Committee a broad knowledge of the practical aspects of the fire problem.

We also regret to report that the Committee has lost the invaluable services of its Executive Secretary, Mr. D. W. Thornhill. This marked the tenth year in which he has managed the affairs of the Committee. It has been a job well done. Your editor thinks that he speaks for Dan Thornhill's many friends in the field in wishing him every success in his new undertaking with the American Association for the Advancement of Science.

Colonel Robert A. Cliffe has been named Executive Secretary of the Committee. Colonel Cliffe has been with the Academy for the past six years, serving as Staff Director for several committees. We welcome him to the Committee on Fire Research.

An Eastern Section of The Combustion Institute was initiated at a meeting on 14 March 1967. This section was set up to provide a forum for members of The Combustion Institute in the eastern United States and Canada. The first meeting will be held in Pittsburgh, Pennsylvania, 27 and 28 November 1967. (See Meetings, page 122.)

This issue contains several special items. It begins with an article entitled "Fire Storms" by Professor R. R. Long, in which he presents an interesting picture of the physical processes of the phenomena. A translation of a Russian article entitled "On an Effect which Stabilizes the Wrinkled Front of a Laminar Flame" by Ya. B. Zel'dovitch has been provided by Mr. L. J. Holtschlag. Dr. A. F. Robertson has furnished a report on a conference, "Burns and Flame-Retardant Fabrics," held at the New York Academy of Medicine, 2 and 3 December 1966. Many aspects of this problem were discussed, with the discouraging conclusion that no socially acceptable solution to many of the problems exists at present. Continued study of this area was recommended.

R. M. Fristrom, *Editor*

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REVIEWS

Fire Storms*

R. R. LONG

Department of Mechanics, The Johns Hopkins University

This paper discusses mass fires as encountered, for example, in some of the incendiary attacks of World War II. We emphasize the conjecture that the fire storm is accompanied by, and influenced by, strong rotational motion. We show that an intense vortex can develop in an hour or less from the rotation present in typical atmospheric eddies of a scale of the order of the size of a city. We follow with an analysis of the modeling problem. Criteria are given for the construction of workable models, both when rotation is important and when it is unimportant.

1. *Introduction*

This paper is concerned with the mechanics of mass fires. A characteristic aspect is the occurrence of sudden increases in intensity and induced wind velocity. The city "fire storm" and the "wildfire blowup" are the best-known examples.

Fire storms are uncommon. Some authors (Bond[1]) believe that all occurred during incendiary attacks of World War II on the German cities of Darmstadt, Kassel, Stuttgart, Hamburg, and Dresden. Others (Sanborn[2]) believe that similar phenomena occurred in Japanese cities as well. In all cases, according to accounts, the fires occurred in areas of the order of one to five square miles with little or no tendency to spread outward. The storms had two main features: (1) The entire region was on fire at the same time, i.e., individual building fires merged into one gigantic blaze; (2) an induced wind was created which may be estimated from the damage to be between one hundred and two hundred miles per hour or more.

The wildfire blowup (Byram[3]) may be similar in that: (1) the fire is more or less confined without a propagated front; (2) it flares up rapidly; and (3) it is accompanied by high wind. In at least some cases of the blowup, one or more fire whirls either accompanied or characterized the fire (Barrows,[4] Berl[5]). The whirls may be small or large. Some are reported to be a thousand feet or so in diameter with winds of one hundred miles per hour. There is always a very thin core of rapidly whirling and ascending air. Small-scale whirlwinds have also been reported in city fires. In Japan they are called *tatsumaki* or *dragons' tails* (Mosley[6]).

2. *General Remarks on Vortices*

In 1961 at a study conference on fire problems at Woods Hole, Massachusetts, sponsored by the National Academy of Sciences,† the author submitted a note containing the suggestion that a basic feature of some, or all, fire storms was a

---

* This paper presents the results of an investigation sponsored by the Office of Civil Defense through the Naval Radiological Defense Laboratory.

† This conference was under the guidance of the Committee on Fire Research of the National Academy of Sciences-National Research Council, Division of Engineering under a grant from the National Science Foundation.—*Editor*

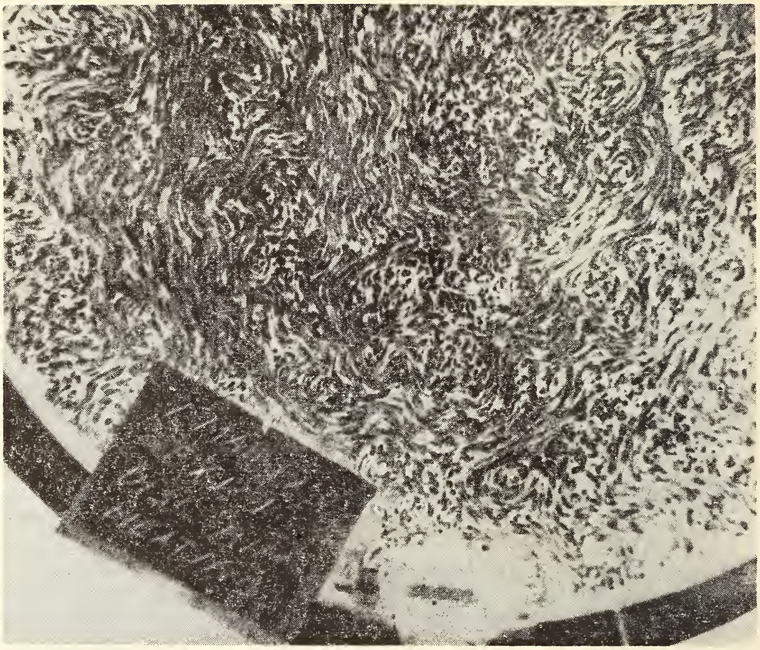

FIG. 1. Jets in the dishpan experiment (Fultz, 1953). A dishpan full of water is rotated about its center and heated at the bottom at the outer edge. The motion is made visible by aluminum powder sprinkled on the surface. The streak photograph shows the surface motion in the form of thin jets. At the proper rotation speed, the fluid motion resembles the atmosphere at levels near the tropopause.

vigorous rotation* induced by the burning and by the presence of rotation in the ambient atmosphere. The suggestion was tentative, and one of the purposes of this paper is to present a brief but detailed discussion, together with proposals for modeling such fire storms.

Consider first a laboratory experiment. If a homogeneous fluid is brought up to solid rotation in a rotating vessel, efforts to create moderately small relative motions, either by thermal or mechanical means, usually lead to flows in which the velocity is concentrated in jet-like patterns or in intense whirls (Long[8]). Examples are shown in Figs. 1 and 2. These jets and vortices reflect a basic tendency for fluid motion to become so concentrated in thin, internal boundary layers that frictional forces increase locally to the same level of importance as internal forces, *no matter how small the viscosity*. To discuss fire storms and blowups, we need consider only the case in Fig. 2. Here, fluid is extracted slowly at the axis of rotation near the free surface of a rotating vessel of water (Long[9]). Quickly, an intense vortex appears, extending from the surface to the bottom of the vessel, with no appreciable vertical variation of its properties (Figs. 2 and 3). The motion in the core of the whirl may be several hundred times the rotation of the vessel. Outside the core, the velocity field is close to that of the vr vortex, i.e., $vr=K$ (constant), where v is the circulating velocity component, and r is the distance from the vortex center.

Let us examine the mechanics of this phenomenon. Evidently the high rotation or vorticity in a core comes from the advection into the center of the vortex lines of

---

* Subsequently, evidence has been offered that this was indeed the case for the Hamburg fire storm (Ebert, Ref. 7).

the fluid's basic vorticity, and from the stretching of these lines through the withdrawal process (Lamb[10]). Just outside the core, the fluid should be relatively free of vorticity; this reasoning is supported by the observation of the irrotational motion $vr=K$. Actually, if the withdrawal process continued indefinitely, and if the fluid had no viscosity, the vorticity near the axis would increase indefinitely. In a real fluid, however, the speeds become so high near the axis that viscosity, no matter how small the coefficient, becomes as important as the inertial forces. Physically,

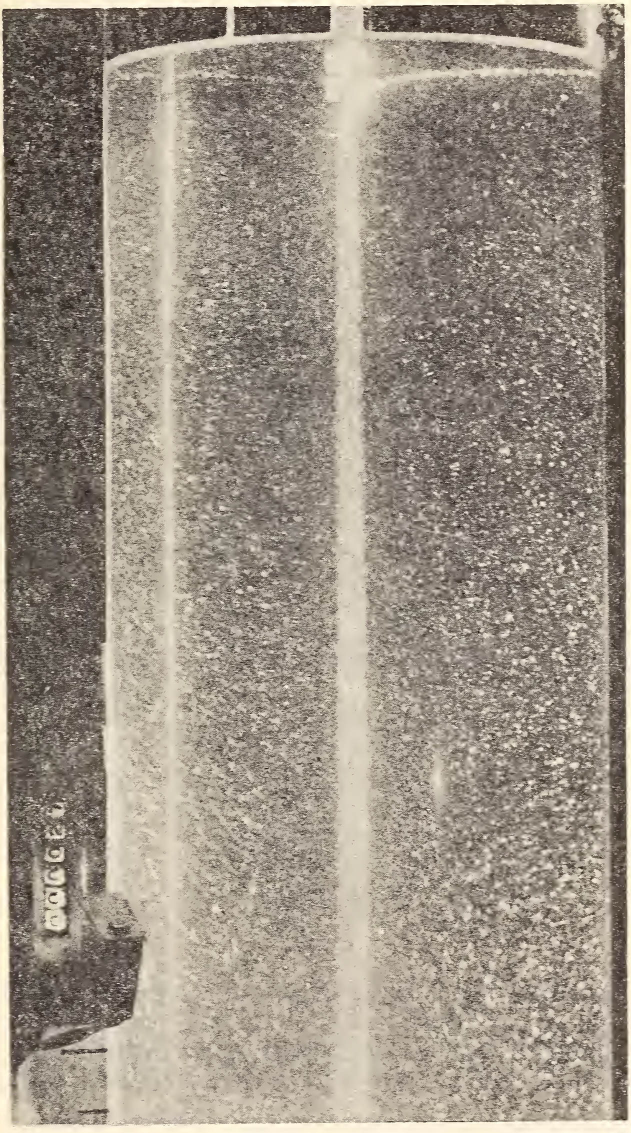

Fig. 2. Vortex at the axis of a rotating fluid (Long, 1961). Fluid is extracted at the axis of a tall cylinder of rotating fluid. The photograph is for low withdrawal rates. The result is an intense vortex at the axis extending from bottom to top.

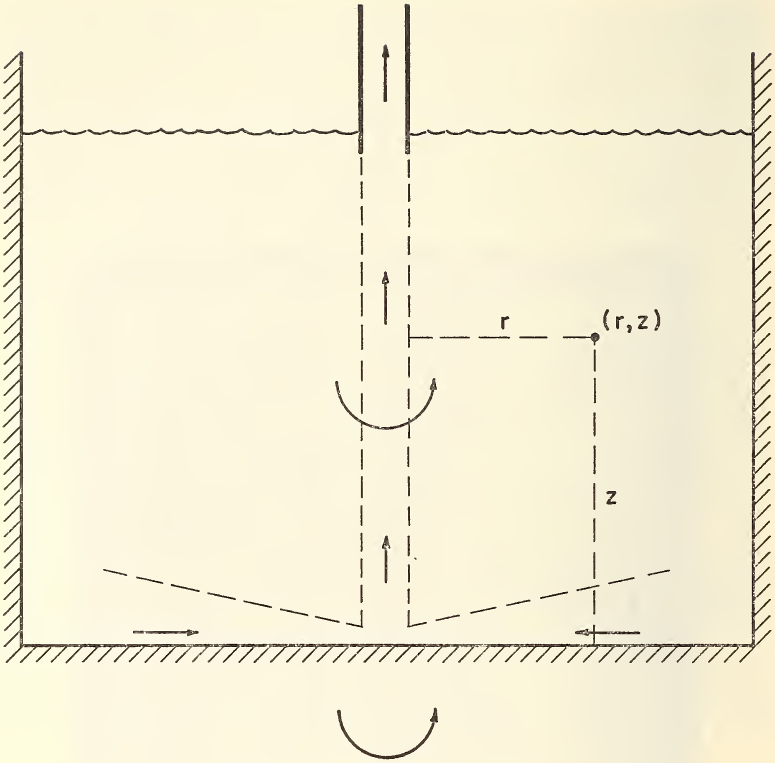

FIG. 3. Schematic drawing of a vortex.

the central region, or core, becomes a boundary layer (Schlichting[11]) in which viscous, inertial, and pressure forces are all of the same order. With this concept, the equations of the problem yield

$$u[\partial(vr)/\partial r]\sim\nu[\partial^2(vr)/\partial r^2] \tag{1}$$

$$w(\partial w/\partial z)\sim\rho^{-1}(\partial p/\partial z)\sim\nu(\partial^2 w/\partial r^2) \tag{2}$$

$$v^2/r\sim\rho^{-1}(\partial p/\partial r) \tag{3}$$

$$w/z\sim u/r \tag{4}$$

$$v\sim K/r \tag{5}$$

In the above,* u is the outward velocity component, v the tangential velocity component, and w the vertical velocity component. The pressure is p, the (constant) density is ρ, the molecular coefficient of viscosity is ν, and the circulation is K. We use a polar coordinate system with z representing elevation and r representing

---

* The symbol $\sim$ is shorthand for "is of the order of magnitude of." Our notation is standard but a bit ambiguous in that we use a given symbol, such as "z", to represent both the height at a given point, and the vertical scale of the motion. Again, "w" is either the vertical velocity, or a speed characteristic of the vertical velocity.

distance from the axis of the vortex. The approximations (1)–(5) lead to:

$$v \sim K/r \tag{6}$$

$$w \sim K/r \tag{7}$$

$$u \sim \nu/r \tag{8}$$

and, if δ_r is a characteristic radius of the core,

$$\delta_r/z \sim \nu/K. \tag{9}$$

The fundamental results of this analysis are that the tangential and vertical velocities are of the same order, but that the outward velocity component is much smaller, if, as is usual, the viscosity coefficient is very small. This reflects the well-known physical principle that a ring of fluid in a vortex resists inward or outward motion. Thus, if a ring of fluid moves inward anywhere in the vortex, it will, in the absence of friction, conserve its angular momentum. If the angular momentum increases outward, it will find itself going faster than the environment.* Since the weaker centrifugal force of the environment just balances the inward pressure-gradient force, the inward moving ring will not be in equilibrium, but will tend to move back out again (Haurwitz[12]). In the case under consideration, the motion "leaks" inward but only because of small frictional forces. The thickness of the core increases linearly along the axis of the vortex if the viscosity is constant, but the cone angle is very small since it is approximately equal to the small nondimensional number ν/K.

The influx in a thin boundary layer at the bottom, as pictured in Fig. 3, also has a simple physical explanation. The outside portion of the vortex well above the bottom is nearly a vr vortex with a balance of centrifugal and pressure-gradient forces. But all velocities must be zero at the bottom so that the rings of fluid close to the bottom lose angular momentum by friction. The resultant reduction of the outward centrifugal force on a given ring permits inward motion. Let us investigate orders of magnitude of quantities in this influx layer. From the equations of motion and continuity, we see that

$$u(\partial u/\partial r) \sim \nu(\partial^2 u/\partial z^2) \sim K^2/r^3 \tag{10}$$

$$u[\partial(vr)/\partial r] \sim \nu[\partial^2(vr)/\partial z^2] \tag{11}$$

$$w/z \sim u/r, \tag{12}$$

so that

$$u \sim K/r \tag{13}$$

$$v \sim K/r \tag{14}$$

$$w \sim (K\nu)^{1/2}/r. \tag{15}$$

Thus, the inward velocity near the bottom is of the order of the tangential velocity, whereas the vertical motion is slight. The boundary layer thickness in the vertical is

$$\delta_z \sim r(\nu/K)^{1/2} \tag{16}$$

---

* The angular momentum is *approximately* constant outside the core, but, in fact, there is a very gradual increase with radius.

This is of the order of 1 mm in a laboratory vortex in water. The inward motion near the bottom is very large, and it is apparent that the inward mass transport for the whole vortex takes place primarily in this boundary layer.

The time for the development of the vortex is of great interest in the problem of fire storms. Observations indicate that the storms form within an hour or two after the burning begins. Given this time period, the problem reduces to (1) finding a source of the initial vorticity, and (2) explaining the vorticity increase to the observed levels by inward motion and vertical stretching. An obvious possibility is that the earth's vorticity can serve as the source. This has been discussed by Nielsen[13] who obtained an expression for the tangential velocity as a function of time for a two-dimensional vortex in which the core is a line sink. The inward motion of a ring is a simple function of the strength of the sink and, from the conservation of angular momentum, the tangential velocity at a given point can be obtained as a function of time. The flux into the sink is assumed to resemble entrainment of air into the core of the fire vortex. Nielsen assumed a flux or entrainment rate constant with height. He concluded that if the fluid is initially at rest with respect to a rotating frame with angular velocity equal to the local angular velocity of the earth, the vortex forms too slowly; 24 hr is required to obtain speeds of 50 mph or so. Actually, in view of the above analysis of the orders of magnitude of vortex quantities, the entrainment is confined mostly to the ground levels, so that a constant entrainment with height is a highly unrealistic assumption. Indeed, Nielsen's conclusion that

$$u \gg \nu / r \tag{17}$$

contradicts (8) and is therefore contrary to the whole concept of the core as a boundary layer. However, if attention is directed to the vortex development near the ground, his results may have some application, although inward-moving rings will not come very close to conserving their angular momentum in this region. In addition, the inward velocity should drop off with distance even faster than $1/r$, since the motion near the ground will not be two-dimensional, and one would expect influx of air from levels above the ground boundary layer. Notice, however, that both of these factors lead to a time for development of the vortex even longer than that yielded by Nielsen's computations.

It has been suggested by the author (Long[14]) and others (Fujita[15]) that the source of vorticity for a tornado may be a local eddy or cyclone with vorticity of the order of 10^{-2} sec^{-1} rather than the vorticity, 10^{-4} sec^{-1}, of the earth's rotation. Eddies of this strength exist (Fujita[15]) and they have been observed to spawn tornadoes. But such eddies are extremely rare in the atmosphere, and, although a sufficient number may exist to explain the infrequent occurrence of tornadoes, it is extremely unlikely that one would be found just over a city at the beginning of an incendiary raid. Indeed, such eddies may not even occur in Europe since tornadoes are virtually unknown in this area.

The typical large-scale vortex (extra-tropical cyclone) of mid-latitudes has a vorticity of 10^{-5} sec^{-1} or one order of magnitude less than the vorticity of the earth's surface (Byers[16]). These are the common storms that bring the day-to-day weather, and meteorological stations have been positioned for the precise purpose of finding and describing storms of this size and intensity. Knowledge of eddy systems becomes poorer and poorer as consideration is given to smaller and smaller systems, but recent work in meso-scale meteorology suggests that smaller eddies are quite common (Landers,[17] Gerhardt[18]).

The investigation of direct application to our problem is the one by Landers who measured vorticity using observational points with various separations. He found that for separations of the order of 200 miles (approximately the distance between standard weather stations), the average vorticity was 2.4×10^{-5} sec^{-1}. This agrees with our remarks about the vorticity of extra-tropical storms. When the observational points were an average of 16 miles apart, the average vorticity was 1.2×10^{-4} sec^{-1}. Finally, when the mean distance between wind reports was about 1 mile, the average vorticity was 0.75×10^{-3} sec^{-1}. *This investigation presents the strongest kind of evidence that rotation one order of magnitude greater than the earth's rotation is available on a scale of a mile or so and is therefore suitable for development into a city fire storm.* Since the *typical* eddy of a size comparable to that of a city has a vorticity of about 10^{-3} sec^{-1}, it must be rather common to have such eddies with strengths several times this. If we use Nielsen's analysis, this would suggest the possibility for development of a fire storm in a period of 1 hr or less; and we have allowed for the likelihood that Nielsen's estimate of 24 hr using the earth's rotation may be too short by a factor of 2 or so.*

On the basis of this discussion, it is altogether possible that the infrequency of fire storms does not arise from the lack of a vorticity source, but rather from the rarity of other necessary meteorological and fuel conditions. The paper by Bond[1] is enlightening in this respect. Bond gives a report of upper-air conditions at Hamburg at the time of the fire storm of July 1943. They are highly unusual for this part of the world, in that the surface temperatures during the day were extremely high (86°F) and the decrease of temperature aloft was almost as rapid as the dry-adiabatic lapse rate. For example, the temperature was 36°F at 10,000 ft as opposed to 32°F for an adiabatic lapse. In addition, winds at all levels were unusually light and the air unusually dry at the time of the Hamburg fire storm. In short, the absence of gravitational stability, the lightness of wind, and the dryness of the air may be the meteorological conditions† necessary for the development of a fire storm.

3. *Turbulence*

The above discussion of viscous vorticities assumed that the fluid was in laminar motion with a constant coefficient of molecular viscosity ν. This is, in fact, the case in small laboratory vortices. In many cases where laminar, laboratory phenomena have larger-scale, turbulent counterparts in the atmosphere, investigators are tempted to assume that the fluid mechanics problems are similar except that turbulence in the larger-scale case acts like molecular viscosity but with a much larger, constant, eddy viscosity coefficient ν_T. Such, for example, is the assumption by Nielsen[13] in the paper discussed above and in the Appendix. There are instances in which this assumption may be reasonably good. But the problem of fire storms is surely not one of these. In the theory of turbulent jets, for example (and the core of the turbulent vortex may be considered a jet with swirl), it is well known, (Townsend[19]) that the eddy viscosity takes on such values that the eddy Reynolds number $\nu_T/\bar{w}L$ is about 0.10–0.01. Here, $\bar{w}$ is the mean velocity in the jet, and L the diameter of the jet. Outside the jet, the eddy viscosity may be zero (laminar motion) or much smaller than in the jet, depending on the particular circumstances. In the fire problem, if we use 100 ft sec^{-1} for $\bar{w}$ and 500 ft for L, we obtain values of ν_T of 500 to 5000 ft^2 sec^{-1} as contrasted with 20 ft^2 sec^{-1} adopted by Nielsen!

* See the Appendix for additional discussion of Nielsen's paper.
† Such conditions are more common in the United States than in western Europe.

The observation that the eddy Reynolds number is of the order of 1 in problems of jets and turbulent boundary layers may be explained in several ways. In the first approach, it may be assumed that the eddies behave like molecules whose speeds are of the order of the fluid velocity. The mean free path or mixing length of the eddies may be assumed to be of the order of the diameter of the vortex or jet. Then, according to molecular theory, the viscosity coefficient is of the order of the product of these two. Thus, $\nu_T \sim w'L'$, where w' is the turbulent velocity and L' is the mean free path. On the basis of our assumptions, this is equivalent to $\nu_T \sim \bar{w}L$, i.e., the eddy Reynolds number is of the order 1. For the second approach, let us use the definition of eddy viscosity which, for our problem, can be expressed as

$$\partial \overline{u'w'}/\partial r \sim \nu_T (\partial^2 \bar{w}/\partial r^2), \tag{18}$$

where the bar indicates an average. In addition, since it is a turbulent boundary layer, the Reynolds-stress terms are of the order of the inertia terms, i.e.,

$$\partial \overline{u'w'}/\partial r \sim \bar{u}(\partial \bar{w}/\partial r) \tag{19}$$

From relation (19), we get

$$\overline{u'w'} \sim \bar{u}\bar{w} \tag{20}$$

This suggests that $u' \sim \bar{u}$, $w' \sim \bar{w}$ and that the correlation is of the order of 1. A combination of (18) and (20) yields

$$\bar{u} \sim \nu_T/r \tag{21}$$

already derived for the laminar case.

4. *Models of Fire Storms*

The problem of creating laboratory models of fires has received considerable attention in the past few years (Berl[20]). The physics of such a complicated phenomenon is almost prohibitively difficult. Indeed, we are far from the point where we have a good idea of the important laws which control the onset and development of fires. Therefore, theoretical approaches, even when combined with the present possibilities for high-speed computing, are unlikely to provide a real understanding of the problem. Because of this, the modeling technique would seem to be the most likely immediate source of future information about the subject of this paper.

The dominant physical process, missing in the analysis so far, is the buoyancy created by the heating of the fluid by the fire. The heat causes an expansion of the air and a lowering of the density. The light air begins to rise until it loses the extra heat by radiation and mixing, or until it reaches a level in the atmosphere at which the density of the environment equals the density of the rising parcel. As the air rises, new air comes in toward the center of the fire in replacement. If, as conjectured in this paper, rotation is important, it will also acquire a swirling component.

Let us now attempt to lay down the conditions for creating a model of this phenomenon. We assume that the model and prototype are in turbulent motion. This is certainly true in the atmosphere, and it is quite obvious that a model can be created large enough for the motion to be turbulent. The ground beneath the fire storm is, of course, rough (buildings, trees, etc.), and the motion near the ground should be determined by a roughness length k and the shear stress τ_0 in the layer near the ground (Townsend[19]). The only external parameter is k, so that a nondimensional number appearing immediately is k/D, where D is a length characteristic of the diameter of the fire. *Our first modeling criteria, therefore, are equality of* k/D, *and geometric similarity of the burning area including geometric similarity of the roughness elements.* These modeling conditions obviously present no difficulties if sufficient pains be taken. The molecular coefficients of momentum and heat conduction are of no importance because the laminar boundary layers are extremely thin compared with any other length in our problem. *Thus, neither the Reynolds number (Goldstein*[21]*) based on the molecular coefficient of viscosity, nor the Prandtl number (Hottel*[22]*) need be modeled.*

There may be ambient turbulence outside the core and the ground boundary layer, both in the model and in the prototype. Indeed, there certainly is such turbulence in the atmosphere under all conditions. A common value of the eddy-viscosity coefficient (Brunt,[23] Nielsen[13]) is 10–20 $\text{ft}^2\ \text{sec}^{-1}$. As we have seen, however, the eddy viscosity in the core and boundary layers jumps enormously to a figure of the order of a thousand times greater than this. Since the eddy-viscosity terms are of the same order as the inertia terms in the core and boundary layers, they must be far smaller than the inertia terms outside. As a result, viscosity can be completely neglected in the ambient air. *In short, a Reynolds number composed of the ambient eddy viscosity (which is one of the external parameters of the problem) need not be modeled.* Indeed, the model itself can be laminar except in the boundary layers and core.

The process of adding heat by the first is a very complicated one. The fire heats the air directly, and at a distance by radiation, but we will adopt a model similar to that of Nielsen[13] in which we assume simply that the ground temperature over the burning area is a certain constant $T_0+\Delta T$, where T_0 is the uniform temperature at the ground outside of the burning area. The region outside of the burning area in the atmosphere is effectively infinite in extent, and we will assume that it is made large enough in the model to eliminate any errors from this source. Probably the outside area should be at least 10 times the burning area.

The problem of rotation has been discussed in some detail above. For the purpose of our model, we will consider that the fluid is in solid rotation with angular velocity Ω at great distances from the burning area. The fluid in both cases will be taken to be air with adiabatic exponent σ and specific heat at constant pressure c_p. The equations that we need for our problem are

$$\rho(d\mathbf{v}/dt) = -\nabla p - \rho g\mathbf{k} \tag{22}$$

$$\rho^{-1}(d\rho/dt) + \nabla\cdot\mathbf{v} = 0 \tag{23}$$

$$p = RT\rho \tag{24}$$

$$[d/dt(p/\rho^{\sigma})] = 0, \tag{25}$$

where ρ is the density, $\mathbf{v}$ the vector velocity, p the pressure, g the acceleration of gravity, $\mathbf{k}$ the vertical unit vector, T the temperature, and R the gas constant for atmospheric air. As discussed above, we have assumed that the processes of molecular diffusion of momentum and heat are negligible. *We have neglected radiation effects, and we have neglected the rotation of the earth.* The latter is easily justified. For example, even if the speeds are as low as 30 ft sec^{-1}, the Rossby number (Fultz[24]), which is the ratio of inertia force to Coriolis force, is

$$c/Lf = 30/(5\times 10^3 \times 10^{-4}) = 60, \tag{26}$$

where c is a characteristic speed, f the Coriolis parameter, and L the horizontal scale of the motion (about 1 mile). The Rossby number, therefore, is very large compared with 1, so that Coriolis forces are quite negligible. We have also adopted a Cartesian coordinate system; the scale of the motion is obviously so small that the spherical shape of the earth is of no consequence.

With a compressible fluid such as air, and for any problem involving buoyancy forces, the density of the fluid is an awkward quantity to deal with. The buoyancy of a parcel is most closely related to a quantity $\bar{\rho}$, called the *potential density*. This is defined to be the density that a parcel would acquire if its pressure was changed adiabatically from the pressure p to a reference pressure p_0. The reference pressure p_0 may be taken to be the pressure at the ground at great distances from the fire. Thus, according to Eq. (25),

$$p/\rho^{\sigma}=p_0/\bar{\rho}^{\sigma} \tag{27}$$

It is also useful to define a quantity which we may call the *virtual pressure*,

$$\bar{p}=[\sigma/(\sigma-1)]p_0^{1/\sigma}p^{1-(1/\sigma)} \tag{28}$$

With use of $\bar{p}$ and $\bar{\rho}$, our Eqs. (22)–(25) may be written

$$\bar{\rho}(d\mathbf{v}/dt)=-\nabla\bar{p}-\bar{\rho}g\mathbf{k} \tag{29}$$

$$\nabla\cdot\mathbf{v}+(\sigma-1)^{-1}(d\ln\bar{p}/dt) \tag{30}$$

$$\bar{p}/\bar{\rho}=\mathcal{J}c_pT \tag{31}$$

$$d\bar{\rho}/dt=0, \tag{32}$$

where $\mathcal{J}$ is the mechanical equivalent of heat. It is obvious from the definition (27) and from (25) that potential density is a conservative quantity.

Let us assume now that the problem of a fire storm is determined by Eqs. (29)–(32), by the condition that the speed,

$$|\mathbf{v}|\rightarrow\Omega r \tag{33}$$

at great distances from the fire (r is the distance from the center of the storm), by the roughness at the ground and by the potential density distribution at the ground and at infinity. The last requires some explanation. We have agreed to adopt a simplification used by Nielsen, in which the temperature at the ground is taken to be a certain constant outside of the fire area and another, higher constant inside the fire area. The pressure will not vary very greatly on the ground, so that from Eq. (31) this amounts to prescribing a constant potential density $\bar{\rho}_0$ outside the burning area and a lower potential density $\bar{\rho}_0-\Delta\bar{\rho}$ at the ground in the burning area. The potential density distribution at great distances from the fire, horizontally and vertically, may be taken to be either a uniform constant $\bar{\rho}_0$ (in which case the atmosphere is neutrally stable) or $\bar{\rho}_0(1-\alpha z)$ corresponding to a stable, linear distribution with height. Since the former is a special case of the latter, obtained by putting $\alpha=0$, we will take

$$\bar{\rho}=\bar{\rho}_0(1-\alpha z)+\bar{\rho}' \tag{34}$$

as the definition of the perturbation potential density $\bar{\rho}'$. We will assume $\bar{\rho}'\rightarrow0$ at great distances from the fire. It is convenient also to define a perturbation pressure by

$$\bar{p}=\bar{p}_0+\bar{\rho}_0 g\tfrac{1}{2}(\alpha z^2)-\bar{\rho}_0 gz+\bar{p}'. \tag{35}$$

Substituting into Eqs. (29)–(32), we obtain

$$d\bar{p}'/dt-\alpha\bar{\rho}_0 w=0 \tag{36}$$

$$(\bar{\rho}_0-\alpha z\bar{\rho}_0+\bar{\rho}')(d\mathbf{v}/dt)=-\nabla\bar{p}'-g\bar{\rho}'\mathbf{k} \tag{37}$$

$$\nabla\cdot\mathbf{v}+(\sigma-1)^{-1}(d/dt)\ \ln[\bar{p}_0-\bar{\rho}_0 gz+\bar{\rho}_0 g\tfrac{1}{2}(\alpha z^2)+\bar{p}']=0 \tag{38}$$

We will now attempt as closely as possible to scale the various quantities in these equations so as to obtain nondimensional variables of the order of one.* For example, we try to find a characteristic velocity, c, such that a nondimensional variable $u^*=u/c$, for example, is of the order 1. This is not really possible in our problem because the orders of magnitude of the velocities change as we go from ground boundary layer to core. Thus, u is very small in the core and very large in the ground boundary layer. An estimate of the vertical velocity may be obtained from the vertical component of Eq. (37) by assuming that the vertical acceleration is of the order of the buoyancy force,† i.e.,

$$w(\partial w/\partial z)\sim g(\Delta\bar{\rho}/\bar{\rho}_0). \tag{39}$$

Thus

$$w\sim[gL(\Delta\bar{\rho}/\bar{\rho}_0)]^{1/2}, \tag{40}$$

and we will scale the other two velocity components, using the same characteristic velocity. As seen in the transition from (39) to (40), we scale z and the other two distances, x and y, with the length L (so far undefined). We have supposed that the fluid is in solid rotation with angular velocity Ω at distances far from the fire. The air moves inward, and there is a tendency for conservation of angular momentum. Thus we should take for the angular momentum in the fire storm, a quantity proportional to Ω and to the square of the distance that the parcels move inward. We do not know this distance, however, so that we use

$$|\mathbf{v}|L\sim\Omega D^2, \tag{41}$$

where D is the diameter of the fire. Using for $|\mathbf{v}|$ the characteristic velocity in (40), we get

$$L=\frac{\Omega^{2/3}D^{4/3}}{[g(\Delta\bar{\rho}/\bar{\rho}_0)]^{1/3}}. \tag{42}$$

Accordingly, let us now define the following nondimensional quantities,

$$p^*=\bar{p}'/gL\Delta\bar{\rho}\qquad \rho^*=\bar{\rho}'/\Delta\bar{\rho}\qquad \mathbf{r}/L=r^*$$

$$\frac{\mathbf{v}}{[gL(\Delta\bar{\rho}/\bar{\rho}_0)]^{1/2}}=\mathbf{v}^*\qquad t^*=\frac{t[gL(\Delta\bar{\rho}/\bar{\rho}_0)]^{1/2}}{L}. \tag{43}$$

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* This is only a convenience and is not necessary for the validity of our modeling criteria.

† This is not the case in most convection problems. Normally the vertical pressure-gradient force and the buoyancy force are in close balance, and the vertical acceleration is the small difference between these. In the fire storm, however, the heat is so great that vertical accelerations are appreciable, at least in lower levels.

Substituting into the Eqs. (29)–(32), we obtain

$$(d\rho^*/dt^*/)-\epsilon w^*=0 \tag{44}$$

$$[1-\epsilon s z^*+s\rho^*](d\mathbf{v}/dt)^*=-\nabla p^*-\mathbf{k}\rho^* \tag{45}$$

$$\nabla\cdot v^*+\frac{-m^2w^*+\epsilon s m^2 z^* w^*+m^2 s(dp^*/dt^*)}{(\sigma-1)[1-m^2z^*+(\epsilon/2)sm^2z^{*2}+m^2sp^*]}=0, \tag{46}$$

where

$$s=\Delta\bar{\rho}/\bar{\rho}_0, \qquad m^2=\frac{g^{2/3}\Omega^{2/3}D^{4/3}}{(\bar{p}_0/\bar{\rho}_0)(\Delta\bar{\rho}/\bar{\rho}_0)^{1/3}}, \qquad \epsilon=\frac{\alpha\Omega^{2/3}D^{4/3}}{g^{1/3}(\Delta\bar{\rho}/\bar{\rho}_0)^{4/3}}, \qquad F=\left(\frac{\Omega^2 D}{g(\Delta\bar{\rho}/\bar{\rho}_0)}\right)^{2/3}. \tag{47}$$

The boundary conditions may be written:

Outside Burning Area:

$$\bar{\rho}'=0 \quad \text{at} \quad z=0$$

$$|\mathbf{v}|\to\Omega r \quad \text{as} \quad r\to 0;$$

Inside Burning Area:

$$\bar{\rho}'=\Delta\bar{\rho} \quad \text{at} \quad z=0. \tag{48}$$

Nondimensionalization yields:

Outside Burning Area:

$$\rho^*=0 \quad \text{at} \quad z^*=0$$

$$|\mathbf{v}^*|\to Fr^* \quad \text{as} \quad r^*\to\infty;$$

Inside Burning Area:

$$\rho^*=1 \quad \text{at} \quad z^*=0. \tag{49}$$

5. *Modeling Conditions*

If we can construct a geometrically similar model such that Eqs. (44), (45), (46), and (49) are the governing equations both for the model and the fire storm, and, if the nondimensional quantities k/D, ϵ, s, F, m^2, and σ are the same in both cases, then we may be said to have created a *strict* model of the fire storm. We may estimate what these nondimensional numbers are and seek to construct a model in which they have the same values.

The first quantity, k/D, has already been discussed, and we have decided that if the model and prototype are geometrically similar with respect to the roughness elements, this quantity will be the same in both cases. The nondimensional number ϵ involves the gradient in the vertical of the potential density distribution. The relevant constant, α, is zero if the atmosphere is neutrally stable, but the common value in the atmosphere is approximately 5×10^{-6} ft^{-1}. Let us consider a possible model in which the burning area has a diameter of the order of 10 ft. The vertical scale will also be about 10 ft, and it is obvious that the decrease of potential density in the undisturbed region is quite negligible over so small a height. In short, it seems impossible to create a model in air in which the stability of the atmosphere is taken into account. This is not a serious matter, however, in the problem under consideration in this paper. As we have already mentioned, there are strong indications that the very existence of a fire storm requires an atmosphere that is nearly neutrally stable.

The constant s presents no modeling difficulties, since it will be the same in both cases if we have a fire of approximately the same temperature in the model as in the fire storm.

The nondimensional number F is all-important for our purposes. Since the acceleration of gravity g, and the percentage density difference $\Delta\bar{\rho}/\bar{\rho}_0$ are the same in model and prototype, modeling this number requires equality of $\Omega^2 D$. Let us take as typical the value $\Omega_a = 10^{-3}\ \text{sec}^{-1}$ and $D_a = 5\times10^3$ ft. We then find that the angular velocity for the model must be $\Omega_m = 2.2\times10^{-2}\ \text{sec}^{-1}$ for a fire diameter of 10 ft, and $\Omega_m = 7\times10^{-2}\ \text{sec}^{-1}$ for a fire diameter of 1 ft. These are of the order of 0.1–1.0 revolutions per minute and such rotations are easily obtainable in a number of ways, for example, by use of a rotating vessel or by injection of air through slits at a distant outer boundary. The quantity $\sigma = 1.4$ is the same in both model and prototype.

Finally, the nondimensional number m^2 rises from the effect of compressibility in the equation of continuity. Using the following sets of values:

Atmosphere	*Model*
$g = 32\ \text{ft sec}^{-2}$	$g = 32\ \text{ft sec}^{-2}$
$\bar{p}_0/\bar{\rho}_0 = 3.4\times10^6\ \text{ft}^2\ \text{sec}^{-2}$	$\bar{p}_0/\bar{\rho}_0 = 3.4\times10^6\ \text{ft}^2\ \text{sec}^{-2}$
$\Omega = 10^{-3}\ \text{sec}^{-1}$	$\Omega = 2.2\times10^{-2}\ \text{sec}^{-1}$
$D = 5\times10^3$ ft	$D = 10$ ft
$s = 1$	$s = 1.$

We obtain for m^2,

$$m_a^2 = 2.5\times10^{-3} \qquad m_m^2 = 5\times10^{-6}. \tag{50}$$

Thus the effect of compressibility is quite negligible both in the fire storm and in the model. Notice that, if we use 1 ft as the size of our model, the value of m_m^2 is even smaller. We see then that the air in both cases behaves like an incompressible fluid.*

A final remark may be made about the modeling problem in cases where no swirl exists. One may easily scale the relevant equations and boundary conditions in a way similar to the scaling in the rotating case. Now, however, there is no condition corresponding to Eq. (33), so that Ω will not occur at all in the problem. Obviously, the characteristic length becomes D, that is, the motion is on the scale of the fire diameter. The new scaling, therefore, is identical to that in Eq. (43) when L in these definitions is replaced by D. The resulting equations and conditions are identical to those in Eqs. (44)–(46) and (49), except that the condition at infinity in (49)

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* This opens the possibility for a model using a liquid such as water. This would have certain advantages; in particular, one could then model the stability of the atmosphere in cases where this seems to be important. We will not explore this aspect of the problem in this paper.

is replaced by

$$\mathbf{v}^* \rightarrow 0 \quad \text{as} \quad r^* \rightarrow \infty. \tag{51}$$

The quantities to be modeled are the same except that F is missing in Eq. (47) and m^2 and ϵ are now defined as

$$m^2 = \frac{gD}{\bar{p}_0/\bar{\rho}_0} \qquad \epsilon = \frac{\alpha D}{\Delta\bar{\rho}/\bar{\rho}_0}. \tag{52}$$

Again, in a neutral atmosphere, ϵ is zero in both model and prototype. In addition, m^2 is still negligible in both cases. The problem of modeling then reduces to obtaining geometric similarity and equality of s.*

6. *Summary*

The above paper discusses the mechanical aspects of mass fires. An analysis is made of the possibility that rotation is an important feature of fire storms. It is shown on the basis of the properties of vortices in homogeneous fluids that a fire storm with swirl will consist of a vertical core with high tangential and vertical velocities and a ground boundary layer with in-rushing air moving at speeds of the order of the tangential velocity. Considerable attention is given to the problem of the generation of the strong rotation. It is shown that the intense swirl can develop in an hour or less from the rotation present in typical atmospheric eddies of a scale of the order of the size of a city.

The modeling problem is also discussed. If swirl is important, the modeling criteria become: (1) geometric similarity of the burning area including similarity of the roughness elements; (2) equality of $\Delta T/T_0$, where T_0 is the temperature of the ambient air, and $T_0+\Delta T$ is the temperature of the fire; (3) equality of

$$F = \left(\frac{\Omega^2 D}{g(\Delta T/T_0)}\right)^{2/3}.$$

When there is no swirl, the modeling criteria are (1) and (2) above.

Appendix

The paper by Nielsen[13] deserves careful analysis in this report because his investigation is directly concerned with the problems of swirl in mass fires. Nielsen uses as his basic equations, the Navier-Stokes equations for a viscous, heat-conducting field. He integrates these equations on a computer, and obtains flow patterns for a number of conditions. His solutions reveal a vortex motion with a "core" and ground "boundary layer" of the order of hundreds of feet in linear dimension. The swirl is never very large, and is quite weak if the vorticity at great distances from

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* This conflicts with conclusions by Byram (Ref. 25), whose results required equality of a nondimensional number that does not appear in the present analysis. Byram, however, did not use the equations of the problem. Indeed, it is often found that some nondimensional constants that appear to be important *a priori*, disappear from the modeling problem when the equations are scaled in the manner of this paper. Of course, the actual boundary conditions at the fire have been ruthlessly simplified here and in Byram's paper. This leads to uncertainties in the analysis which may make desirable the equality of the nondimensional number derived by Byram. Obviously no harm is done if it can be modeled conveniently.

the center is of the order of 5×10^{-5} sec^{-1} (approximately the earth's vorticity), or 5×10^{-4} sec^{-1}.

It is possible to make two major criticisms of Nielsen's paper. Most importantly, he has solved a set of difference equations, and *these solutions do not approximate solutions of the corresponding differential equations.* For example, outside of the ground boundary layer, as illustrated by his Tables VII and VIII, the computations yield an inward velocity of $u=2$ ft sec^{-1}. If we use his value of $\nu=20$ ft^2 sec^{-1}, this corresponds to a viscous core of radius

$$\delta=\nu/u\sim10 \text{ ft}.$$

Of course his data do not reveal a core of this dimension since his grid size is seven times larger than this! The use of such a coarse grid means that viscous forces are nowhere important in his numerical solution. This is revealed by a check of his tables of data which show clearly that there is a very close balance of all non-viscous terms in his difference equations. Thus he has really solved the difference equations corresponding to the *perfect-fluid differential equations of motion.* The latter, together with viscous boundary conditions, have no non-trivial solution in the problem posed by Nielsen.

There is a second, fundamental objection to Nielsen's results. In order to obtain a finite region for the integration, he imposes an upper boundary and an outer cylindrical boundary. As he points out, the artificiality of the upper boundary is not important because, when its position was changed from 1250 ft to 2500 ft, the results were substantially the same. He makes no such claim for the artificial outer boundary, and for good reason, since his results show that the strength of the vr vortex just outside his "core" depends utterly on the distance d of this boundary from the axis. In all cases, the strength of the vortex precisely equals Ωd^2, where Ω is his assigned angular velocity at the outer boundary. In brief, Nielsen has introduced a new artificial length into his problem which plays no role in the actual fire problem and which has a fundamental importance in his results.

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Subject Headings: *Fire storm; Meteorology, interaction of fire; Vortex, formation in fire; Atmosphere, eddys; Mass fire.*

ABSTRACTS

I. Ignition Phenomena

Cullis, C. F., Fish, A., and Gibson, J. F. (Imperial College, London, England) "The Oxidation of Hydrocarbons: Studies of Spontaneous Ignition. II. Ignition Limits in Large Vessels," *Proceedings of the Royal Society* **A292**, 575–587 (1966)

This paper presents results obtained in experimental studies of the spontaneous ignition of *n*-heptane + oxygen + nitrogen mixtures at temperatures in the region of 500°C in vitreous vessels up to 10 l in volume. Previously, the authors reported[1] that similar experiments in smaller vessels (volume < 500 cm^3) indicated a dependence of limiting ignition pressure on temperature different from the predictions of Semenov's[2] simple thermal ignition model. However, there was some evidence that thermal factors became important in larger vessels, where the rate of heat loss is small compared to the rate of energy production.

Experimental results are presented, showing the effects of temperature, mixture composition, and size and shape of the reactant vessel on the minimum pressure required for ignition, as well as the effect of various parameters on the pre-ignition induction period and the maximum rate of non-isothermal pressure rise and associated temperature rise. Various reaction mechanisms are presented and discussed in the light of the experimental evidence, leading to the selection of the probable mechanism. The results indicate that thermal factors are relatively unimportant and that surface reactions can be rate-determining even in large, unpacked vessels.

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Subject Headings: *Hydrocarbons, ignition of; Ignition, spontaneous, of hydrocarbon; Ignition, limits of, in large vessels.*

T. C. Adamson, Jr.

Dittmar, P., Voigtsberger, P., and Conrad, D. (Mitteilung aus der Bundesanstalt für Materialprüfung, Berlin-Dahlem, Germany) "Development and Use of a Method for Establishing the Ignition Limits of Flammable Gases and Vapors in Mixtures with Air or Oxygen," *Arbeitschutz* **3**, 58–63 (1965) (In German)

The apparatus and methods of measurement are described. Results are discussed. The ignition vessel was roughly spherical in shape, with a large opening fitted with a cellophane diaphram. This vessel was filled by flowing the gas mixture through it. The gases used were obtained from cylinders. Gaseous mixtures of flammable liquids were prepared by saturating a portion of the air stream with the vapor, and varying the proportions of air with and without the vapor. The gas handling train included a section for preparing calibrating mixtures. Fuel concentrations in the gaseous mixtures were measured interferometrically. Spark ignition was used; the energy of the spark could be controlled and accurately measured. The spark was initiated between two main electrodes by a low energy, high voltage discharge from a third electrode. It was judged that ignition has occurred if, following the spark, a pressure in excess of 200 Torr was indicated on an electrically registering mercury manometer. When the pressure increase exceeded one atmosphere, the cellophane membrane of the explosion vessel failed.

Ignition limits and electrical spark parameters are reported for the following substances: for both air and oxygen as oxidants—ethylene oxide, hydrogen cyanide, deuterium, difluoroethane, methyl chloride, octafluorocyclobutane, trichloroethylene, tetrachloroethylene, vinyl chloride, vinyl fluoride, and vinylidene fluoride; for air only as oxidant—benzene, difluoromonochloroethane, methyl bromide, methyl mercaptan, methyl nitrite, and hydrogen; for oxygen only as oxidant—ethylene. The spark energy was systematically increased close to the limits to assure that the limits quoted would be the widest possible. The ignition diagram for the ternary system ethylene oxide–carbon dioxide–air is given.

The effect of the shape of the ignition vessel was investigated, using a 5 cm i.d. tube. Only hydrogen-air mixtures were used in these experiments. A spark ignition source was employed. Data were obtained with the tube in a horizontal and also in a vertical position. In the vertical position, the effect of having the ignition source either at the top or at the bottom of the tube was determined. Ignition at the bottom of the vertical tube yields a lower value for the lower ignition boundary for hydrogen-air mixtures than ignition at the top of the tube.

The authors conclude that the ignition limits determined, using a spherical ignition vessel with centrally located spark electrodes, are the widest possible limits, an important point in considerations of safety.

Subject Headings: ***Ignition, limits of, flammable gases; Ignition, spark.***

P. R. Ryason

Hulanicki, S. and Glowiak, B. "Dynamic Determination of the Ignition Temperature of the Coal Dust/Air Clouds," *Archiwum Gornictwa* **11** (1), 87–97 (1966)* (In Polish)

The apparatus methods of measurement are described. Results of measurements of the ignition of coal dust/air clouds (brown coal dust) are given. It is shown that the temperature of dynamic ignition in the case of a coal dust/air cloud is not a constant value, but lies between the lower dynamic ignition temperature (DSZ^d) and the upper dynamic ignition temperature (GSZ^d). The influence of the concentration of dust in the cloud, of the intensity of cloud flow, of the content of volatile matter and of ash and water in the dust, as well as of the inner surface area of the dust on the temperature of dynamic ignition, was also investigated. (From authors' summary)

Subject Headings: ***Coal dust, ignition of; Ignition, temperature, of coal dust.***

* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15* (3), 14. By Permission.

Kuchta, J. M., Bartkowiak, A., and Zabetakis, M. G. "Hot Surface Ignition Temperatures of Hydrocarbon Fuel Vapor-Air Mixtures," *Journal of Chemical and Engineering Data* **10,** 282–288 (1965)

This paper contains a considerable amount of new data on autoignition temperatures of hydrocarbon fuel vapor–air mixtures. Ignition was achieved by means of heated Pyrex vessels (spheres and cylinders), heated Nichrome wires, Nichrome rods, and Inconel tubes. The experimental apparatus and procedure is described in detail in the paper. The fuels tested were *n*-hexane, *n*-octane, *n*-decane, JP–6, and an engine oil MIL–L–7808 (an adipate ester). Tables and curves are given, showing the dependence of ignition temperature on fuel/air ratio, on vessel surface area/volume ratio, on radius and surface area of heat source, and on flow rate of the gas (for low flow velocities, between 0 and 0.5 cm/sec). Flow velocity and fuel/air ratio exerted negligible effects on ignition temperature, except at the highest flow rates and the lowest fuel/air ratios (less than 0.1 weight ratio). Ignition temperatures were found to increase appreciably with decreasing heat source dimensions. The results are discussed in terms of the Frank-Kamenetskii and Semenov theories of thermal ignition. Qualitative agreement with these theories is demonstrated. Correlation formulas are given for the observed dependence of ignition temperature on heat source size, in limited ranges of the source dimension. The results should be useful for studies of fire safety of aircraft and of other systems that employ hydrocarbon fuels.

Subject Headings: *Ignition, temperature; Hydrocarbon-air, ignition of; Ignition, surface.*

F. A. Williams

Leuschke, G. (Federal Institute for Material Testing (BAM), Berlin-Dahlem, Germany) "Investigating the Fire and Explosion Hazards of Flammable Dusts," *Staub* **26,** No. 2, 6–16 (1966) (English edition)

The use of effective safety measures in plants exposed to dust explosion hazards frequently requires better knowledge of the dangerous properties of the dusts concerned. The fire and explosion hazards in the case of these dusts may be determined by safety investigations. After a brief general survey of the properties of inflammable dusts and hazards caused by them, and a report on investigation results available, test methods are described which are used in the "Bundesanstalt für Material prüfung" (Federal Material Testing Institute) for the determination of inflammability and explosibility of dusts. The importance of the characteristic values obtained is shown and their applicability for safety rules is discussed.

Subject Headings: *Dust, fire and explosion hazard; Explosion, of dust; Fire, dust; Hazards, fire, of dust.*

Author's Abstract

Salooja, K. C. ("Shell" Research Ltd., Chester, England) "Studies of Combustion Processes Leading to Ignition of Some Oxygen Derivatives of Hydrocarbons," *Combustion and Flame* **10**, 11–21 (1966)

The pre-ignition behavior of eleven oxygen derivatives of hydrocarbons was studied experimentally, and the results were interpreted on the basis of various molecular models and compared with analogous results with hydrocarbons. The compounds studied included acetic acid, propionic acid, some salts of these, salts of formic acid, and acetone and derivatives. The temperature range over which reactions were noted was from about 400°C up to the ignition temperature, which in most cases, was between 500° and 600°C. Measurements were performed by passing the vapor-air mixtures through a quartz reactor and analyzing the products by chromatography. At the ignition temperature, the reactions were so fast that no ignition time-temperature relationship could be measured. All mixtures were twice stoichiometric.

In contrast with hydrocarbons, the compounds tested in this work yielded amounts of CO_2 equal to or greater than the amounts of CO produced as oxygen was consumed. Under the same circumstances, hydrocarbons will yield 6 to 10 times as much CO as CO_2. By separate tests in the absence of oxygen, thermal decomposition was shown not to be the primary cause of this phenomenon. Detailed examination of the structures of the various compounds revealed the existence of carbonyl groups. Easy removal of these by oxidative degradation was considered to be controlling. Additional steps are the formation and oxidation by HO_2 and OH radicals.

The compounds studied fell into different classes, according to the following three considerations: a carbonyl group causes a greater activation of adjacent alkyl groups than does an oxygen atom in an ether linkage; peroxy radicals formed in the initial stages of oxidation can readily undergo 1,5 and 1,6 intramolecular hydrogen transfer; and the oxygen atom in the carbonyl group tends to form hydrogen bonds intramolecularly.

Subject Headings: ***Ignition, of oxygenated hydrocarbons; Hydrocarbons, oxygenated, ignition of; Ignition, pre-ignition behavior.***

J. K. Richmond

Salooja, K. C. ("Shell" Research Ltd, Chester, England) "Influence of Potassium Chloride on Combustion Processes Leading to Ignition," *Combustion and Flame*, **10**, 45–49 (1966)

Pre-flame oxidation studies of organic combustibles were made in Pyrex vessels using twice the stoichiometric ratio of fuel to air at temperatures up to approximately 600°C to determine, on a quantitative basis, the influence of potassium chloride (KCl) on the oxidation processes. These studies showed that:

(1) KCl raises the ignition temperature of organic fuels significantly above their

"normal" ignition temperature as is illustrated in Figs. 1 and 2. The fuels examined were:

Hydrocarbons—pentane; hexane; 2-methyl-pentane; 2,2-dimethylbutane; iso-octane; cyclohexane; and methyl cyclohexane.

Organic acids and acid esters—propionic acid, methyl formate, ethyl formate, and methyl acetate.

(2) KCl inhibits the oxidation process of the above-mentioned hydrocarbons at temperatures below the fuel's ignition temperature. Results, typical of the hydrocarbons, are shown in Fig. 1.

Other analyses showed that KCl:

Did not alter the nature of hydrocarbons and carbonyl intermediates. Reduced the concentrations of peroxides significantly when compared to tests under "clean glass" conditions. Hydrogen peroxide was not detectable and organic peroxides were present in much lesser amounts.

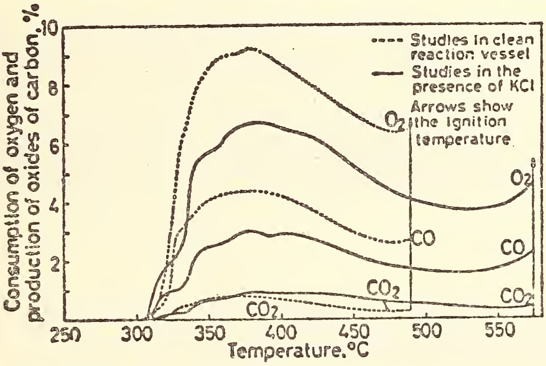


FIG. 1. Effect of potassium chloride on combustion of pentane.

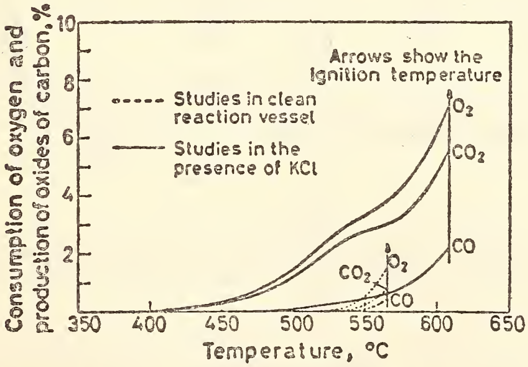


FIG. 2. Effect of potassium chloride on combustion of propionic acid.

(3) KCl promotes the pre-flame oxidation of the above-mentioned organic acid and acid esters plus acetic acid and ketones (acetone). These fuels tended in one of two directions:

To generate more carbon dioxide (CO_2) than carbon monoxide (CO)-acetic acid (up to ca. 600°C), propionic acid, methyl acetate, and acetone (up to ca. 560°C, then the next situation applies). To generate more CO than CO_2-methyl formate and ethyl formate (in the early pre-flame stages only, in later stages the reverse situation developed).

Results cited for propionic acid are shown in Fig. 2.

(4) KCl has virtually no effect on the pre-flame combustion of aldehydes and ethers. Compounds tested were acetaldehyde and diethyl ether.

(5) KCl does not:

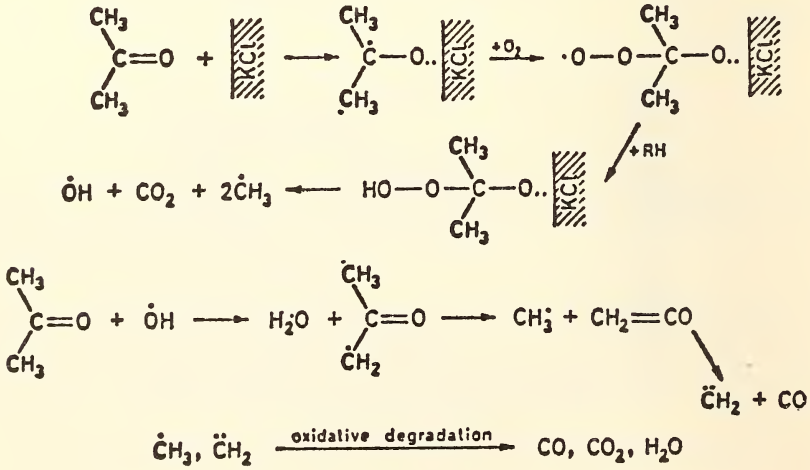
Appear to degrade under pre-flame oxidation conditions. No potassium hydroxide was detectable. Promote thermal degradation of the examined fuels. Significantly catalyze CO to CO_2.

(6) KCl causes acetic acid to form considerable amounts of alcohol, whereas in the absence of the salt, negligible quantities of alcohol are formed.

In addition to the above observations, two hypotheses are presented for the "promoting" effect of KCl on the two groups of carbonyl compounds in item 3 above where the ratio of CO_2/CO tends to be greater or smaller than one.

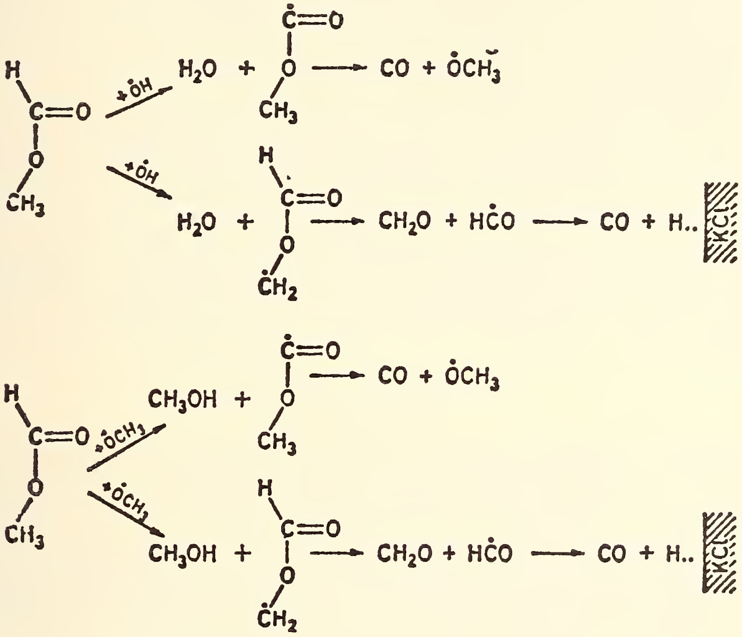
Group where $CO_2/CO>1$

(Note: The attack of the fuel is through the carbonyl group on the surface rather than through the methyl group where KCl is not present.)



Group where $CO/CO_2 < 1$

(Note: The initiation of oxidation of the formates is probably the same as shown above. Once the OH radicals are produced, however, the oxidation process probably proceeds as shown here.)



Subject Headings: *Ignition, effect of potassium chloride surfaces; Potassium chloride, effect on ignition; Ignition, pre-ignition behavior.*

R. A. Gorski

Walker, I. K., Harrison, W. J., and Hooker, C. N. (Chemistry Division of D.S.I.R., Wellington, New Zealand) "The Heat Balance in Spontaneous Ignition. Part 3. Application of Ignition Theory to a Porous Solid," *New Zealand Journal of Science* 8, 319–332 (1965)

An experimental study was made of temperature changes and, in particular, the onset of spontaneous ignition occurring within masses of wool in the presence of oxygen. The equipment used and the procedure followed have been described in detail previously.[1,2] Two spherical glass reaction vessels having volumes of 1.0 and 24 liters and one cylindrical stainless-steel vessel (having the diameter equal to the length) of 5.9 liters were employed. These reaction vessels, tightly packed with scoured wool (bulk density 0.108 g/ml), were submerged in baths maintained at a series of temperatures. Oxygen was circulated through the wool at sufficient rates to insure unchanging oxygen partial pressure. A nitrogen purge was provided to quench reactions leading to ignition. Two different batches of dry scoured wool were used.

The changing temperature at the center of the wool mass was recorded. Graphs are given showing the temperature difference Δ (°C) between that at the center and that of the surrounding bath as a function of time ϕ. The initial condition is $\Delta=0$ at $\phi=0$. At bath temperatures below 143°C for one batch of wool, the temperature at the center of the mass passes through a maximum (thermally stable); at higher bath temperatures the curves ultimately turn sharply upward (thermally unstable, i.e., the onset of ignition). The highest value of Δ under thermally stable conditions was found to be about 39°C. This critical condition was achieved in about 3 hours. For the other batch of wool the same critical condition ($\Delta=39$°C) was reached, also in about 3 hours but at a bath temperature of 141°C.

The rate of heat generation Z (cal/sec g), the reaction rate, was evaluated as a function of the time ϕ (sec) for the tests which did not result in thermal instability. The computation of Z was based on a mean temperature τ_M midway between the bath temperature and the peak central temperature. This calculation is described in detail in an earlier publication.[1] The values obtained are represented approximately by

$$Z=2.4\times10^{-6}\ (2^{0.08\tau}/\phi^{0.282}).$$

As a criterion for ignition in gases, Frank-Kamenetskii first proposed the critical state where heat gains and heat losses are equal.[3] For reaction orders greater than zero there is an increasingly severe diminution of reaction rate at the center in comparison with that at the surface as ignition is approached. On the other hand, in a porous mass, the situation is reversed for an appreciable period before ignition occurs. The ignition theory for gases can be applied to porous solid ignition only when the reactions are at zero order, i.e., when the rate is uninfluenced by reactant consumption. Hence in the present work the conventional conceptions of reaction order and activation energy E may not be applied. The form of the empirical equation given above is sometimes used for representing the kinetics of oxidation reaction in solids.

In reactions of zero order, E will relate to the critical state. For porous solids, however, the parameter y is proposed; y is the temperature interval empirically demonstrated to change the reaction rate by an arbitrary factor 2 under the conditions of the experiment.[4] In the present tests $y=12.5$°C (from above equation); hence here the highest temperature rise without ignition (39°C) is $3.1y$. This value can be compared with the value $2.32y$ predicted for the maximum central temperature rise for the critical state in a sphere of material undergoing zero-order reaction.

The value of the reaction rate at the vessel perimeter in the critical state was calculated independently on the basis of a theoretical equation for ignition.[4] When this value of Z is substituted in the above empirical equation, the critical ambient (bath) temperature can be calculated. The temperature thus determined matches precisely the observed value, indicating agreement between theory and experiment.

Calculations show that the heat release either at the temperature maximum in tests displaying thermal stability or at the onset of instability in other tests does not exceed 50 cal/g. Indeed, the reaction is so slight that the wool at the center of the mass is only moderately discolored at the end of a nonignition test. This heat release is less than one-tenth of the value determined for the total reaction between wool and oxygen. This fact, in addition to the observation that the dimunition of reaction rate with time steadily decreases with the passage of time, suggests that the heat release for total reaction is not always relevant in porous-solid ignition.

In some experiments the central temperature did not continue to rise vertically after thermal instability had commenced. In these instances, it was found that a hollow spherical region, 8 cm diameter, had developed at the center. Evidently this is due to fusion and partial combustion of the wool.

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Subject Headings: *Heat balance, in spontaneous ignition; Ignition, spontaneous, of porous solids; Porous solids, spontaneous ignition of.*

G. A. Agoston

II. Thermal Decomposition

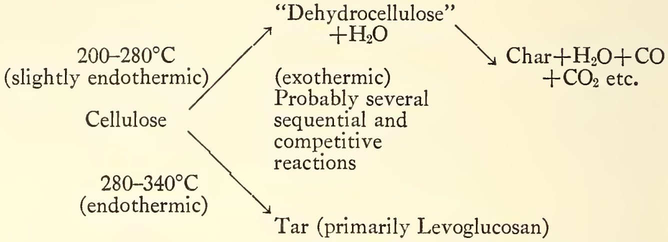
Kilzer, F. J. and Broido, A. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service, Berkeley, California) "Speculations on the Nature of Cellulose Pyrolysis," *Pyrodynamics* **2**, 151–163 (1965)

This paper considers recent results, obtained both by the authors themselves and by other workers, and attempts to account for them.

Differential thermal analysis (DTA), thermogravimetric analysis (TGA), mass spectrometric thermal analysis (MTA), and paper chromatographic separation of products, are all techniques currently applied in studying the pyrolysis of cellulose. The authors point out that the variable ash content of samples studied markedly affects the pyrolysis behavior; thus, TGA curves reveal a difference of some 30°C in the temperature at which the first detectable weight change occurs (with a heating rate of 6°C per minute in a flowing nitrogen atmosphere) for samples with 0.1% ash and so-called ash-free (less than 0.01% ash) cellulose, respectively.

The authors refer to TGA and DTA curves for "ash-free" cellulose and point out that an endothermic process starting at 220°C is concurrent with a slight weight loss and is not merely a rearrangement without weight loss. (This weight loss reaction has been confirmed independently using MTA, and attributed to a dehydration of the cellulose yielding a "dehydrocellulose.")

A much sharper endotherm at about 280°C can be attributed to the tar formation resulting from the depolymerization of the cellulose molecule. A sharp exotherm beginning at about 320°C, which results in the major weight loss, corresponds to a char-forming reaction with the evolution of water and a variety of small carbon-containing compounds. Thus, a general scheme for the pyrolysis of cellulose is postulated to be:



During the second endothermic process, which competes with the first for native cellulose, levoglucosan, the major component of the tar, is postulated to arise from the rearrangement of 1:4 anhydro-α-D-glucopyranose formed in an "unzipping reaction." The final exothermic process is ascribed to reactions of the "dehydrocellulose," which suffers carbon–carbon and carbon–oxygen bond ruptures and hydride ion transfers with the formation of volatile carbon-containing compounds and hydrogen, and intermolecular condensation to produce char.

On the basis of currently held views on the structure of cellulose, possible mechanisms for the above processes are discussed in the paper.

The authors claim that many of the observations noted with impure cellulose can be explained by assuming that the effect of inorganic impurities is to catalyze the dehydration and char-forming reactions at the expense of the depolymerization reaction. Previous work has shown that there is a large increase in char and decrease in tar observed with impure cellulose or with cellulose treated with certain fire-retarding agents. The reactions proposed to account for the dehydration and decomposition of cellulose are known to be affected by Lewis acids or bases. The authors point out that salts such as $KHCO_3$ might be expected to catalyze the rate of formation of "dehydrocellulose" and since this competes with the depolymerization, less cellulose remains to depolymerize as the sample temperature is increased. It also catalyzes the decomposition of "dehydrocellulose" leading to an increased rate of formation of CO, CO_2, and char.

Further experimental work aimed at characterizing the individual reactions and determining the structures of unidentified intermediates is suggested by the author.

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

R. Long

Simionescu, Cr. and Rozmarin, Gh. (Polytechnical Institute of Jassy, Jassy, Rumania) "Some Views on the Mechanism of Cellulose Photodestruction," *Chemistry and Industry* **15**, 627 (1966)

Simionescu and Rozmarin comment on an exchange of views between Béelik and Hamilton[1] and Bera[2] about the theory of the mechanism of cellulose photodestruction advanced by Bera and Agarwal.[3] Concepts of the ways of photochemical destruction of cellulose generally limit the action of ultraviolet radiations to photolysis effects on C(1)–C(2) bonds of the elementary ring or on 1–4 glucosidic bonds, and to oxidation effects on the C(2), C(3), and C(6) atoms by means of atmospheric oxygen, through reactions of the chain type.

Bera and Agerwal postulated that the cellulose macromolecules are split into monoses, cellobioses, and oligosaccharides and are decomposed into simple glycoses through decarboxylation and subsequent photolysis. That part of the theory was confirmed previously by Simionescu, Rozmarin, and Bulacovschi[4] by spectroscopic and chromatographic studies. The present paper presents infrared spectra of galacturonic, gluconic, and mucic acids, each both before and after irradiation in thin films for 1000 hours by two bactericide lamps ($\lambda \sim 253.7$ mμ). The spectra reveal a process of gradual decarboxylation that is a function of the position of the carboxylic group in the ring.

But Bera and Agarwal's theory limits photochemical destruction to two effects only—photolysis and decarboxylation; the yellowing or browning of the model substances and of cellulose by photooxidation is neglected. The studies of Simionescu and Rozmarin indicate that there are four aspects of the mechanism of cellulose photodestruction. They are (in the order of decreasing importance) photolysis, oxidation, chromophore formation, and internal changes. The light quanta have been found to cause conformational changes that weaken the physical structure of the cellulosic frame and render it more liable to photochemical destruction.

The four aspects cannot be treated separately because they are interconnected. The whole supermolecular architecture undergoes the destruction process in its entirety.

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Subject Headings: ***Cellulose, photo destruction of; Photo destruction, of cellulose.***

F. L. Browne

III. Heat and Material Transfer

Abel, W. T. (U. S. Bureau of Mines, Morgantown, West Virginia), **Bluman, D. E.** (West Virginia University, Morgantown, West Virginia), **and O'Leary, J. P.** (Tufts University, Medford, Massachusetts) "Gas-Solids Suspensions as Heat-Carrying Mediums," *Pyrodynamics* **2**, 15–23 (1965)

Suspensions of micronized graphite in inert gases were studied as heat transport mediums for high-temperature systems such as nuclear reactors. A closed recycle system was used in which a centrifugal compressor circulated suspensions of graphite in helium or nitrogen through heat exchangers to determine the flexibility of the method and heat-transfer capabilities of the medium.

Graphite (2 microns average size) was circulated in helium or nitrogen for more than 200 hours with concentrations up to 3 lb of solids per cubic foot and with

Reynolds numbers (based on gas properties) from 800 to 6000. No pipe abrasion or impeller weight was evidenced. Graphite deposition on the walls of the heat exchanger substantially reduced the over-all heat-transfer coefficient relative to circulating helium alone. The reduction in heat-transfer coefficient increased with increasing graphite concentration in the carrier gas. The power required for circulating the suspensions per unit of heat transferred was significantly higher than with helium only, except for the case of 0.13 lb/ft^3 graphite loading. Unsuccessful elimination of wall deposition was tried by using more stringent drying procedures, loop operation at higher minimum temperatures, loop grounding, and particle irradiation. The use of larger particles (85 microns) of aluminum silicate was effective in preventing wall deposition, but erosion of the walls and impeller occurred. Larger graphite particles disintegrated after being temporarily effective.

Higher velocities and nitrogen at 25 psi were used to produce Reynolds numbers in the turbulent regime (based on gas properties) $2.2–6.5 \times 10^4$. The suspensions were heated to 300°F and cooled to 100°F in the exchanger. No accumulation occurred on the walls, and the over-all heat transfer was slightly higher than that obtained with nitrogen alone. The heat-transfer effectiveness in terms of power required to transport given quantities of heat per unit time was equal to that with nitrogen alone. However, the improvement in heat-transfer characteristics was offset by the increase in power required to move the suspension.

It was concluded that solid deposition is not a problem until particles are reduced to micron size. However, it appears that in any practical system involving a high-speed compressor, friable materials such as graphite will be broken so that micron size particles will predominate. The flow must be kept in the highly turbulent range to minimize film buildup in the exchanger. The substantial increase in the power input to the compressor may offset any benefit attributable to increased heat-transfer rates. Application appears limited to systems where circulating cost is not the primary factor.

Subject Headings: *Gas, solids suspension, heat transfer by; Heat transfer, by suspension.*

L. A. Povinelli

IV. Diffusion Flames

Meier zu Köcker, H. and Verheesen, H. (Institut für Brennstoffchemie der Technischen Hochschule, Aachen, Germany) "Combustion Rate of Free Falling Hydrocarbon Droplets in Pure Oxygen at Atmospheric Pressure," *Erdöl und Kohle* 18, 881–885 (1965)

The combustion rate of free falling hydrocarbon droplets in pure oxygen at atmospheric pressure: In conclusion of the investigations of the combustion-behavior of various pure hydrocarbons and marketable multi-component fuels, the combustion time of freely falling droplets of hydrocarbons of different structure in pure oxygen in a vertical, cylindrical combustion-chamber at atmospheric pressure and temperatures between 650° and 800°C was tested. Particular attention was given to the correlations between the combustion rate and the temperature of the combustion chamber, the droplet diameter, and various fuel properties. The experimental results are discussed together with the theoretical relations.

Subject Headings: *Flame, free falling droplets; Droplets, free falling flames; Droplets, hydrocarbon flames.*

Authors' Abstract

V. Combustion Principles

Günther, R. (Technische Hochschule, Karlsruhe, Germany) "Combustion in Turbulent Gas Flames," *Gaswärme* **14,** 6–13 (1965)

In order to define precisely the characteristics of a flame, it is necessary to specify the distribution of both combustion and mixing processes. Since this precise characterization is possible only for the isothermal case, the author has devised a method for defining the flame characteristics in terms of burnout ratio and "unmixedness," both of which are dependent upon the conventional distribution of gaseous species in the flame. Moreover, complete description of the combustion zone permits pointwise variation of energy sources (heat evolution) along the flame axis.

Degree or completeness of combustion is defined as the combustion factor

$$\alpha = \text{weight of combustion products/total weight of gas}$$

at the sampling location.

The fallacy of equating regions of time-averaged stoichiometric mixture ratio with the combustion reaction is explained by differentiating between the concurrent mixing processes of turbulence and molecular diffusion. Whereas the former is dependent primarily on aerodynamic properties of the gas stream, the latter depends on molecular structure of the various gaseous species and is hence impossible to specify accurately in most actual cases. The impossibility of accurate description of the diffusion process is particularly evident for the case of town gas, which is the subject of the author's experimental investigation.

In order to circumvent the obviously impossible task of quantifying the complex diffusion processes, the author proceeds to describe the variation of combustion in turbulent flames by defining a "Maximum Mixture Factor" (M), leading to an "Unmixedness Factor" (u):

$$M = \text{combustion products} + \text{time-averaged stoichiometric mixture}$$
$$\text{(which can be determined by sampling)}$$

and

$$u = (M - \alpha)/M.$$

From the foregoing definitions, it is apparent that the degree of turbulence is related to the unmixedness factor.

Typical variation of α, M, and u for town gas are shown in Fig. 1, and the average (over the pertinent cross sections) variations are shown in Fig. 2.

For comparison purposes, the corresponding variation of unmixedness factor for a glass melting furnace is included in Fig. 2, thus indicating how various flames can be effectively compared by this technique.

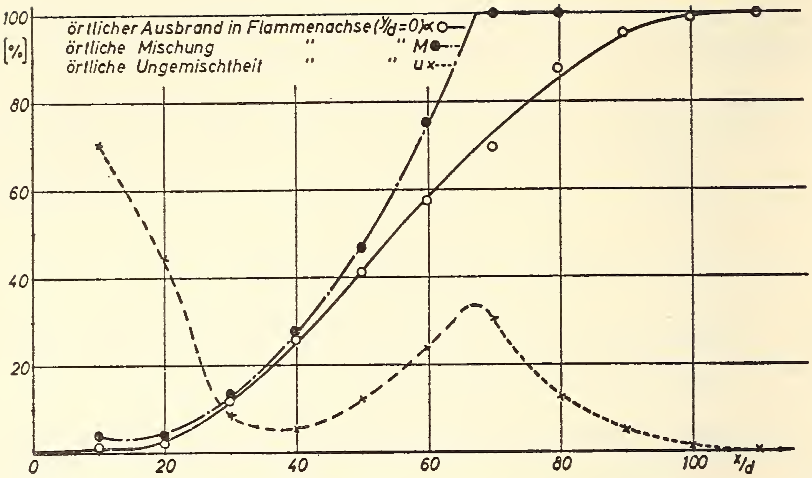

FIG. 1. Longitudinal variation of burnout, maximum mixture, and unmixedness in town gas flame.

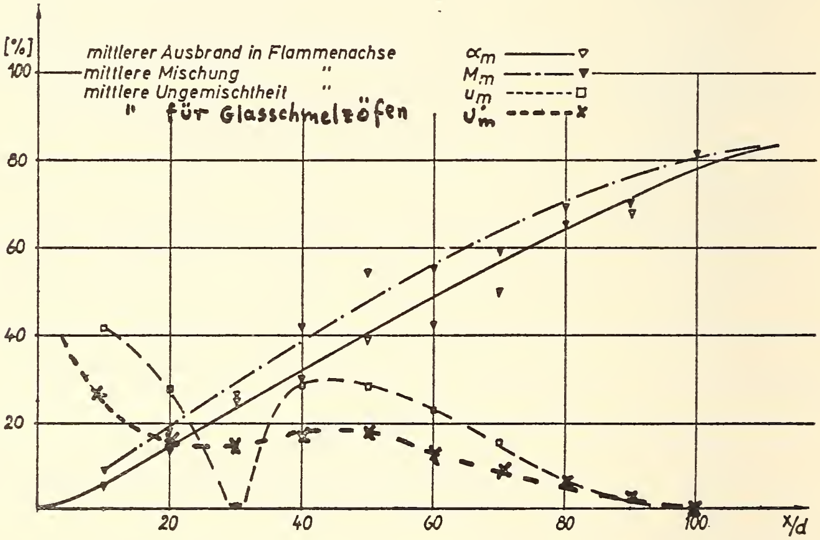

FIG. 2. Longitudinal variation of average burnout, maximum mixture, and unmixedness in town gas and producer gas flames

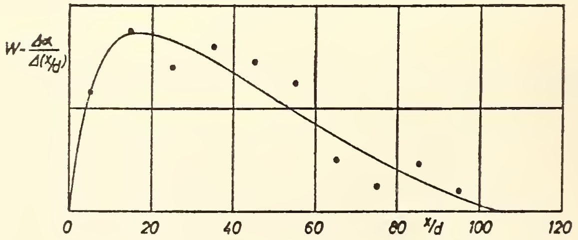

FIG. 3. Heat evolution in a town gas flame

The report concludes with the derivation of the variation of heat evolution (W) from the combustion factor:

$$W = BH(d\alpha/dx),$$

where B is the mass flow rate, and H the specific heat. Variation of W/BH with x/d for the town gas flame represented by Fig. 2 is shown in Fig. 3, which indicates the applicability of this technique to the determination of the effectiveness of various combustors.

Subject Headings: *Combustion mechanism; Flame, turbulent; Turbulence, in flame.*

C. C. Miesse

Kogarko, S. M., Lyamin, A. G., and Mikhailov, V. A. (Institute of Chemical Physics, Academy of Sciences, USSR) "Spontaneous Transition to Detonation in Pure Acetylene at Low Combustion Pressures," *Proceedings of the Academy of Sciences of the USSR, Doklady Physical Chemistry* **162,** 430–433 (1965)

The authors briefly review studies of spontaneous transition in pure acetylene (omitting much work reported by other investigators—for example, see Ref. 1) and describe their own experimental investigation and results. Decomposition of pure acetylene within the range of initial pressures 0.89 to 1.56 atm was initiated at one end of a steel tube 300 mm diameter and 100 m long by a capacitance spark (approximately 200 Joules). The initial flames accelerated to steady detonation within 100 tube diameters. Pressures in the tube did not increase before arrival of the detonation wave. Ease of transition to detonation was attributed to the highly roughened flame front surface, and to great rate of expansion of hydrogen, one of the decomposition products.

Reference

1. Zabetakis, M. G.: Flammability Characteristics of Combustible Gases and Vapors, Bulletin 627, Bureau of Mines, 1965, 121 pp.

Subject Headings: *Acetylene, detonation of; Detonation, transition to; Transition, to detonation.*

J. M. Singer

Laud, B. B.* and Sathe, L. N. (University of Poona, Poona, India) "Spectroscopic Study of Some Organic Flames: Part I. Variation of Band Intensity of Different Radicals with Air-Fuel Composition and Influence of Diluents. Part II. Flame Temperatures, Burning Velocities and Radical Formation," *Indian Journal of Pure and Applied Physics* 4, 4–12 (1966)

* Present address: Department of Physics, Marathwada University, Aurangabad, India.

Part I. Variation of Band Intensity of Different Radicals with Air–Fuel Composition and Influence of Diluents

The processes involved in the production and excitation of free radicals in flames are important in understanding the chain reaction mechanism and chemical kinetics. Emission spectra may be used to determine radical concentrations and composition profiles in the various stages of the flame. Burshane, a mixture of butane, butylene, and a small percentage of propane and propylene, is a suitable fuel since it allows following the four molecular radicals, C_2 (5165 Å), CH (4315 Å), OH (3064 Å), and HCO (3377 Å), simultaneously.

A stable, premixed, laminar burshane-air flame at atmospheric pressure was formed on a 0.75 cm diameter Pyrex tube 80 cm long feeding from an appropriate flow monitoring and regulating system. For the diluent studies CO_2 or Cl_2 were added to the combustible mixture at a constant rate and in definite proportion. Band intensity spectra were taken, with and without diluents, on a small quartz Gaertner instrument for 11 different air–fuel compositions. Exposure times were adjusted so that film densities were in the straight line part of the characteristic curve, and microphotometer traces were taken on a Kipp and Zonen Moll microphotometer and optical densities determined from them.

The spectrum of the inner cone of the flame showed all four radicals noted above. The light from the outer cone was much weaker than that from the inner cone and showed mainly the OH bands. All the radicals exhibit a maximum of intensity over the range of mixture compositions examined (air-fuel ratios from 16 to 27). However, the shape of the intensity/air–fuel mixture curves differ to an appreciable extent from molecule to molecule. The maxima for the intensities of C_2, CH, and HCO radicals all lie on the rich side of the stoichiometric mixture, and this suggests that the presence of excess fuel is conducive to the formation of excited radicals.

The introduction of CO_2 as a diluent has a strong quenching effect on the C_2 band intensity, by a factor of 2. With the CO_2 the increased carbon formation gives rise to continuum radiation while with the Cl_2 diluent the reaction zone becomes intense green, indicating enhancement of C_2 band intensity. There is a slight shift in the maximum of the C_2 band intensity to the rich side with CO_2 and to the lean side with Cl_2. The intensity of the CH band is reduced by both CO_2 (to $\frac{1}{3}$) and Cl_2 (to $\frac{2}{3}$). This cannot be considered to be a measure of their quenching action since the diluent flows were different. No shift in the maximum of the CH intensity occurred with either diluent. In the OH case both CO_2 and Cl_2 caused quenching of almost the same order and, considering the relative flow rates, it may be concluded that Cl_2 has a greater quenching action on OH than CO_2. Both CO_2 and Cl_2 have quenching effects on HCO intensity but it is stronger and more marked in the case of CO_2. In general, the magnitude of the quenching effect as well as the enhancement, wherever noticed, is different for different mixture strengths and is maximum at the air–fuel ratio at which the band intensity of the radical under consideration is maximum.

Part II. Flame Temperatures, Burning Velocities and Radical Formation

The relative band intensities of the free radicals in a flame depend upon the burning conditions of the flame and consequently a knowledge of the combustion parameters that are characteristic of the burning mixture is necessary to determine the optimum conditions for observation of a particular band system.

A stable, premixed, laminar burshane-air flame at atmospheric pressure was formed on a 0.75 cm diameter Pyrex tube 80 cm long feeding from an appropriate flow monitoring and regulating system. For the diluent studies CO_2 or Cl_2 were added to the combustible mixture at a constant rate and in definite proportion. Flame temperatures were measured by the sodium D-line technique, the sodium introduced by placing a sodium chloride bead on a platinum loop in the flame. Temperature readings could be reproduced within ±10°C. Burning velocities were measured by Guoy's technique, the flame cone area being determined by shadow photographs.

The maximum temperature observed in the outer cone corresponded to a rich mixture, 2137°K for an air–fuel ratio of 21.0. This temperature was slightly lower than anticipated for a burshane-air flame, probably due to the technique used to introduce the sodium salt. The maximum temperature occurs for the fuel rich mixture as a result of dissociation of the intermediate species. The maximum inner cone temperature of 2086°K was found in an air–fuel ratio of 19.0. This departure from the stoichiometric ratio is probably a consequence of the energy loss to the C_2 molecule by dissociation. The addition of CO_2 diluent lowers the maximum temperature of the outer cone and the inner cone to 2055°K and 1980°K, respectively. Alternatively, the addition of Cl_2 diluent raises the maximum temperature of the outer and inner cone to 2170°K and 2125°K, respectively. The conclusion is that CO_2 has a quenching effect on flame processes, while Cl_2, acting like a catalytic agent, supports the chemical reactions taking place in flames and causes an enhancement of the heat content of the flame.

The burning velocity of the mixture increases rapidly with increasing air–fuel ratio reaching a maximum of 41.2 cm/sec at an air–fuel ratio of 21.5 before falling off in a symmetrical manner. The addition of both CO_2 and Cl_2 reduces the burning velocity, Cl_2 to 37.5 and CO_2 to 39.2 cm/sec. The addition of Cl_2 shifts the position of the maximum burning velocity slightly more toward the fuel-rich side.

It is worthwhile to compare the above data with the intensity variation of the C_2, CH, OH, and HCO radicals given in Part I. The position of the maximum intensity of the C_2 band coincides with that of the maximum temperature of the inner cone, although the intensity maxima of the other molecular radicals do not show any such temperature correlation. Thus, there appears to be a close dependence of temperature on the production of the C_2 radical. Although it is acknowledged that there is a relation between CH and C_2 radicals in flames, the variation of band intensity of the CH radical with temperature is different from that of the C_2 radical. The inclination is to conclude that the reaction $C_2+OH \rightarrow CH^*+CO$ is operative in the formation of CH radical, and this indicates the expected relation between C_2 and CH radical formation. The intensity of the OH band does not seem to bear any relationship to temperature and it is generally assumed that the OH radical in the inner cone results from chemiluminescence. The band intensity variation of the HCO radical is similar to that of the OH radical and is independent of the temperature.

Subject Headings: *Burning velocity; Flame, temperatures; Radical, in flames; Spectroscopy, of radicals.*

T. P. Anderson

Maksimov, E. I., Merzhanov, A. G., and Kolesov, Yu. R. (Institute of Chemical Physics, Academy of Sciences, USSR) "Distribution of the Density of Matter in the Zone of Combustion of Condensed Systems," Translated from *Doklady Akademii Nauk SSSR* **162**, 1115–1118 (1965)

A decomposition reaction in an organic liquid was investigated to determine the role played by foam formed in the process on the reaction mechanism.

The problem was approached experimentally using X-ray absorbtion as a measure of density and motion picture photography as a measure of reaction zone, foam location, and X-ray beam location as a function of time. X-ray absorbtion was selected for density measurement since it is independent of the chemical nature and phase (liquid or gas) of the substance. The principal experimental challenge was to provide a narrow field of X-ray radiation parallel to the reaction front. This was achieved by a 50-μ-thick slit, which provided a 75-μ-thick beam through the sample under investigation. Alignment of the beam was audited by photography to an accuracy of about 200 μ. Any data falling outside this range were not used. The measured length of the region of density variation was 500 to 2000 μ, so for most cases the beam width was effectively small.

The substance selected for this study was hexogen,* which has a boiling point of 340°C and heat of vaporization of 26,000 cal/mole. Thermal decomposition in the liquid phase proceeds as a first-order reaction with a constant,

$$K = 10^{18.5} \exp(-47{,}500/RT) \text{ sec}^{-1}.$$

The experiments were conducted at a temperature of about 20°C and pressures of 0.5 to 5 atm. The principal experimental results are shown in Fig. 1. The position at which maximum radiation occurs is further from the point of initial density variation than the zones of density variation, indicating reaction beyond the region of density variation.

Foam was formed in the decomposition reaction of hexogen. The main cause of foaming was the reaction in the liquid phase. Calculations using the rate constants of the reaction showed the degree of reaction in the liquid phase may be substantial. Measurement of temperature profile through the reaction zone showed a near-isothermal region near the boiling point, indicating substantial heat evolution in the liquid phase. Calculation of the amount of liquid-phase decomposition required to support evaporation showed about a quarter of the liquid as decomposed.

Calculation of the rate of propagation of reaction in the liquid phase at the boiling temperature produced values an order of magnitude lower than the experimentally measured value. The limiting reaction rate is therefore in the gaseous phase. The reaction in the liquid phase may, however, affect the rate of reaction through change of composition of the gas phase.

The decomposition reaction of hexogen is therefore described as a distributed phenomenon with some decomposition occurring in the liquid phase, forming foam, but with the rate-determining reaction being in the gaseous phase.

Subject Headings: ***Combustion, in liquids; Flame, liquid, structure of; Flame, structure of, in liquids.***

A. E. Noreen

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* Hexogen is hexahydro-1, 3, 5-trinitro-*s*-triazine.

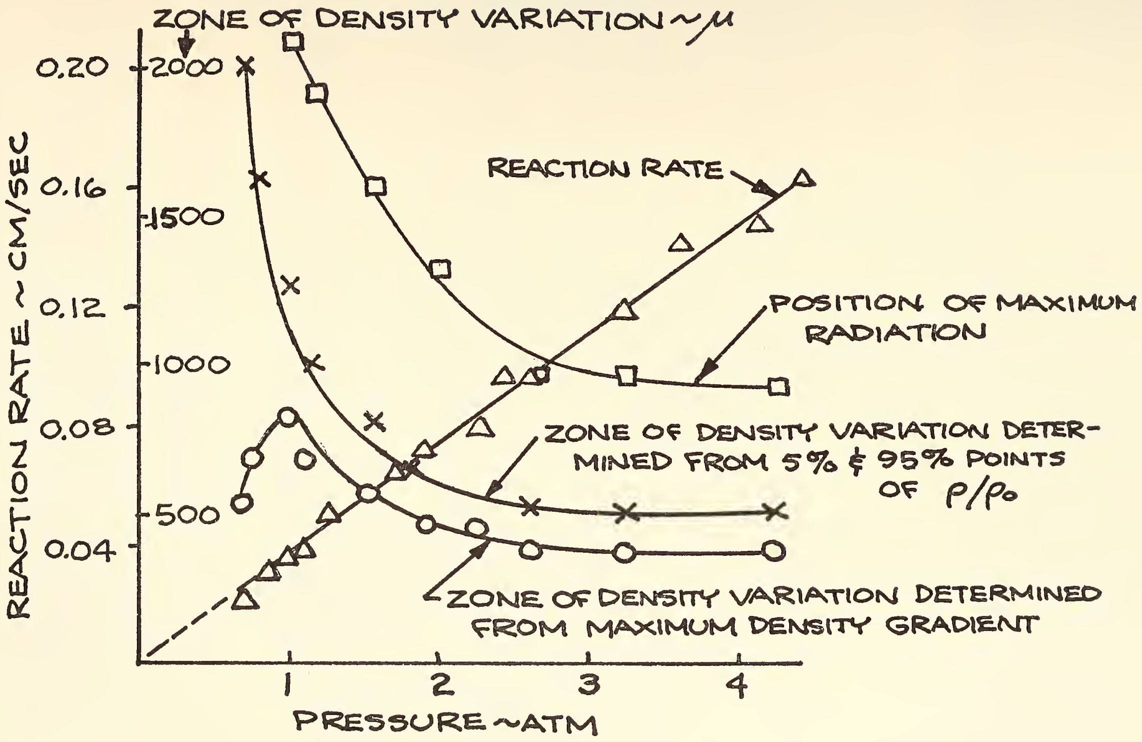

FIG. 1. Experimental Results

Poppleton, B. J. and Mulcahy, M. F. R. (University of Melbourne, Melbourne, Australia) "Catalysis of the Slow Combustion of Acetaldehyde by Alkali Halides," *Australian Journal of Chemistry* **19**, 65–74 (1966)

A coating of alkali chloride on the inside of a Pyrex or quartz vessel notably decreases the rate of slow combustion of a hydrocarbon or of hydrogen in the vessel. The effect is attributed to a more efficient destruction of free radicals and labile peroxide intermediates at the surface of the salt.

Some work of Pease in 1933[1] indicated that the slow combustion of acetaldehyde vapor is accelerated by potassium chloride. This observation has been reinvestigated by the authors who conclude that solid alkali halides do catalyze the slow combustion of acetaldehyde vapor at 100° to 125°C.

The catalysis (by chlorides) is not sensitive to the nature of the cation (Li^+, K^+, Cs^+, Ca^{2+}, Ba^{2+}) but changes drastically with a change in anion, the relative catalytic effect being in the order $Br^- \gg Cl^- > F^-$, I^- probably exerts an inhibitory effect.

A positive catalytic effect of sodium chloride on the oxidation of acetylene, a reaction kinetically similar to aldehyde oxidation has also been noted and there are indications of the effect in the low temperature oxidation of formaldehyde. The catalysis is attributed tentatively to the sensitizing action of free halogen produced by reaction of acetyl hydroperoxide with the halide. There is a general kinetic similarity with the much weaker catalysis by glass observed by other workers.

While the present results do not permit discussion of the mechanism in detail, the general idea that the catalysis is brought about by the interaction of hydroperoxide with the surface provides a reasonable explanation of the kinetic behavior over both alkali halide and glass surfaces.

If a detailed examination of the reaction were to substantiate this then the catalyzed acetaldehyde oxidation would constitute a case of the homogeneous-heterogeneous type of catalysis discussed by Kovalskiĭ, Semenov, and others.

Reference

1. R. N. Pease: J. Am. Chem. Soc. *55*, 2753 (1933).

Subject Headings: *Acetaldehyde, slow combustion of; Alkali halides; Catalysis, of slow combustion, by alkali halides.*

G. S. Isles

VI. Radiation

Bracciaventi, J., Heilferty, R., and Derksen, W. (U. S. Naval Applied Science Laboratory, Brooklyn, New York) "Radiant Exposures for Ignition of Tinder by Thermal Radiation from Nuclear Weapons," *Final Report under Defense Atomic Support Agency Subtask 12,009* (July 1966)

The radiant exposure to ignite tinder materials by thermal radiation from nuclear weapons was measured. The experiments involved 41 materials commonly encountered in urban areas and are to provide basic data of direct use in the determination of fires caused by nuclear weapons and to provide basic information for ignition prediction models.

The radiant exposures for ignition of the most susceptible common material, newspaper (dark picture) ranged from 5.1 cal cm^{-2} to 31 cal cm^{-2} for bursts of 20 kt to 100 Mt, respectively. Black roll roofing, a common material representing an important but less susceptible fuel, ignited at 38 cal cm^{-2} for a 1 Mt pulse and 45 cal cm^{-2} for a 10 Mt pulse. Other thin fuels ignited at various intermediate or higher exposures.

Thick wood fuels, such as might be used as building siding, were ignited to sustained flaming by the simulated detonation pulses. Cedar shingle was ignited at 15 cal cm^{-2} by a 1 Mt pulse, and at 26 cal cm^{-2} by a 10 Mt pulse.

Subject Headings: *Ignition, of tinder, by thermal radiation; Tinder, ignition of; Nuclear weapons, ignition of tinder.*

Authors' Abstract

Gibbons, M. G. (U. S. Naval Radiological Defense Laboratory, San Francisco, California) "Transmissivity of the Atmosphere for Thermal Radiation from Nuclear Weapons," *Report under Office of Civil Defense Work Order No. PS-64-200, Work Unit 5700. USNRDL-TR-1060* (August 12, 1966)

The transmissivity of the atmosphere is estimated for thermal radiation from a nuclear weapon of any given yield and height of burst under various atmospheric conditions. Situations in which the effective source height (for thermal radiation) is less than one-quarter mile,* the atmosphere is unclouded and the surface of the earth (or its covering) is of low albedo are considered first. The transmissivity for these situations is given in terms of a formula derived from earlier experiments of the author. Situations in which the effective source height (for thermal radiation) is equal to or greater than one-quarter mile are then considered, and basic transmissivity values are given in terms of effective fireball height and zenith angle for the case of an unclouded atmosphere, a visibility of about 12 miles and a low surface albedo. Factors are then given for modifying the basic transmissivity values to apply to other situations, such as ones with cloud cover or haze, and for taking into account high surface albedo. The factors for taking account of a cloud layer above the fireball and/or a high surface albedo are found to apply also to situations in which the effective height is less than one-quarter mile.

Subject Headings: *Atmospheric transmissivity, of thermal radiation; Transmissivity, of atmosphere; Radiation, thermal, transmissivity through atmosphere.*

Author's Abstract

Herman, B. M. and Browning, S. R. (The University of Tucson, Tucson, Arizona) "A Numerical Solution to the Equation of Radiative Transfer," *Journal of the Atmospheric Sciences* **22,** 559–566 1965)

The solution of the equation of radiative transfer for a plane parallel, horizontally homogeneous medium is presented, utilizing an iterative technique such that no

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* The "miles" used in this report are statute miles.

restrictions as to the form of scattering or length of optical path exists. Practical application of the method does, however, set up an upper limit of 4 in. on the optical path width and does place rather restrictive conditions upon the type of Raleigh scattering allowed.

The method of calculation assumes a nonabsorbing atmosphere that is subjected to plane parallel radiation travelling in the direction of propagation of the light with respect to the normal or right point angle of entry into the top of the atmosphere. A second direction-defining parameter is the value of the solid angle subtended by the incident radiation upon an arbitrarily oriented x-axis, which may be at any level or height within the scattering medium. The depth of the atmosphere is divided into as many layers as desired. Solution of the scattering phase matrix separated the contributions of the scattering due to travel into and out of the medium. Part of the light leaving the top of the atmosphere is directly reflected or actually scattered on its way out from an inner reflective layer. Initially we do not know anything of the outward scattered radiation flux, therefore the first solution of the iterative equation assumes that this value of re-emitted radiation is zero. The procedure is continued until there are values for the emergent radiation at all levels of the layer with the total reflected radiation equalling, or nearly equalling, that of the incident radiation. This solution is, of course, for a conservative scattering system. The size of the increment of depth used in the above iterative computation was restricted so that the maximum deviations from tables derived by others to $\pm 1\%$ on polarization and $\pm 0.01\%$ total intensity for an incident unpolarized beam of a certain number of arbitrary light intensities per unit area. An incremental depth of 0.020 and solid angle width of 30° was used. This is with respect to a maximum depth of 1.0 and scattering angle range of from 0° to 60°.

Curves of total intensity and percent scattering as a function of a single reflective direction and zero azimuthal angle are presented. In addition plots are given showing the variation of transmitted and reflected total intensities as a function of the depth of the layers. The smaller the angle of incidence of the incoming radiation, the earlier does the peak intensity of total transmitted light occur. However, at large depths this fact is reversed, that is, the transmitted total intensities rise with increasing angle of incidence.

Other data presented show the variation of transmitted and reflected scattering only as a function of depth. A maximum value for polarization of 10% of the incident flux is obtained at large (up to 4.0 in.) depths. Similar results are shown for the percent polarization of the reflected or emerging beam.

The variations of intensities and percent polarizations of the reflected light with optical depth are quite valuable for the study of planetary atmospheres, assuming they are conservative scattering systems. The connection is between the optical depth and the wavelength of the scattering. A measure of the polarization of reflected light at various values of optical depth and comparison with theoretical values obtained here and elsewhere for a perfect scattering medium will enable one to measure indirectly the depth of such atmospheres.

Subject Headings: *Radiative transfer, equation for; Equation, for radiative transfer.*

P. Breisacher

VII. Suppression of Combustion

Arseneau, D. F. (Xavier College, Sydney, Nova Scotia) "A Differential Thermal Analysis Study of Fire Retardants in Cellulose," *Proceedings Canadian Wood Chemistry Symposium, 1st, Toronto 1963*, 155–160 (1965)

The research described in this paper used the technique of differential thermal analysis to study the effects of ammonium chloride and borax on the decomposition of cellulose. The technique includes: (1) a rate of temperature rise of approximately 7.8°C/min; (2) temperatures within the range 75° to 450°C; and (3) the use of no inert material for sample dilution owing to the observation that alumina (often used for dilution) absorbs primary decomposition products.

The thermograms obtained for cellulose exhibit two overlapping exothermic peaks: the author interprets the lower-temperature peak as representing the decomposition of surface impurities, chain ends, or miscelle surfaces, and the other peak as representing the decomposition of miscelle interiors, i.e., α-cellulose. Cellulose impregnated with ammonium chloride exhibits a slight endothermic nadir and a distinct exothermic peak. Cellulose with borax exhibits two distinct exothermic peaks.

Activation energies of the decomposition processes which give the thermogram deflections were calculated using measurements of the effect of rate of temperature rise on the temperatures at which the deflections occur. An example of the results is that treatment with borax increases the activation energy of the reaction represented by the higher-temperature peak from 34.5 to 40.3 kcal/mole, an effect which the author believes should reduce the probability of the occurrence of this reaction.

Another observation of practical importance is that borax retards the rate of temperature rise in cellulose by forming a foam. This effect might delay a real fire long enough to permit the arrival of fire extinguishing equipment.

Information presented in the paper includes a schematic representation of the equipment, thermograms, Arrhenius plots, and tables of activation energies.

Subject Headings: *Cellulose, fire retardants in; Differential analysis, thermal; Fire retardants, in cellulose.*

J. B. Howard

Back, M. H. and Laidler, K. J. (University of Ottawa, Ottawa, Canada) "Theories of Inhibition by Nitric Oxide," *Canadian Journal of Chemistry* 44, 215–222 (1966)

The three theories of Voevodsky,[1,2] Norrish and Pratt,[3] and Wojciechowski and Laidler,[4,5] on the inhibition of pyrolysis reactions by nitric oxide are critically discussed by the authors. By reference to experimental results of various researchers it is concluded that it is necessary to postulate hydrogen abstraction by nitric oxide, as in the Wojciechowski-Laidler mechanism.

The scheme of Voevodsky assumes that inhibition is caused by suppression of an irreversible surface initiation reaction. In addition, it assumes a non-inhibited surface initiation and a surface termination. Recent results on ethane pyrolyses showing very little effect of surface/volume ratio on the rate of initiation are at variance to this. Since nitric oxide can cause a 90% decrease in the pyrolysis rate, a very strong effect of surface/volume ratio should have been found if this mechanism were correct.

The Norrish-Pratt mechanism involving oximes, with nitric oxide adding to a radical, rearranging to an oxime, followed by unimolecular decomposition, was originally applied to pentane pyrolysis with qualitative success in explaining many features of the reaction. The authors of this paper show, however, that the scheme is incapable of predicting fractional orders for the maximally inhibited reaction and, furthermore, that for ethane and dimenthyl ether decompositions, activation energies calculated from this mechanism are quantitatively in disagreement with measured values.

The Wojciechowski-Laidler mechanism on the other hand is shown to be in substantial agreement with experimental facts. The mechanism assumes an abstraction of hydrogen by nitric oxide to form HNO and a radical. The chain-ending step involves the radical and HNO, or a rearranged oxime from RNO, to produce the original molecule and NO. With the most probable chain-ending step for each reaction it is shown that the calculated overall order of the maximally inhibited reaction agrees with experiment for the decomposition of ethane, propane, butane, dimethyl ether, diethyl ether, acetaldehyde, and propionaldehyde. Further support for this scheme is found in the close agreement between the measured activation energies in the region of acceleration and the endothermicity of the postulated initiation reaction, i.e., the hydrogen abstraction.

The evidence appears conclusive that, while some modifications and additions to the Wojciechowski-Laidler mechanism may be required in a more detailed treatment of these reactions, the nitric oxide-hydrogen extraction must be important in pyrolyses occurring in the presence of nitric oxide.

References

1. V. V. Voevodsky: Trans. Faraday Soc. *55*, 65 (1959).
2. V. V. Voevodsky: Kinetics Catalysis USSR—Engl. Transl. *5*, 603 (1964).
3. R. G. W. Norrish and G. L. Pratt: Nature *197*, 143 (1963).
4. B. W. Wojciechowski and K. J. Laidler: Can. J. Chem. *38*, 1027 (1960).
5. B. W. Wojciechowski and K. J. Laidler: Trans. Faraday Soc. *59*, 369 (1963).

Subject Headings: ***Inhibition, by nitric oxide; Nitric oxide, inhibition by; Radical, reactions, inhibition by nitric oxide.***

F. Falk

Blackmore, D. R., Clark, D. R., and Simmons, R. F. (Manchester College of Science and Technology, Manchester, England) "Inhibition of the Thermal Reaction between Hydrogen and Oxygen," *Final Scientific Report under Grant AF EOAR 62–88 by the Air Force Office of Scientific Research through the European Office of Aerospace Research, (OAR) United States Air Force.*

The kinetics of the inhibiting action of hydrogen bromide and hydrogen chloride on the thermal reaction between hydrogen and oxygen has been investigated. Hydrogen bromide was found to be a very effective inhibitor of the reaction, while hydrogen chloride was relatively inefficient. The kinetic characteristics of the inhibition have been examined, and it has been shown that in the case of hydrogen bromide the primary inhibition step is:

$$H+HBr \rightarrow H_2+Br \qquad (14)$$

Only a fraction of the bromine atoms produced in reaction (14) react to give chain termination, however, and the majority react to give chain propagation by:

$$Br+H_2 \rightarrow HBr+H \qquad (16)$$

It is suggested that chain termination occurs by:

$$Br+HO_2 \rightarrow HBr+O_2 \qquad (18)$$

The corresponding mechanism is also operative when hydrogen chloride is the inhibitor, but a second primary inhibition step is also important in this case:

$$OH+HCl \rightarrow H_2O+Cl \qquad (15a)$$

The reason for the marked difference in efficiency of hydrogen bromide and hydrogen chloride is discussed.

Subject Heading: *Inhibition, of H_2–O_2 reaction by HBr and ACL.*

Authors' Summary

Broido, A. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service, Berkeley, California) "Thermogravimetric and Differential Thermal Analysis of Potassium Bicarbonate Contaminated Cellulose," *Paper Presented at Spring Meeting of the Western States Section of The Combustion Institute, Denver, Colorado* (April 1966)

When samples undergo a complicated set of simultaneous and sequential reactions, as cellulose does on heating, results of thermogravimetric and differential thermal analyses are difficult to interpret. Nevertheless, careful comparison of pure and contaminated samples, pyrolyzed under identical conditions, can yield useful information. In these experiments TGA and DTA curves were obtained, in air and in an inert atmosphere (nitrogen), with "ash-free" cellulose (ash content $<0.01\%$) "pure" cellulose (ash content $\sim 0.15\%$) and "treated" cellulose (1.5% $KHCO_3$ added). The results show that as little as 0.15% inorganic contamination can significantly affect the pyrolysis reactions undergone by cellulose. The addition of 1.5% $KHCO_3$ lowers by some 80°C the temperature at which significant decomposition begins but essentially eliminates the flame-producing reactions in favor of those leading to glowing combustion.

Subject Headings: *Cellulose, pyrolysis, effect of potassium bicarbonate; Differential analysis, thermal; Potassium bicarbonate, effect on cellulose pyrolysis; Thermogravimetric analysis.*

Author's Analysis

Byrne, G. A., Gardiner, D., and Holmes, F. H. (The Cotton Silk & Man-made Fibers Research Association, Shirley Institute, Manchester, England) "The Pyrolysis of Cellulose and the Action of Flame-Retardants. II. Further Analysis and Identification of Products," *Journal of Applied Chemistry* **16,** 81–88 (1966)

This paper describes very detailed results of extensive analysis of pyrolysis products of various cotton celluloses with and without treatment by flame retardants. The objective of the work was to determine the mode of action of the retardants. The stimulus for the approach used (careful analysis of products) was stated to have been derived partly from the enormous contribution of gas-liquid chromatography to the identification of pyrolysis products. However, other techniques were used in addition to GLC. These included thin-layer chromatography and infrared absorption for determination of laevoglucosan in tars, copper number as an estimate of reducing power, fluidity to estimate (inverse) chain length, and measuring fabric temperatures burning in air with 0.006 in. Pt/Pt–Rh thermocouples.

Analysis was concentrated on the chars and tars although CO, CO_2, and water were also identified after removal in traps at temperatures down to −190°C. The products for analysis were obtained by heating samples (mostly for 6 min) at various temperatures, mostly in a vacuum, although some were heated by hot air or hot nitrogen. Two vacuum systems were used, one fully described in a previous paper,[1] but both consisting essentially of a sample in a pyrolysis tube with appropriate arrangements for heating it, and appropriate traps to catch the products. The materials used were cotton fabrics of various types such as: cotton poplin, cotton winceyette, cotton typewriter cloth, cotton canvas, cotton sateen, and for some subsidiary investigations, a cotton/viscose rayon mixture, a cotton cloth, and a partially acetylated cotton cloth. Flame retardants used included Proban, APO–THPC, BAP–THPC, Antiflamm, and Borax/boric acid mixture. Details of cloth weights, cotton mixtures, retardant percentage are given.

Results of the experiments are far too detailed to attempt to summarize them here. They included determination of maximum tar yields, laevoglucosan yields, and char yield under various conditions of temperature, flame retardant percentage, etc. However, a characteristic behavior of flame retardants was reported to be increase of the proportion of char and decrease of the tar yield. For details of the analytical results, yields, compositions of the chars and tars, and elements distribution from the flame retardants, the reader is referred to the paper. It was again, however, an apparent characteristic of the retardants that, of the nitrogen and phosphorus not volatilized, most was found in the char, but chlorine was more usually found in the tar.

Of the materials identified other than laevoglucosan, several are indicative of pyrolysis by Madorsky's Process I in which glucose units are preserved as hexose units, e.g., in the form of 1,6-anhydro-β-D-glucopyranose or 1,6-anhydro-β-D-glucofuranose (found by GLC). The alternative process (Madorsky II) involves irreversible decomposition by chain scission and fragmentation (which the authors note was reviewed recently by Broido and Kilzer[2]). The decreased production of tar and increased production of char by flame retardants is regarded as support for the proposition that retardants promote the fragmentation process II (possibly in some instances by free-radical mechanisms). The ability of flame retardants to operate effectively at temperatures well below that of rapid pyrolysis of cellulose is given as evidence in support of the belief that flame retardants act mainly in the solid phase (particularly the Borax/boric acid mixture and the APO–THPC) with Proban also perhaps acting partly in the vapor phase.

References

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Subject Headings: *Cellulose, pyrolysis, and flame retardants; Flame retardants, cellulose; Pyrolysis, modification by flame retardants.*

R. H. Essenhigh

Clark, D. T. and Tedder, J. M. (The University, Sheffield, England) "Reaction of Hydrogen Atoms with Halogeno-Methanes. Part 1. Carbon Tetrachloride. Part 2. Bromotrichloromethane and Fluorotrichloromethane. Part 3. Chloroform, Deuterochloroform and Bromodichloromethane.," *Transactions of the Faraday Society* **62,** 393–414 (1966)

The reactions between hydrogen atoms and CCl_4, CCl_3Br, CCl_3F, $CHCl_3$, $CDCl_3$, and CCl_2BrH were studied in a steady-state flow system at 0.22 mm Hg. The hydrogen atoms were generated in a Wood's tube while each of the reactants was introduced into the flowing stream of atomic and molecular hydrogen through a concentric injector nozzle. The concentration of the reactant was determined by assuming saturation in a hydrogen stream bubbling through a liquid pool of the halomethane. Analysis was performed by gas chromatography, mass spectrometry and infrared techniques. Flow rates were determined using gas burettes, and all runs were performed at room temperature.

The data were recorded by calculating the percentage of reaction of the specific scavenger used. The relative concentrations of reactant and hydrogen were varied in order to assist in determining the actual mechanism of the reaction.

The products of the reaction of $H\cdot + CCl_4$ were HCl, $CHCl_3$, CH_2Cl_2, and traces of CH_3Cl. The concentration of H· was assumed to be around 20% in the poisoned tube. This is over 8 times greater than the concentration of CCl_4 in any experiment. Not over 8% of the CCl_4 was ever reacted. The first step in the reaction sequence is the abstraction of a chlorine atom by H·;

$$CCl_4 + H\cdot \rightarrow \cdot CCl_3 + HCl \qquad (1)$$

followed by H· recombination with CCl_3 to form vibrationally excited CCl_3H^*

$$H\cdot + CCl_3\cdot \rightarrow CCl_3H^* \qquad (2)$$

Unimolecular decomposition of the CCl_3H^* follows one of two paths to yield another molecule of HCl and CCl_2: ;

$$CCl_3H^* \rightarrow CCl_2 + HCl \qquad (3)$$

$$\rightarrow CCl_2H + Cl\cdot \qquad (4)$$

Reaction (3) is more likely when looked at from a study of the thermal decomposition of $CHCl_3$ itself. The $:CCl_2$ or dichlorocarbene radical reacts swiftly with molecular hydrogen to form $CCl_2H_2^*$;

$$:CCl_2 + H_2 \rightarrow CCl_2H_2^* \qquad (5)$$

The unimolecular decomposition of the excited $CCl_2H_2^*$ occurs by abstraction of yet one more HCl molecule and CClH: The complicating reaction $HCl+H\cdot$ is disregarded since it is estimated to be 20 times slower than the abstraction of $Cl\cdot$ from CCl_4. When HCl is added to the molecular H_2 bubbling through the CCl_4 an additional reaction of $:CCl_2$ must be recognized;

$$:CCl_2+HCl \rightarrow CCl_3H \qquad (6)$$

The ratio of $CHCl_3/CH_2Cl_2$ was independent of changes in the concentration of CCl_4 or $\cdot H$. This confirms the fact that both $CHCl_3$ and CH_2Cl_2 are produced from the common intermediate $CHCl_3^*$ as shown in Eqs. (2), (3), and (5), above. When HCl is added to the molecular H_2, Reaction (6) begins to compete readily with Reaction (5). Thus $:CCl_2$ will favor conversion to $CHCl_3$.

A plot of $CHCl_3/CH_2Cl_2$ vs. HCl/H_2 results in a straight line if the concentration of HCl is artificially enhanced as described above. The intercept (4.30) corresponds to the ratio of $CHCl_3/HCl$, from the slope of 33.5 we arrive at a calculated value of 6.34 for the ratio of $CHCl_3/CH_2Cl_2$. This result fits in well with the experimental data found.

A study of the reaction of $H\cdot$ with CCl_3Br and CCl_3F resulted in a similar reaction sequence as described for $H\cdot+CCl_4$. The percentage of reaction of CCl_3Br was greater than that of CCl_4. On the other hand CCl_3F showed a slightly lower degree of reaction than CCl_4. Products actually found were CCl_3H, CCl_2H_2, $CClH_3$, $CBrH_3$, CFH_3, CCl_2BrH, CCl_2FH, $CClFH_2$, $CClBrH_2$. The detailed reaction sequence given below assumes steady-state theory and is applicable to CCl_3F by substitution of Br by F in all reaction sequences involving the bromine atom.

$$CCl_3Br+H\cdot \xrightarrow{K_1} CCl_3\cdot+HBr$$

$$\left\{\begin{array}{lcl} CCl_3\cdot+H\cdot & \xrightarrow{K_3,\,K_4} & CCl_3H^* \\ CCl_3H^*+M & \xrightarrow{K_3} & CCl_3H+M \\ CCl_3H^* & \xrightarrow{K_4} & CCl_2{:}+HCl \end{array}\right.$$

$$CCl_2{:}+HCl \xrightarrow{K_{15}} CCl_3H$$

$$\left\{\begin{array}{lcl} CCl_2{:}+H_2 & \xrightarrow{K_8,\,K_{10}} & CCl_2H_2^* \\ CCl_2H_2^*+M & \xrightarrow{K_8} & CCl_2H_2 \\ CCl_2H_2^* & \xrightarrow{K_{10}} & CClH{:}+HCl \end{array}\right.$$

$$\left\{\begin{array}{lcl} CClH{:}+H_2 & \xrightarrow{K_{13}} & CClH_3^* \\ CClH_3^*+M & \xrightarrow{K_{13}'} & CClH_3+M \end{array}\right.$$

$$CCl_3Br+H\cdot \xrightarrow{K_2} CCl_2Br\cdot+HCl$$

$$\left\{\begin{array}{lcl} CCl_2Br\cdot+H\cdot & \xrightarrow{K_5,\,K_7} & CCl_2BrH^* \\ CCl_2BrH^* & \xrightarrow{K_5} & CCl_2{:}+HBr \\ CCl_2BrH^*+M & \xrightarrow{K_7} & CCl_2BrH+M \end{array}\right.$$

$$CClBr{:}+HCl \xrightarrow{K_{16}} CCl_2BrH$$

$$\left\{\begin{array}{lcl} CClBr{:}+H_2 & \xrightarrow{K_9,\,K_{11},\,K_{12}} & CClBrH_2^* \\ CClBrH_2^*+M & \xrightarrow{K_9} & CClBrH_2+M \\ CClBrH_2^* & \xrightarrow{K_{11}} & CClH+HBr \\ CClBrH_2^* & \xrightarrow{K_{12}} & CBrH+HCl \end{array}\right.$$

$$\left\{\begin{array}{lcl} CBrH{:}+H_2 & \xrightarrow{K_{14}} & CBrH_3^* \\ CBrH_3^*+M & \xrightarrow{K_{14}'} & CBrH_3+M \end{array}\right.$$

Experimental results showed that the ratios of the concentrations of the above products correspond well with those calculated from the mechanism. Again it is permissible to conclude that the ratios of the products is independent of the relative concentrations of H· or CCl_3Br and CCl_3F.

With CCl_3F, no CFH_3 or $CClH_3$ was found; therefore, the extent of the stabilization reactions K_8 and K_9 must greatly overpower the decomposition sequences K_{12} and K_{13}. When CCl_3Br was the reactant a ratio of 5–10 CH_3Br/CH_3Cl was observed. This indicates that K_{12} is the favored decomposition route over that shown in K_{11}. The favored route is dictated by the stability of the halogen acid produced.

The final series of compounds studied were $CHCl_3$, $CDCl_3$, and CCl_2BrH. The products found were CCl_3H, CCl_2H_2, and $CClH_3$ for starting reactant $CHCl_3$. $CDCl_3$ yielded $CHCl_3$, CCl_2DH, CCl_2H_2, $CClDH_2$, and $CClH_3$. With CCl_2BrH products were CCl_2BrH, $CClBrH_2$, CCl_2H_2, and CBr_3H. A similar assumption of the mechanism outlined above for CCl_3Br was assumed and resulted in reasonable correlations of the product ratios found in each of the above reactions. The ratio of $CHCl_3/CH_2Cl_2$ was roughly the same for CCl_3D and CCl_3H as found in the experiment using CCl_4. With CCl_2BrH the ratio of CCl_3H/CCl_2H_2 is 7.4. An interesting comparison of the relative rates of H, Cl, or Br abstraction from CCl_3Br, CCl_3D, or CCl_3H and CCl_2BrH shows that K^H/K^{Cl} for the latter two compounds is equal to >3. Chlorine abstraction in the case of these compounds is more exothermic than H abstraction. Despite this the H or D abstraction process is preferred. The difference is cited as being due to the greater coulombic repulsion of the $2P_z$ electron of carbon atoms in the methyl group and the unbound $1s$ electrons of the electron pairs of the particular halogen involved. During hydrogen atom approach this repulsive force is much less due to the ability of small H atoms to come close enough to the halogen atom to form a partial H–X bond.

In summary, the extent of reaction in each of the systems studied was always closely proportional to the concentration of H atoms and inversely proportional to the concentration of the reactant. The decomposition of the di- or trihalogenomethanes always proceeds through the carbene structure. This decomposition route apparently has a lower activation energy than normal carbon-halogen bond fission. Also the carbene route involves a cyclic transition structure, which invariably means a lower exponential factor. This means that at low temperatures such as employed here decomposition of the CX_2H_2 or CX_3H type molecules go through the CX_2: transition state.

Subject Heading: *Atom reaction, hydrogen, with halo methanes.*

P. Breisacher

Fry, J. and Lustig, R. E. (Joint Fire Research Organization, Boreham Wood, England) "Water Used in Fire Fighting," *Fire International* 6, 25–30 (1964)

A study was made of the quantities of water used in fire fighting by eleven fire brigades in England and Wales. These brigades were selected to give a good geographical spread and include different types of areas. The information was compiled during the period from April 1960 to March 1961. Tables are listed showing the actual water used in some 7200 fires during this period. From the tabulation, several interesting conclusions can be drawn.

1. While there was a general similarity in the distribution patterns, there were definite differences between brigades. For example, one brigade used between 30 and 100 gal on almost 40% of its fires, which was a much higher proportion than any of the other brigades. In addition, there were several other brigades that used between 100 and 300 gal much more often than any of the other nine.

2. The summary, insofar as the over-all use of water was concerned, was as follows:

(a) Thirty per cent of the fires were extinguished with three gal of water or less.
(b) An additional 20% of the fires were extinguished with between 30 and 100 gal of water.
(c) The figures showed a marked decrease in the amount of water used on dwelling fires than on those in other buildings. For example, 75% of all dwelling fires were extinguished with 30 gal or less.
(d) Four hundred gallons of water, the amount carried in one tank on many appliances, was sufficient to extinguish 95% of the fires in dwellings; 81% of those in other buildings, and about 86% of all the fires listed.

A general conclusion was drawn to the effect that a very large proportion of fires can be extinguished with no more water than the amount carried in the tank of a water tender. It would, however, be impossible to rely on the water carried by the first appliances, even in entirely residential areas, because of the need for considerably larger quantities on many occasions. On the other hand, a large proportion (over 80%) of the fires were extinguished by less than 100 gal of water and if a small first vehicle carrying quantities of this order were available, it might be useful in answering the first alarm in congested areas or country districts where narrow or rough roads slow down larger vehicles.

Subject Headings: *Water, in fire fighting; Fire, suppression, by water.*

J. J. Ahern

VIII. Model Studies and Scaling Laws

Atallah, S. (Tufts University, Medford, Massachusetts) "Model Studies of a Forest Fire," *Pyrodynamics* **2**, 53–63 (1965).

A simplified theoretical model of a spreading fire is presented, in which the propagation of a vertical flame zone across a homogeneous thin horizontal combustible slab suspended in still air is described by a nonlinear second-order differential equation. This equation is derived by writing an energy balance for a volume element in the slab located at a distance x from the base of the advancing flame. The element gains heat by radiation from the flame and by conduction horizontally through the slab; it loses heat by radiation and by convection. The boundary conditions are:

$$T=T_b \quad \text{at} \quad x=0$$

$$T=T_a \quad \text{at} \quad x=\infty,$$

where T is the temperature of the slab element, T_a is ambient temperature, and T_b the temperature at the flame base.

The governing equation can be linearized by making a rough approximation for the temperature relationships in the term for radiation loss. This procedure permits an algebraic solution which yields the temperature distribution in the slab ahead of the advancing flame. However, a more precise solution was obtained without linearization by means of a digital computor.

By restricting the governing equation by the additional boundary condition

$$dT/dx=0 \quad \text{at} \quad x=0,$$

an equation can be found for the velocity of propagation of the flame. This relationship is

$$VH=\alpha(H^2/L)-\beta, \tag{1}$$

where V is the rate of flame propagation, H the height of the flame, and L the slab thickness. The quantities α and β can be regarded as "constants" although they vary inversely as the slab density and their values also depend on (1) the thermal properties of both the flame and the slab, (2) the surface convection heat transfer coefficient between the slab and the surroundings, and (3) the various temperatures in the system.

The experimental model was a thin horizontal slab of pine which burned from the edge. A thermocouple embedded in the slab gave the experimental temperature distribution ahead of the advancing flame. The experimental temperature distribution curve differs considerably from the theoretical curves—especially the curve based on the algebraic solution of the linearized form of the basic differential equation.

If the quantity VH is plotted against H^2/L, the data from the burning pine slab indicates a linear relationship which agrees with Eq. (1). This equation is also in agreement with the data from fires in two other kinds of fuels.

Subject Headings: *Forest fire, model for; Model, forest fire.*

G. M. Byram

IX. Atomization of Liquids

Shagalova, S. A. and Reznik, V. A. (Central Boiler-Turbine Institute—TsKTI—Leningrad, USSR) "The Influence of Initial Pressure on the Development of Natural Fuel Dust Explosions," *Teploenergetika* **12,** 63–65 (1965)

Dusts burning in suspension in air are generally believed to burn faster the higher the pressure. In power engineering this can be of economic importance, and this was the stimulus for the work reviewed here.

The specific point investigated was the influence of the initial pressure on the final pressure developed in a dust flame, and the method of investigation was to explode a dust/air suspension in an appropriately pressurized steel bomb. This was a cylinder of 15 cm i.d. and 40 cm ht but containing, internally, another concentric cylinder of 10.6 cm i.d. to divide the chamber volume in two. At the bottom of the bomb was an axial fan to circulate the dust/air mixture up the annulus between the bomb casing and internal cylinder, and back through the cylinder center. This is reminiscent of a device developed by Gliwitzky[1] about 30 years ago. Ignition of a dust dispersion by an electrically heated coil (at 800°C) generated pressure changes that were recorded as indicator diagrams. In this specific sequence of tests, the fuel was the sieve fraction 53–74 μm of dried peat.

The principal results are summarized in two tables and four diagrams, and concentrated in the 2 following points: the pressure developed; and the completeness of combustion of the fuel components. Tests were run at 4 levels of initial pressure: 1, 1.5, 2, and 2.5 atm and the principal measurement reported was the maximum pressure developed for dust concentrations in the range 0 to 28 kg/m^3 [oz/cu ft] (which is very high). The data were normalized in pressure by taking the ratio ($p_{\max}/p_{\text{init}}$); and normalized in concentration by the ratio (α) of the stoichiometric to the actual concentration (both expressed in kg/cm^3 for the appropriate pressure). All values of ($p_{\max}/p_{\text{init}}$) plotted against α were then found to lie on a common line. (This implies that the temperature rise depends only on α; and that the fraction of dust burned for a given concentration depends only on the fuel/air weight ratio and not on pressure.)

The maximum pressure developed was at very fuel-rich concentrations with $\alpha \simeq 0.08$–0.1 (roughly 10 times the stoichiometric concentration) from which it was concluded that combustion was therefore incomplete and with only a small proportion of the fuel participating.

Detailed gas analysis showed CO_2 maximizing and O_2 minimizing close to the concentration developing maximum pressure. Calculations from these data of the percentage of each fuel component consumed (fixed carbon, V.M., volatile carbon, etc.) indicated that not all the gasified fuel was burned, and the authors concluded that the main component involved in the combustion was the volatile carbon.

Two observations would seem to be in order. The maximum explosibility at a significantly fuel-rich concentration is behavior that has often been assumed, though the authors seemed to find it surprising. If it occurs (e.g., as in the peak flame speed observed by Essenhigh and Woodhead[2]) a reasonable explanation is that there is increased surface area so that more particles of dust burn at the same specific rate to a smaller extent, but allowing a greater over-all rate of energy release.

The second point concerns the validity of the experimental method. There is much to be said for developing continuous flow systems but closed-circuit devices suffer from a number of disadvantages discussed in detail by Brown and Woodhead.[3] In the Gliwitzky-type apparatus there is doubt that all the dust is fully dispersed before ignition. Anyone contemplating construction of a closed circuit system would be well advised to examine the Brown and Woodhead paper[3] beforehand.

References

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2. Essenhigh, R. H. and Woodhead, D. W.: Safety in Mines Research Estab. Res. Report No. 166 (1959); Combust. Flame *2*, 365 (1958).
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Subject Headings: ***Dust, flame, effect of pressure; Pressure, effect on dust flame.***

R. H. Essenhigh

Burgoyne, J. H. (Imperial College, London, England) "The Flammability of Mists and Sprays," *Proceedings of the Second Symposium on Chemical Process Hazards, Institution of Chemical Engineers, 1963*, Published 1964.

In this paper measurements of the effect of drop size (uniform) on the lower flammability limit, principally for tetralin-in-air suspensions, are presented. In addition, some data are reported showing the proportion of diluent gas (nitrogen) required to suppress flammability. Most of the data given were obtained, using an open-ended vertical 2-inch-diameter tube with ignition at the bottom.

In tetralin suspensions in which the drop diameter is less than 0.010 mm, the lower flammability limiting concentration is 0.045 g/l and the limiting addition of nitrogen gas is about 40%. These values are essentially equal to those for homogeneous systems, probably because the drops are able to evaporate forming a homogeneous phase before the arrival of the flame front. This is of practical interest in the case of suspensions formed by the condensation of saturated vapor, because the resulting drop sizes are generally less than 0.010 mm.

In suspensions formed mechanically (e.g., by the use of atomizing nozzles), the drop diameters generally exceed 0.010 mm. In such cases the sedimentation velocity toward or away from the advancing flame influences the effective fuel concentration at the flame front. Therefore a "kinetic" concentration C_k (g/l) of suspended liquid in air is defined:

$$C_k=[(V_f+V_s)/V_s]C_s,$$

where C_s is the "static" composition (g/l), V_f the flame velocity, and V_s the sedimentation velocity relative to the air. (V_s is positive for upward flame propagation; negative for downward flame propagation.) Data are presented which support this concept.

For suspensions with drop sizes exceeding 0.010 mm, the flame front concentration at the limit decreases significantly as the drop size increases. Here flame spread occurs in a heterogeneous system and the "vapor" (homogeneous) flame propagation mechanism no longer applies. When the spray becomes very coarse, with drop diameters somewhere between 0.6 and 1.5 mm, normal flame propagation becomes impossible. The amount of diluent gas required for suppressing flammability passes through a maximum (57%) when the drop size is increased to 0.045 mm.

Subject Headings: *Flammability, mists and sprays; Mists, flammability of; Sprays, flammability of.*

G. A. Agoston

X. Meteorological Interactions

Fahnestock, G. R. (Southern Forest Experiment Station, U. S. Forest Service, New Orleans, Louisiana) "Texas Forest Fires: In Relation to Weather and Other Factors," *U. S. Forest Service Research Paper SO-16* (1965)

This paper describes results from a computer analysis of fire reports and weather records of the Texas Forest Service for the years 1958 through 1960.

The analysis showed that the final size of nonincendiary fires varied directly with wind speed and attack time and inversely with relative humidity and hour of discovery (10 a.m. to 6:00 p.m.). Occurrence of nonincendiary fires was correlated with burning index or relative humidity or both. The dependency varied from strong to weak and one or the other variable was replaced in two instances by a function of wind speed.

The size of incendiary fires increased with wind and decreased as hour of discovery became later. Attack time and relative humidity had no effect. The number of incendiary fires was not related significantly to any of the variables tested.

The frequency of large fires and the area burned were concentrated at relative humidities below 40% and at burning indexes of 50 to 100. Strong evidence existed that few large fires could be expected when the humidity was 40% or higher. Days when 5 or more fires occurred in a district tended to be characterized by humidities below 40 and burning indexes between 20 and 45. More certain identification and measurement of the factors affecting each fire should clarify apparent cause and effect relationships, thereby permitting sharper definition of significant levels of relative humidity.

Fires discovered by aerial observers were attacked less promptly, on an average, than those discovered by towermen, patrols, or the public. With increasing fire danger, attack time increased for aerial discoveries, decreased for tower discoveries, and stayed essentially constant for patrol discoveries. Attack time on fires discovered by the public was constant up to a burning index of 50, then more than doubled. On fires discovered by patrols, attack was much faster than on any of the others, and did not vary with burning index. Despite slower attack, aerial discoveries averaged slightly smaller in final size than did tower or public discoveries. Average final size of fires discovered from towers increased linearly with burning index throughout its range. Up to about burning index 50, aerial and tower discoveries behaved similarly; above that point, size of aerial discoveries increased disproportionately. Lumbering and debris-burning fires discovered from towers were larger than aerially discovered fires attributed to the same causes. Without exception, fires that reached large size primarily because of excessive attack time were discovered by aerial observers or the public.

Three general conclusions were drawn that have significance for both fire control operations and future investigations: (1) Some measure of atmospheric moisture is essential for rating fire danger in the South. The new National Fire Danger Rating System replaces direct measurement of fuel moisture content with estimation based on relative humidity and should provide more accurate ratings of probable fire occurrence. (2) Occurrence and potential size of incendiary fires are governed more by undetermined human factors than by any natural influences that are being measured. (3) Detection is a key area to study in efforts to reduce area burned. Study of detection in relation to the total suppression operation may show the way to accelerate control in critical situations and to reduce the acreage burned.

Subject Headings: *Forest fire, Texas; Forest fire, and weather; Texas forest fire; Weather, and forest fire.*

L. A. Povinelli

Kao, S. K. and Niemann, B. L. (University of Utah, Salt Lake City, Utah) "Analyses of Isotropic and Anisotropic Turbulent Dispersion of Particles in the Atmosphere," *Journal of the Atmospheric Sciences* **22**, 85–90 (1965)

This paper compares the field measurements of turbulence in the atmosphere carried out by Edinger[1] with the theory for anisotropic turbulent diffusion given by Lin.[2] The measurements were of the trajectories of many individual particles diffusing near the 500 ft level in the atmosphere. The particles were soap bubbles approximately 6 cm in diameter and the positions of the soap bubbles were recorded every fifth of a second using a motion picture camera. The experiments were carried out in the Mojave desert during a period of active convection.

The auto-correlation of the vector velocity and the vector acceleration for a single particle are calculated from the positional measurements of the bubbles. The results agree well with theoretical predictions by Lin and others. For pairs of bubbles the mean auto-correlation of the vector relative acceleration, the mean cross-covariance of the relative acceleration, the eddy diffusivity, and a component of the diffusion tensor are determined. Predictions by Lin regarding these quantities are reasonably consistent with the measurements.

References

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Subject Headings: *Diffusion, turbulent; Dispersion, of particles, in the atmosphere; Turbulence, dispersion of particles; Particles, diffusion of.*

D. L. Turcotte

Le Quinio, R. and Hugon, J. (Center for Nuclear Studies, Saclay, France) "Atmospheric Diffusion Experiments on an Actual Scale: Methods and Results," *La Mētērologie, Quatrieme Série* 69, 177–192 (1963)

The authors first describe a method of study mainly based on the autonomy and flexibility of the sampling appliances. In opposition with previous studies, they have endeavored, in about a hundred tests, to emit a tracer in conditions as near as possible to real conditions—for instance from the top of stacks. Samples were taken in all weathers, in all types of surroundings and especially inside villages and towns.

The usual theories are then difficult to apply, diffusion being on the whole better than was accepted until then. This difference can be explained on one hand by the nature of surroundings and on the other hand, by the duration of sampling—an often neglected factor. On the other hand it was shown that wind velocity has less importance than was thought, due to resulting contrary phenomena.

Subject Headings: *Atmosphere, diffusion in; Diffusion, in atmosphere.*

Editor's Summary from *La Méteorologie*

Lugt, H. J. and Schwiderski, E. W. (U.S. Naval Weapons Laboratory, Dahlgren, Virginia) "Convection Flows Due to Local Heating of a Horizontal Surface," *Journal of the Atmospheric Sciences* **23**, 54–55 (1966)

Fire storms caused by massive forest fires and updrafts over sun-heated islands represent typical instances of convective flow processes over locally heated surfaces. In this article, the authors present the initial phase of their study of steady laminar convetion caused by nonuniform axisymmetric heating (or cooling) of a horizontal surface.

Following their previously developed mathematical approach, the authors start their analysis with a dimensionless formulation of the Navier-Stokes equations for steady laminar incompressible flow. Boundary conditions of nonslip at the rigid surface and a finite heat flux source are imposed upon the system of elliptic partial differential equations. The surface temperature distribution is synthesized by a monatonically decreasing series expansion, which falls off rapidly with distance from the center of the heated surface. By means of an adjustable local boundary layer assumption and certain transformations, the remaining differential equations are changed to their equivalent integral expressions. These are solved by Volterra integral equations and an iteration process starting with small Grashof numbers.

The numerical results of the computer program are presented by a series of nine plots of dimensionless flow field velocities and temperatures against altitude, for a zero Coriolis parameter.

The heated surface produces convection away from the surface which grows in strength and extent as the Grashof number (i.e., temperature difference) increases. By contrast, a cooled surface produces flow towards the surface which diminishes in spatial extent but increases in strength with Grashof number.

For constant Grashof number but increasing Eckert number (i.e., heat flux) convective motion from the heated surface is enhanced in strength and extent, and the temperature difference between the surface and the rising fluid is reduced.

A parametric study using various types of fluids (i.e., different orders of magnitude of Prandtl number) shows that flow from a heated surface becomes spatially unstable beyond a critical Rayleigh number (i.e., product of Prandtl and Grashof numbers) of about 120 (for an Eckert number of zero), and is virtually independent of Prandtl number.

As the positive sign Eckert number increases, this instability occurs at a lower Rayleigh number. Typically, instability begins at a Rayleigh number of 70 for a critical Eckert number of about 0.02. The effect of increasing Prandtl number is to enlarge the strength and extent of heated surface convection. These effects are reversed for cooled surfaces. For the latter situation (i.e., corresponding to negative Eckert number) the resultant flow becomes heated by frictional processes and the temperature difference between the surface and the convecting fluid increases to the point where the temperature in the descending flow exceeds that in the fluid environment far above the surface.

Another conclusion of the study is that the heat flux (Nusselt number, Nu) for a cooled surface is related to Rayleigh number, Ra, by a 1/6 power law, almost independent of Prandtl number, or

$$\mathrm{Nu} \rightarrow 0.87\,|\,\mathrm{Ra}\,|^{1/6}.$$

For heated surfaces, the Nusselt number decreases with Rayleigh number until the critical (unstable) value is reached at

$$\mathrm{Nu(crit)} \approx 1.6.$$

Abstracter's Note: The authors recently have reported on the extension of the material contained in this *J. Atmos. Sciences* article.[1] It is found that consideration of a positive Coriolis parameter in the solution of the heated surface flow field results in cyclonic motion for the radial inflow near the surface, and anti-cyclonic motion for the convective radial and axial outflow above and away from the heated area. Hence, in the northern hemisphere a counterclockwise vortex is produced in the lower part of the boundary layer and clockwise vorticity exists in the upper part. These flow field characteristics are reversed for a cooled surface.

As the Coriolis parameter increases from zero, the tendency of motion to become unstable decreases. Thus, a higher Rayleigh number accompanies the critical Coriolis parameter for which instability commences.

Reference

1. Lugt, H. J. and Schwiderski, E. W.: "Atmospheric Convection Produced by Local Heating or Cooling of a Horizontal Surface," NWL Report No. 1999, U.S. Naval Weapons Laboratory, Dahlgren, Va., Oct. 1965.

Subject Headings: ***Flow, convective; Heat, induced convective flow by.***

K. M. Foreman

Walters, T. S. (University of Wales, Swansea, Wales) "Diffusion from an Elevated Point Source into a Turbulent Atmosphere," *Mathematika* **12,** 49–57 (1965)

This paper presents a theoretical study of a steady diffusion problem. Some airborne substance diffuses from an elevated point source into a turbulent atmosphere while the air flow is parallel to the ground. The Cartesian axes are chosen such that $z=0$ is the ground level and $0X$ points in the direction of the mean wind velocity of a turbulent flow in $z>0$. The diffusion equation being considered is simply written as

$$V(\partial\phi/\partial X)=(\partial/\partial y)[K_y(\partial\phi/\partial y)]+(\partial/\partial z)[K_z(\partial\phi/\partial z)],$$

where ϕ is the concentration of the airborne substance, V the mean velocity, K_y and K_z are the coefficients of eddy diffusivity in the y and z directions, respectively. It is assumed that the mean velocity is a function of z only and the diffusion velocity in X direction is small compared with the mean velocity V. Based on the mechanism of the turbulence considered by Davies,[1] the expressions for V, K_y and K_z are assumed as

$$V=V_1(z/z_1)^m$$

$$k_y=a_yV_1^{(1/2)n}z^m$$

$$k_z=a_zV_1^{1-n}z^{1-m},$$

where V_1 is the mean velocity at a reference height Z_1, m and n are constants and are related by $m=n/(2-n)$, and a_y, a_z are constants. Because of the expression of V, the author points out that the region in which the theory can apply is only in the boundary layer near the ground.

By the use of the Fourier cosine and the Hankel transforms, an analytical solution is obtained. Predictions of the solution are that the maximum concentration at ground level of the diffusing substance varies with $h^{1.8}$ as $m=1/7$, where h is the height of the source, and that the distance in the downstream from the source to the point where this maximum concentration is attained varies with $h^{1.3}$.

Reference

1. Davies, D. R.: Quart. J. Mech. Appl. Math. 3 (1950).

Subject Headings: *Atmosphere, turbulent diffusion in; Diffusion, turbulent, in atmosphere.*

S. J. Ying

Zimmerman, S. P. (Air Force Cambridge Research Laboratories, Bedford, Massachusetts) "Turbulent Atmospheric Parameters by Contaminant Deposition," *Journal of Applied Meteorology* **4,** 279–288 (1965)

This paper compares the available contaminant or smoke-puff experiments with the theories for atmospheric turbulence. It is concluded that the similarity theory of Batchelor[1] is applicable when the turbulent field is uniform. However, when a mean shear field is present and the square of the vorticity is small compared with the square of the mean shear, the theory of Tchen[2] is found to be applicable.

References

1. Batchelor, G. K.: Quart. J. Roy. Meteorol. Soc. *76,* 133 (1950).
2. Tchen, C. M.: Advan. Geophys. *6,* 165 (1959).

Subject Headings: *Atmosphere, turbulence in; Smoke, puff experiments, on atmospheric turbulence; Turbulence, in atmosphere.*

D. L. Turcotte

XI. Operational Research Principles Applied to Fire Research

Jarrett, H. F. (System Development Corporation, Santa Monica, California) "Fire Data from the Watts Riot: Results of Preliminary Analysis and Evaluation," *Work Unit No. 2611C under Office of Civil Defense Contract OCD-PS-65-71 Technical Memorandum* (May 1966)

This volume documents the results of a preliminary analysis and evaluation of data from the Watts Riot provided by the U.S. Department of Agriculture, U.S. Forest Service. Recommendations regarding future studies of the data, including its relation to Emergency Operating Center research, are offered.

Subject Headings: *Fire, data from Watts Riot; Riot, Watts, fire data from; Watts Riot, fire data from.*

Author's Abstract

John, F. I. and Passell, T. O. (Stanford Research Institute, Menlo Park, California) "Evaluation of Nuclear Weapon Thermal Heat," *SRI Project 4949-360 under Office of Civil Defense Contract No. OCD-PS-64-201* (August 1966)

The threat to urban areas from fires produced by the detonation of a nuclear weapon may be measured in terms of the proportion of structures that will contain one or more significant fires, i.e., fires producing a flashover. In the study, this proportion is determined for uncrushed structures in which the ignition of an interior fuel by thermal radiation from a nuclear weapon results in at least one significant fire. The proportions of structures containing a significant fire in different land-use areas are expressed as functions of the radiant exposure outside structures. The functions depend on such parameters as the weapon yield, height of burst, atmospheric conditions, number of fuels, and exposure of fuels. Scaling relationships for determining parameter values are given.

Atmospheric transmission factors for completely overcast skies are given for different elevation angles of the fireball. In addition, a preliminary estimate is made of the conditions under which clouds will be burned out by thermal radiation.

Subject Headings: *Thermal, effects of nuclear weapons; Nuclear weapons, thermal effects.*

Authors' Abstract

XII. Instrumentation

Bernard B. (Huggins Laboratories, Inc., Sunnyvale, California) "Flame Temperature Measurements," *Instruments & Control Systems* **38,** 113–115 (1965)

Techniques for flame temperature measurements by various means are compared, and a new instrument called the "Infrascope" precision radiometer is described. The statement is made that most standard optical techniques are not practical because of the "high transmission characteristics of flames and exhausts," but the meaning of this statement is not clear. If it means that the flame is nearly transparent, then standard line-reversal techniques are applicable; if it means that the flame is nearly opaque, then a standard radiation bolometer will read the blackbody temperature.

Useful radiation regions for optical measurements are radiation due to H_2O at 2.7 microns and that due to CO_2 at 4.45 μ. The new instrument isolates the 4.45-μ band with an interference filter and utilizes a sensitive infrared detector, either of the thermal or quantum type, with a short time response. Mirrors are used instead of lenses and a chopper to produce an AC signal for ease in amplification. A separate light source provides a reference, although its role is not described.

Because flames vary considerably in emissivity, this factor must be determined in order to measure the gas temperature. An auxilliary mirror placed behind the flame will permit determination of the gas transmission at the selected wavelength, and hence its emissivity, assuming the reflectivity is negligible. Since the apparent emissivity of a flame also depends on its thickness and the amount of solid particles, this effect can be taken into account by use of the usual relation for absorption coefficient. The absorption coefficient then may be determined separately by use of flames of different thicknesses, where the other factors are held constant.

Subject Headings: *Flame, temperatures, optical pyrometry; Pyrometry, optical; Temperature, measurement in flames.*

J. K. Richmond

XIII. Fire-Fighting Techniques, Equipment

"Flame Resistance with Polymers," *Rubber and Plastics Age* 47 (4), 395 (1966)*

Summaries of papers presented at the Plastics Institute Conference on Flame Resistance with Polymers, 15–16 March 1966. The papers covered the subjects of fire hazards and health hazards, the lack of international coordination of tests, the merits of additives, smoke and toxic products produced at fires and specific flame retardants.

Subject Headings: *Flame resistance, of polymers; Polymers, flame resistance of.*

Castrantas, H. M. (FMC Corporation, Princeton, New Jersey), **Banerjee, D. K.** (U.S. Industrial Chemicals Co., Cincinnati, Ohio), **and Noller, D. C.** (Wallace and Tiernan, Inc., Buffalo, New York) "Fire and Explosion Hazards of Peroxy Compounds," *American Society for Testing and Materials Special Technical Publication No. 394* (1965)

The detonation theory is used to clarify the explosive characteristics of both organic and inorganic peroxy compounds. Some typical accidents are described. The hazards involved in the use of a large number of peroxy compounds are tabulated for use by laboratory workers handling these compounds for the first time. All commercially available peroxides are covered together with those that may be synthesized for occasional use in the laboratory. One hundred thirty-four references are included.

Subject Headings: *Fire hazards, of peroxy compounds; Explosion hazards, of peroxy compounds; Peroxy compounds, fire and explosion hazards of.*

Authors' Abstract

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* Taken from *Safety in Mines Research Establishment Abstracts of Current Publications 15* (3), 23. By Permission.

Nelson, R. M. (Southeastern Forest Experiment Station, Asheville, North Carolina) "The National Fire Danger Rating System," *U.S. Forest Service Research Paper SE-13* (1964)

Stockstad, D. S. and Barney, R. J. (Intermountain Forest and Range Experiment Station, Ogden, Utah) "Conversion Tables for Use with the National Fire-Danger Rating System in the Intermountain Area," *U.S. Forest Service Research Note INT-12* (1964)

Barney, R. J. (Intermountain Forest and Range Experiment Station, Ogden, Utah) "Calculating the National Fire-Danger Rating Spread Index by Computer," *U.S. Forest Service Research Note INT-19* (1964)

The National Fire-Danger Rating System for forest fires is specified in the U.S. Forest Service Handbook 5123.3, which will ultimately describe four basic indexes: the fire spread index, the ignition index, the fire risk index, and the fuel energy index. To date on the national scale, only the spread index has been developed. The purpose of the fire-danger rating indexes is to provide means for predicting fire behavior as a function of weather and fuel.

Implementation of the fire spread index has caused concern in the U.S. Forest Service wherever other rating systems have been used, with respect to the interpretation of the new index in terms of the old.

Three research papers have been prepared to aid in the appreciation and implementation of the national system:

1. *The National Fire Danger Rating System*—R. M. Nelson

This paper discusses the merits of the fire spread index and includes a digest of the instrumentation and procedures used in computation. Both the spread index and the burning index previously used in the East and South are based on the same variables—fuel moisture, wind speed, and conditions of lesser vegetation—but these variables are given different weights in the two systems.

Figure 1 shows the relationships between inputs and the computational steps in deriving the fire spread index. The spread index ranges in numerical value from 0 to

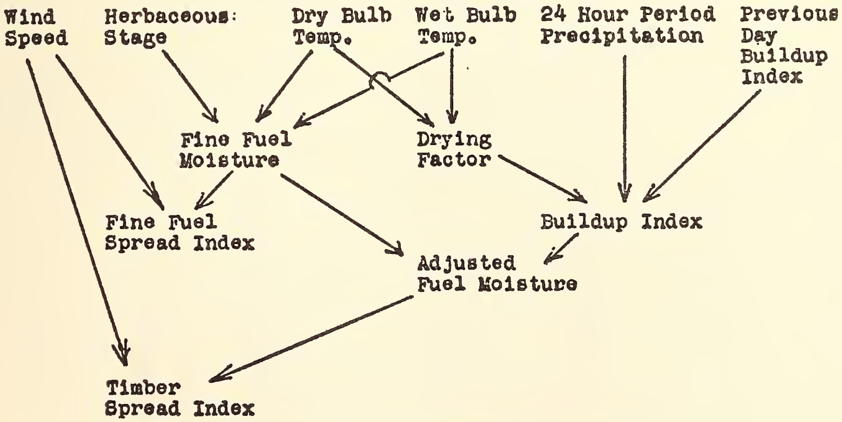

FIG. 1. Factors in the computation of spread index.

100. The buildup index cited in Fig. 1 is a cumulative index of numerical value ranging from zero but unlimited in the maximum accumulated value, and the value computed for a given day is dependent upon the value computed for the previous day. The herbacious stage cited in Fig. 1 may be one of three stages, i.e., green, transition, or cured.

Tables required in the computation of spread index are included, along with examples of details of computations based on parameters in Fig. 1. It is required that daily fire spread index values be computed from data gathered at the same time of day. Other technical requirements are discussed, such as the location of the basic instrumentation for the measurement of wind speed, temperatures, etc.

The author notes that the buildup index is by itself a good fire hazard rating, since its value is not reduced significantly by light rains which quickly evaporate and lose their effectiveness in reducing hazard.

Correlation of the old burning index and the spread index with actual fire experience is presented in Tables I and II. In Table I, percentages of days and fires are cumulated and grouped by five-unit increments for both burning and spread indexes using fire experience from the most severe fire months, January through April, for the years 1958 through 1960 in a Southeastern state fire protection district. The fire size classification used in Table I is as follows:

Class	*Size (acres)*
A	$\frac{1}{4}$ or less
B	$\frac{1}{4}$ to 10
C	10 to 100
D	100 to 300
E	300 or more

Tables I and II show that in the lower range indexes, spread index correlation with fire incidents is better than the burning index correlation. Since C, D, and E fires represent larger fire areas, it follows that these classes indicate a greater ten-

TABLE I

Comparison of cumulated days, fires, and C, D, and E fires by burning index and spread index ranges for a Southeastern protection district

	Burning index			Spread index		
Index range	Days	All fires	C, D, E fires	Days	All fires	C, D, E fires
			Percent			
0– 5	53	18	14	24	1	2
0–10	73	38	34	35	6	3
0–15	81	52	49	53	21	15
0–20	88	68	64	76	51	44
0–25	93	78	73	90	71	67
0–30	96	87	83	96	91	90
0–35	98	93	90	98	93	95
0–40	99	97	94	99	98	98
0–45	99	99	98	99	99	99
0–50	100	100	100	100	100	100

dency for fire spread. Thus interpreted, the superiority of fire spread index over burning index for fire spread is shown in Table I.

Adjective classification of fire danger is also discussed. A suggested correlation of adjective rating with fire spread indexes is shown in Table III.

TABLE II

Comparison of cumulated days and fires by burning index and spread index ranges for a Northeastern protection unit[1]

Index range	Burning index Days	Burning index Fires	Spread index Days	Spread index Fires
		Percent		
0– 5	29	5	17	1
0–10	40	10	32	3
0–15	52	18	46	13
0–20	69	33	64	31
0–25	76	49	70	58
0–30	84	62	78	81
0–35	88	77	95	94
0–40	91	80	100	100
0–45	94	84	—	—
0–50	100	100	—	—

[1] The burning index range of 0–200 used in the Northeast has been converted to a 100-point range.

TABLE III

Fire danger classes based on spread index

Class of danger		Color code	Spread index
Low	(1)	green	0 to 4
Moderate	(2)	blue	5 to 9
High	(3)	yellow	10 to 19
Very high	(4)	orange	20 to 39
Extreme	(5)	red	above 40

NOTES:

(1) Low: Fuels do not readily ignite from small fire brands, hence there is little danger of spotting. Intense heat sources including lightning may start fires in duff and punky wood. Open curled grassland fires may burn freely for a few hours after rain. Wood fires spread slowly by creeping and smoldering, burning in irregular fingers.

(2) Moderate: Fires may start from most accidental causes, but with the exception of lightning fires in some areas, the number of starts is generally low. Open cured grassland will burn briskly and spread rapidly with wind. Woods fire-spread is slow to moderate. Short distance spotting may occur. In general, control is relatively easy.

(3) High: Cured fine fuels ignite readily. Unattended brush and camp fires are likely to spread. Fire spread is rapid, and short distance spotting is common. Fires on slopes may develop high intensity. Control at best is difficult on all but small fires.

(4) Very high: Ignition is easy and spread is rapid. Intensity of fire increases rapidly. Spot fires are a constant danger, and with heavy fuels they may develop over long distances. Direct attack is rarely possible, except within a few minutes of ignition.

(5) Extreme: Ignition and initial development is extremely rapid. Fire spread is furious in intensity and rate. Control action is possible generally only on the flanks, except for incipient fires, or changes in fire environment such as lessening of fuel density and abrupt favorable change in weather.

2. *Conversion Tables for Use with the National Fire-Danger Rating System in the Intermountain Area*—D. S. Stockstad and R. J. Barney

The authors present a table for predicting actual fire spread in terms of chains per hour perimeter increase (1 chain equals 22 yards) as a function of fuel rate of spread type, steepness of slope, and spread index. Tables for converting spread index values determined at one specified time of day and location (such as mountain top, or valley site, etc.) to values for other hours and locations are included. Examples showing the application of the Tables are given.

3. *Calculating the National Fire-Danger Rating Spread Index by Computer*—R. J. Barney

This paper reports the development of a computer program for both the burning and fire spread indexes, using IBM 1620 computer with 40K storage capacity. This work was done at the University of Idaho Computer Center by H. W. Crowley.

Subject Headings: ***Fire danger rating; National fire rating system.***

J. E. Malcolm

Heselden, A. J. M. (Joint Fire Research Organization, Boreham Wood, England) "Fully-Developed Fires in a Single Compartment. Part II. Experiments with Town Gas Fuel and One Small Window Opening," *Joint Fire Research Organization Fire Research Note No. 568*

Heselden describes a continuation of his work in developing modeling techniques for compartment fires. One objective is to determine the fire resistance requirements of structures. This paper discusses the development of a sample mathematical model incorporating the rate of heat release within a compartment, the rate of sensible heat of effluent gases, radiation losses through openings, net radiation transfer of the flame to the compartment walls, and the rate of convection transferred from the flame to the walls.

His experimental work consisted of burning a regulated flow of town gas in a small compartment instrumented for measuring fire characteristics and heat transfer. He defined the point at which flames emerged from the window as being the critical gas flow rate. When the gas flow rate was low, an increase in flow caused an increase in heat release rate within the compartment until the critical flow rate was reached; thereafter, the heat release rate decreased. When gas flow rates were high, insufficient air mixed with the gaseous fuel so it could not burn completely within the compartment. The unburned gases mixed with entrained air, burned outside and would have contributed to the spread of fire beyond the compartment.

His calculated values agreed reasonably close to measured values. He found that the rate of heat release within the compartment depends on the rate of flow of air into the compartment; consequently, as the rate of air inflow falls with the rate of fuel flow, the heat release rate drops. He concludes that when windows are large the heat release rate within the compartment may be limited by the rate of air entrainment by the flame, but when openings are small, the rate at which air can enter the compartment may limit the combustion rate.

Tests with insulated walls by Simms and calculations for concrete by Heselden are cited.

Agreement between the model and measured values warrant extension of this work to larger, more complex models and an approach toward actual scale fires.

Subject Headings: *Compartments, fire in; Fire, in compartments; Modeling, compartment fire; Windows, in compartment fire.*

A. P. Brackebusch

Schleicher, A. R. (The Western Company of North America, Dallas, Texas) "Rapid Gelling of Aircraft Fuel," *Final Report under U.S. Army Aviation Materiel Laboratories, Fort Eustis, Virginia Contract DA 44-177-AMC-112*(*T*) (February 1966)

Experimental evidence has shown that the severity of accidental hydrocarbon fuel fires can be reduced by chemically solidifying the liquid fuel. The purpose of the subject work was to determine the feasibility of utilizing this principle to reduce the dangers of postcrash aircraft fires.

The feasibility of rapidly gelling large quantities of aircraft fuel has been investigated and established. The types and quantities of chemical gelling agents required were investigated. The times required for the gelling of 50-gallon quantities of fuel have been determined.

Mechanisms and power sources for mixing gelling agents with fuel have been evaluated. The hazards and penalties associated with these systems have been established.

Impact tests were made to determine the reduction of fire hazard with gelled fuel under dynamic conditions. These tests showed radical differences in performance between gels which behave similarly under static tests.

Soap type and amine-isocyanate gels have about equal effectiveness in reducing fire hazards in small scale experiments. The performance of the coal system was decidedly superior in terms of achieving rapid gelling of large quantities of fuel.

A visual presentation of this final report has been made in the form of a narrated color motion picture. This film presents a summary of results of the subject contract and a state-of-the-art report on fuel gelling.

Subject Headings: *Aircraft, fuel, gelling of; Fuel, aircraft, gelling of; Gelling, of aircraft fuel.*

Author's Abstract

Sukharevskii, V. M. "Fundamental Problems Concerning the Reduction of the Fire Hazard in Coal Mines"—"Osnovnye voprosy snizheniya pozharnoi opasnosti v ugol'nykh shakhtakh" Moscow, Nedra, (1964)* (In Russian)

The book deals with practical data and scientific investigations of combating the fire hazard in coal mines. Part I gives recent data of the actual hazard and of the

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main causes of mine fires. Part II discusses methods of preventing dangerous heat impulses in mine workings, the occurrence of fires and their development, whilst Part III is concerned with the main available means of fighting fires in mine workings and their special properties. Each part is divided into a number of chapters (which are in turn sub-divided into sections), discussing the various aspects of the three parts of the book.

Subject Headings: *Coal, mine, fire; Fire, coal mine; Mines, coal, fire in.*

XIV. Miscellaneous

Broido, A. (Pacific Southwest Forest and Range Experiment Station, U.S. Forest Service, Berkeley, California) "Effects of Fire on Major Ecosystems," Reprinted from *Ecological Effects of Nuclear War, BNL 917* (*C-43*) G. M. Woodwell, Editor, Brookhaven National Laboratory, Upton, New York (1965)

The catastrophic impact that a nuclear war is expected to have upon major ecosystems can result from two sources: ionizing radiation, chiefly from fallout, and large fires started principally by thermal radiation emitted by the nuclear detonations. As yet no large land areas have ever been covered with high levels of radioactive fallout. Consequently there is little evidence on which to base conclusions about the ecological impact of fallout, and the subject is necessarily controversial. On the other hand, fire has long been recognized as a primary agent affecting major ecosystems. Fires involving large areas have produced their impact frequently since prehistoric times, contributing in large part to the development of many of our present ecosystems. Many hundreds of studies have been conducted on the ecological effects of such fires, with greatly varied results. Consequently, statements that can be made about the ecological impact of large-scale fires are, if possible, even more controversial than are those about fallout.

This paper describes the initial thermal radiation and fire effects of a nuclear detonation—a subject with which the author has had some experience. It will then discuss some ecological consequences of fire—a subject for which the author's primary qualification is a complete lack of prejudice due to no experience whatever. Since thermal and fire effects on the ecosystem of prime concern to man, the urban complex, have already received considerable attention, this paper deals primarily with ecosystems in which man's presence is secondary.

Subject Headings: *Ecosystems, fire effect on; Fire, effect on ecosystems.*

Authors' Abstract

Broido, A. and Nelson, M. A. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service, Berkeley, California) "Ash Content: Its Effect on Combustion of Corn Plants," *Science* **146,** 652–653 (1964)

Broido has previously shown that the reactions leading to flaming combustion of pure cellulose are minimized or eliminated by adding inorganic ash constituents.

This result is attributable to lowering the temperature range for the reactions which produce glowing combustion.

After a plant dies, its inorganic substances may be leached by weathering, and its reaction to fire may thus be changed. One such instance is described. Several green stalks of sweet corn cut in October were stored in an open barn while several others were left uncut in the field until March when they too were cut and stored for one month with the fall cuttings.

Burning tests were made when both samples had 8% moisture content. When a match was held to a leaf of the fall cutting (sample F), the leaf flamed fairly readily, but when the match was withhrawn the flames died. The charred section continued to glow and formed a powdery white ash. There was little spread of combustion beyond the initial ignition. In contrast, when a match was held to a leaf of the spring cutting (sample S), the leaf flamed readily and it was completely enveloped. After flaming the black charred remains did not glow. A red hot wire in contact with a leaf of sample F caused glowing combustion, which burned a hole larger than the wire but produced no flame. When the wire momentarily contracted sample S, it burned a sharp, clearly defined hole the size of the wire with no glowing; if the wire remained longer in contact, the leaf ignited and continued in flames.

Sample S had one-third as much ash as sample F. All of the ash components were reduced about the same degree; no specific ash component was completely eliminated. The authors concluded that although there were some differences in organic composition of the two samples, especially in water-soluble fractions, these could not account for all of the differences in combustion. The enhanced glowing combustion but decreased flaming of sample F was attributed to its greater ash content.

Subject Headings: ***Ash content, effect on combustion of corn plants; Corn plants, ash content and combustion.***

W. G. Morris

O'Dogherty, M. J. (Joint Fire Research Organization, Boreham Wood, England) "The Shock Hazard Associated with the Extinction of Fires Involving Electrical Equipment," *Joint Fire Research Organization Fire Research Technical Paper No. 13* (1965)

The hazard of electrical shock during the extinguishment of fires with various agents near live electrical equipment is discussed by the author. Experimental work on this subject is reviewed and summarized.

A greater part of the paper deals with the shock hazard associated with water as an extinguishing agent. The other agents, i.e., foam, carbon dioxide, dry chemicals, and vaporizing liquids, are only briefly discussed. In general, carbon dioxide, dry chemicals, and vaporizing liquids are considered nonconducting; water, with or without additives, and foam are considered conductors.

Based on his reviews, the author comes to a number of conclusions and recommendations. These conclusions and recommendations are based on the criterion that the current liable to pass through the body of an equipment operator should never exceed 1 mA. This level gives, in the opinion of the author, the greatest margin of safety. His conclusions and recommendations are as follows:

1. As nozzle diameter and conductor voltage increase the safe distance for solid hose streams must be increased. A table of recommended safe distances for different nozzle diameters and voltage is given.
2. Water sprays do not conduct dangerous electric currents. A distance sufficient to avoid flashover or direct contact with the high voltage equipment is recommended. The author emphasizes that only nozzles designed for spray production should be used; combination solid stream and spray nozzles could be dangerous.
3. Portable extinguishers containing water without additive can be used safely down to 1 foot for voltages up to 1 kV, provided there is no danger of direct contact. Portable extinguishers containing highly conductive solutions may present a serious hazard even at voltages below 1 kV. It is important to train personnel in the use of and to distinguish between various types of portable extinguishers.
4. Because it is possible to have widely varying specific resistances with foam solutions, the same precautions that were emphasized for water should also be applied to foam
5. Normally there is no electrical hazard involved in the use of carbon dioxide, dry chemicals, or vaporizing liquids as extinguishing agents. Precautions should be taken to avoid flashover or direct contact with live electrical parts.

Subject Headings: ***Electric shock, hazards in fire; Fire, in electrical equipment, shock hazards; Shock hazards, in fires.***

W. Y. Pong

Spalt, K. W. and Reifsnyder, W. E. (Yale University, New Haven, Connecticut) "Bark Characteristics and Fire Resistance: A Literature Survey," *Prepared at the School of Forestry, Yale University, in cooperation with the Southern Forest Experiment Station, U.S. Forest Service.* (1962)

This is a summary of the field with 75 references. 19 pages.

Subject Headings: ***Bark, fire resistance of; Fire resistance, of bark.***

Editor

Waisel, Y. and Friedman, J. (Tel-Aviv University, Tel-Aviv, Israel) "The Use of Tamarisk Trees for the Restriction of Fires," *La'Yaaran* **15**, No. 3 (1965)

Field and laboratory observations and tests showed that some species of Tamarisk trees inhibit growth of non-halophytic herbaceous plants, which are usually a high fire hazard during dry hot months. Furthermore, the litter of Tamarisk is much more resistant to ignition, spread, and smoldering of fire than is litter from either pine needles or grass straw.

Laboratory tests on strips of oven-dry material showed that ignitions of Tamarisk litter will go out after a few seconds but in similar strips of pine needles or hay the ignitions continued to spread. Tests of 10-gram oven-dry samples of these fuels showed that: (1) Tamarisk burns only about one-fourth as long from ignition to extinction of flame; (2) Tamarisk glows only about one-fortieth as long after extinction of flame; (3) Tamarisk loses only 4% in weight by burning while hay loses 64% and pine needles 84%; (4) Tamarisk contains 19.6% ash (dry weight basis) while hay and pine needles contain only 7% to 8%. After Tamarisk litter was thoroughly leached to 15.6% ash content it burned longer than the other fuels, glowed much longer than the unleached, and lost 50% in weight by burning. Its resistance to fire appears related to its high ash content.

An additional factor in fire resistance of Tamarisk litter is that salty drops drip from the trees at night. In addition to inhibiting non-halophytic herbaceous growth, this salt forms hydroscopic crystals on the litter which then gathers moisture and remains damp from an hour or two before sunset until a few hours after sunrise.

Tamarisk trees are easy to propagate and the large number of species spread over the world makes them available in many regions. They should be considered for use where a cover is desirable on firebreaks.

Subject Headings: *Fire resistance, of tamarisk trees; Tamarisk trees, fire resistance of; Trees, tamarisk, fire resistance of.*

W. G. Morris

BOOKS, BULLETINS, TRANSLATIONS, MEETINGS

Books

Mavrodineanu, R. (Philips Laboratories, Irvington-on-Hudson, New York) and Office of Standard Reference Data, National Bureau of Standards, Washington, D. C.) *Bibliography of Flame Spectroscopy* (*Analytical Applications*) *1800 to 1966*. NBS Miscellaneous Publication No. 281. 250 pages, 5,113 references. U.S. Government Printing Office, Washington, D. C. 20402 (Superintendent of Documents.)

Subject Headings: *Bibliography, of flame spectroscopy; Flame spectroscopy, bibliography of, Flame spectroscopy, analytical uses of; Spectroscopy, of flame.*

Bulletins

Mass Spectrometry Bulletin (Mass Spectrometry Data Centre, AWRE, Aldermaston, Berkshire, England) First issue November 1966. Sold on subscription only. Annual subscription $40.00 including air mail (2nd class). Available from Her Majesty's Stationery Office, London, England

The aim of the Bulletin is to help the working scientist keep abreast of research involving mass spectrometry. Each month will provide relevant references derived from a comprehensive and critical search of the world's literature in subjects including Biology, Chemistry, Engineering, Geology, Instrumentation and Physics. Over 150 journals will be completely scanned, the remainder being covered via abstract journals. Books and reports will also be included. Additionally, the Bulletin will give information of Data Centre activities, notes of conferences, meetings, etc. and other items of general interest to mass spectrometrists.

Subject Heading: *Mass spectrometry.*

JANAF Thermochemical Data Tables Tables issued August, 1965, including:
Supplement 17: Hard Copy $10.00 #PB 168 370, Microfiche $3.50
Supplements 18-21 issued September 1966: Hard Copy $4.00 #PB 168 370–1
Available from Clearinghouse for Federal Scientific and Technical Information, U.S. Department of Commerce, Springfield, Virginia 22151 (Subscription Desk/410.12)
Magnetic Tapes: Complete set of tables, including Supplement 22, $295.00
Individual Supplements beginning with #14, $45.00
Available from Dow Chemical Company, Thermal Research Laboratory, 1707 Building, Midland, Michigan 48440 Attn: Dr. Harold Prophet

These tables present reliable thermodynamic data on propellants and related compounds and species, with sources referenced and critically reviewed. Quarterly supplements are issued containing updated and new data. At present the tables contain data for over 800 species.

Subject Headings: *Thermochemical data; JANAF thermochemical data.*

Translations

The Physics of Combustion Processes (Fizika Goreniya i Vzryva) Published by the Siberian Division of the Academy of Sciences USSR, M. A. Lavrent'ev, Editor. Translation by Faraday Press. Available through The Faraday Press, Inc. 84 Fifth Avenue, New York, New York 10010 $100/year, 4 issues

This journal covers theoretical and experimental work on the combustion and detonation of gaseous mixtures, solid and liquid explosives and propellants, physical phenomena relating to detonation and shock waves, wave propagation, ultrastrong magnetic fields, high-velocity jets and the properties of materials under shock loading. (*See Fire Research Abstracts and Reviews* 7, 152 1965)

Subject Headings: *Combustion process, physics of; Soviet journals, translation, "Physics of Combustion Processes."*

Zel'dovitch, Ya. B. "On an Effect which Stabilizes the Wrinkled Front of a Laminar Flame," *Zhurnal Prikladnoi Mekhanikii Tekhnicheskoi Fiziki* (Journal of Applied Mechanics and Technical Physics) No. 1, 102–104 (1966) Translation 1925 under Bureau of Naval Weapons Contract NOw 62-0604-c by Applied Physics Laboratory, The Johns Hopkins University (L. J. Holtschlag)

Subject Headings: *Flame, wrinkled front, stabilization of; Stability, wrinkled flame front.*

Meetings

Conference on Burns and Flame-Retardant Fabrics—New York Academy of Medicine, New York, New York, December 2–3, 1966. Reported by A. F. Robertson, National Bureau of Standards, Washington, D. C.

A most successful meeting on this subject was held on December 2–3, 1966 at the New York Academy of Medicine. It was jointly sponsored by American College of Surgeons, The New York and Brooklyn Trauma Committee; and New York Academy of Medicine, Section on Plastic Surgery; the United States Public Health Service, Division of Accident Prevention; and the National Fire Protection Association. The National Safety Council, the American Public Health Association, and the American Academy of Pediatrics also served as "cooperating sponsors." Among the 160 registrants and participants at the meeting were representatives of the medical profession, textile industry, chemical industry, fire protection groups, clothing retailers, public consumer interests, and several Governmental agencies.

The problems presented by the continuing use of flammable clothing fabrics were explored in some detail. It was reported that among the roughly 12,000 fire fatalities and 250,000 serious burn injuries experienced by the public each year, an estimated 2,400 fatalities and a much larger fraction, perhaps two fifths (100,000), of the serious burn injuries can be associated with the use of flammable clothing. The National Fire Protection Association was reported to be currently compiling more detailed statistical data on fire fatalities than have been previously available, while the Public Health Service is, through regional survey teams, trying to secure comprehensive information on burn accidents being experienced by the public. Such data are essential as an indication of whether the burn injury experience can be modified by techniques other than public education and a requirement that all clothing be of flame retardant-treated or nonflammable materials.

The seriousness of burns was described by Dr. Curtis Artz of the Medical College of South Carolina. He reported that under the best of current medical care techniques, the initial hospital stay of persons suffering 50 percent burns of second and third degree character involves 14–30 and 30–100 days, respectively. The fifty percent of such patients who survive usually require further surgical corrective procedures later. While great progress has been made in our ability to treat and keep injured people alive, the physical, economic, emotional, and psychological damage suffered by burn accident victims and their families is usually severe. The medical profession considers it due time that more attention be given to preventing burn injuries. It was pointed out that the British have had some experience in this line with their legal requirement that children's nightwear be of retardant-treated material. Dr. Artz stated that one can at least buy retardant-treated fabrics and nightwear in Britain; one cannot easily do so here.

It is true that the United States does have a Flammable Fabrics Act designed to prevent commercial distribution of very flammable nitrocellulose-finished and brushed fabrics. However, most of the clothing items being worn by the public and complying with the standard set by the Act, are flammable and can cause serious burn injuries if ignited. The Act was not originally intended, nor does it do anything, to prevent distribution of such items and fabrics. Thus, there is little if any incentive for industry to produce and distribute fabrics of less flammable nature. The clothing industry, like the automobile industry, sees little public enthusiasm for, but probably many legal hazards in, advertisements or sales promotion campaigns emphasizing the safety of a retardant-treated or fire-safe garment. As a result, few if any retardant-treated garments are available to the public through commercial retail trade.

At the present time, about 13×10^9 yards of textile materials are produced annually in this country. Of this production, fully 75% makes use of cotton fibers. It was reported that, although permanent flame-retardant treatments are available for cotton, they have had a tendency to change the "hand" or feel of the fabric to such an extent that only treated fabrics in the weight range of 8 to 11 ounces per yard can be considered as commercially acceptable. In other words, the treatment methods currently used are acceptable only when applied to fabrics of weight corresponding to work clothing. The annual production of such fabrics amounts to

400×10^6 yards. They are significantly heavier than most clothing materials, other than suiting. This, together with the fact that for a given fabric material the flammability is inversely related to weight, presents a serious problem to modification of the flammability of clothing fabrics.

New treatment methods are obvious necessary. However, new, inherently flame-retardant fiber materials may also prove to be an effective approach to increased fire safety. Progress on such developments was described by several producers—E. I. du Pont de Nemours & Company, Borg Fabrics Division of Amphenol Corp., Owens Corning Fiberglas Corp., and Union Carbide Corporation.

The need for more adequate information on current fire accident experience, prior to broadening the influence of the Flammable Fabrics Act, was stressed. There is now no information to show that fire accidents are most frequently associated with the lighter, more flammable clothing fabrics. Thus, in the absence of any information on the relationship between clothing type, construction or weight of fabric and burn injury experience, it is only possible to suggest that very drastic changes in fabric flammability would probably be required in order to reduce clothing burn injuries. As a result, it seems important that a public demand for flame retardant-treated fabrics be encouraged. This might be done effectively if a treatment could be developed combining flame resistance with some other desirable attribute such as wrinkle resistance, wash and wear, or permanent press. It was emphasized that the public will pay for a labor-saving feature, but is seldom inclined to buy safety without strong encouragement.

A warning to textile producers was voided by a representative of the American Trial Lawyers Association. He pointed out that the legal changes which have taken place in the last twenty years are greatly to the advantage of the public as users of manufactured products. He mentioned a recent case in which a textile manufacturer was ordered to pay damages of $140,000 to a housewife for burns she sustained when her cotton pajamas brushed a kitchen burner and caught fire.

The conference closed on a note of unanimity in accepting a proposed introduced by Dr. George F. Crikelair, Professor of Surgery and Director of Plastic Surgery Services, Columbia—Presbyterian Medical Center of New York, that a permanent organization be established to encourage both a public demand for, and commercial production and distribution of, more flame retardant clothing materials.

Publication of the papers presented at the Conference, together with the discussion of them, is planned for an early issue of the "Bulletin of the New York Academy of Medicine."

The following papers were presented:

Why We Are Here—R. A. Prindle, M.D., U.S. Public Health Service
The Medical Aspects of Burns—Curtis Artz, M.D., Medical College of South Carolina
Statistics and Epidemiology of Burns—A. P. Iskrant, U.S. Public Health Service
A Survey of Fatal Clothing Fires—E. E. Juillerat, Jr., National Fire Protection Association
Development of Clothing for Protection Against Hazardous Thermal Exposure—R. E. Seaman, E. I. du Pont de Nemours and Company
Flame-Retardant Textiles—Past, Present, and Future—G. L. Drake, Jr., U.S. Department of Agriculture
Pile Fabrics as Related to Flammability—H. A. Freedman, Amphenol Corporation

Research and Application in a Textile Mill—J. W. Weaver, American Textile Manufacturers Institute
Developments in the Cotton Industry—W. M. Segall, National Cotton Council of America
Developments in the Wool Industry—H. J. Wollner, A. C. H. Fiber Service, Inc. Representing American Wool Council
Developments in the Fiber Glass Industry—J. F. Ferger, Owens-Corning Fiberglas Corporation
The Use of Synthetic Modacrylic Fibers—R. S. Brissette, Union Carbide Corporation
The Fire Protection Agency's Role—L. Segal, National Fire Protection Association
Federal Flammable Fabrics Act—H. D. Stringer, Federal Trade Commission
Department of Commerce and Fabrics Flammability—A. F. Robertson, National Bureau of Standards
An Observation of the British Experience—E. L. Lehr, U.S. Public Health Service
Industrial Experience in the Use of Flame-Retardant Fabrics—R. S. B. Holmes, U.S. Steel Corporation
Developments in Flame Resistant Textiles at U.S. Army Natick Laboratories—T. D. Miles, U.S. Army Natick Laboratories
Program Activities of the Division of Accident Prevention, U.S. Public Health Service—A. F. Schaplowsky, U.S. Public Health Service
Viewpoint of National Retail Merchants Association—P. J. Fynn, National Retail Merchants Association
Legal Aspects of the Clothing Fire Problem—A. B. Elkind, American Trial Lawyers Association
Action and Program for the Future—G. F. Crikelair, M.D., Columbia-Presbyterian Medical Center

Subject Headings: ***Burns, fire retardant fabrics; Fabrics, fire resistant.***

A. F. Robertson

Meeting of the Eastern Section of The Combustion Institute—University of Pittsburgh, Pittsburgh, Pennsylvania, November 27 and 28, 1967.

This meeting is co-sponsored by the Bureau of Mines, the Committee on Fire Research, and the University of Pittsburgh. The subject of the meeting is DISCUSSION ON SCIENTIFIC ASPECTS OF FIRE HAZARDS (emphasizing solids and liquids). Following is a provisional program.

Monday, 27 November 1967

Morning	Flame Spread	*Chairman*, R. Friedman Atlantic Research Corporation
Afternoon	Ignition Mechanisms	*Chairman*, D. Burgess Bureau of Mines

Tuesday, 28 November 1967

Morning	Flame Retardation and Extinction	*Chairman*, C. Fenimore General Electric Company
Afternoon	Round Table Discussion	*Moderator*, R. Levine

Members: R. Friedman, D. Burgess, C. Fenimore, H. Wolfhard, R. Van Dolah

The meeting is planned on the basis of invited summaries of the critical aspects of the topics named above, and short contributions which are herewith solicited. One-page abstracts should be sent to either—

Hans G. Wolfhard
Institute for Defense Analyses
400 Army-Navy Drive
Arlington, Virginia 22202

or

R. M. Fristrom
Applied Physics Laboratory
The Johns Hopkins University
8621 Georgia Avenue
Silver Spring, Maryland

The deadline for abstracts is September 15.

Organization of the Eastern Section of The Combustion Institute will be discussed at the meeting. Pending an election, the following have agreed to serve as officers:

Chairman:	R. Levine, NASA Headquarters, Washington, D. C.
Vice-Chairmen:	A. L. Thompson, McGill University, Montreal, Canada R. Friedman, Atlantic Research Corporation, Alexandria, Virginia
Secretary:	R. H. Essenhigh, Pennsylvania State University, University Park, Pennsylvania
Treasurer:	R. Roberts, Office of Naval Research, Washington, D.C.
Program:	H. G. Wolfhard, Institute for Defense Analyses, Arlington, Virginia
Arrangements:	T. Wolfson, Air Force Office of Scientific Research, Arlington, Virginia
Papers:	R. Fristrom, APL/The Johns Hopkins University, Silver Spring, Maryland

ERRATUM*

"Soot Production by Diffusion Flames"

In the abstract that appears in *Fire Research Abstracts and Reviews* **8**, 192 (1966), Fig. 1 should be replaced by the following figure:

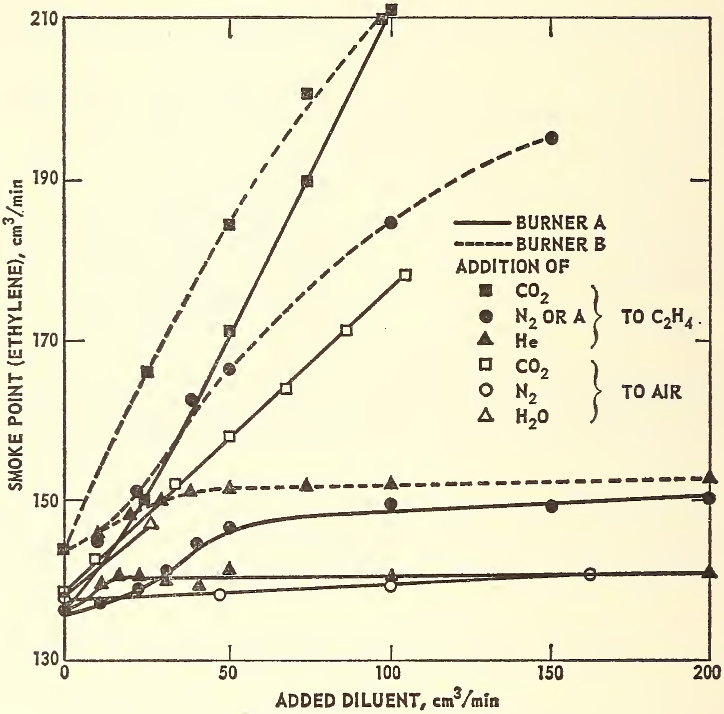

Fig. 1. Effect of adding CO_2, N_2 or A, He to ethylene and CO_2, H_2O, N_2 to air on the smoke point of ethylene-air diffusion flames. Flow rate of air: 1000 cm³/sec.

Subject Headings: *Diffusion flame, soot in; Flame, ethylene, smoke point of; Smoke point of hydrocarbon flame; Soot, formation by diffusion flame.*

U. Bonne

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* Due to editorial oversight—*Editor.*

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Volume 9 Number 3

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.
1967

FIRE RESEARCH ABSTRACTS AND REVIEWS is published three times a year by the Committee on Fire Research of the Division of Engineering—National Research Council, 2101 Constitution Avenue, Washington D. C. It is supported by the Office of Civil Defense of the Department of the Army, the U. S. Department of Agriculture through the Forest Service, the National Science Foundation, and the National Bureau of Standards. The opinions expressed by contributors are their own and are not necessarily those of the Committee on Fire Research.

Library of Congress Catalog Card Number 58-60075 rev

Available without charge from the
Office of the Committee on Fire Research
National Academy of Sciences—National Research Council
Washington, D. C. 20418

FOREWORD

Unwanted fires continue to plague our society. The severity of this problem is periodically underlined by disasters such as the tragic accident on the Aircraft Carrier Forrestal. It is estimated that this may cost the taxpayer as much as fifteen million dollars. Spectacular disasters make newspaper headlines and tend to obscure the main problem, which is the daily accumulation of individual tragedies in our cities and countryside. Each may involve and disrupt only a few lives and receive only a line or two in the local paper, but taken together they cost our society tens of thousands of lives, lost or scarred, and two billion dollars a year. These are the important losses that are crying for attention.

Efforts are being made to combat this problem. An Interagency Committee on Fire is being formed. This hopefully will coordinate federal efforts in fire prevention and research and encourage more effort. An even more promising development is the Fire Research and Safety Act of 1967 (Bill S. 1124), being considered in Congress. This envisions setting up a research effort under the Bureau of Standards with the simultaneous appointment of a committee to study the fire problem. Your Editor hopes that this bill will be passed in a useful form and that this will mark renewed constructive Congressional interest in this major social problem.

This issue of *Fire Research Abstracts and Reviews* also contains a report on the Office of Civil Defense Contractors Conference (see p. 238). It is one of the largest groups working in fire research in this country and many interesting projects were reported.

The Letters to the Editor Section continues with comment by Dr. A. Broido of the U. S. Forest Service on the relations between urban and woodland fires. This issue also contains a review article by your Editor covering the literature of Combustion Suppression. It is keyed to abstracts in *Fire Research Abstracts and Reviews* covering the period from 1958 to 1967.

R. M. Fristrom, *Editor*

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REVIEWS

Combustion Suppression

(A Literature Survey with Commentary)

R. M. FRISTROM

Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland

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INTRODUCTION

The goal of this paper is to provide a guide to the literature of combustion suppression. Background information has been included for the benefit of those new to the field. The primary source of material has been the Combustion Suppression section of *Fire Research Abstracts and Reviews*, Volumes 1–8 (1958–1966). The material has been subdivided into nine sections each of which represents a relatively restricted and coherent area. These are: A—Reviews; B—Gaseous Extinguishers; C—Liquid Extinguishers; D—Reactant Separators; E—Flame Traps;

F—Chemical Inhibitors, Homogeneous; G—Chemical Inhibitors, Heterogeneous; H—Mixed Extinguishers; and I—Unusual Fire Systems and Extinguishers.

If this selection represents an unbiased sample of the fire literature one would conclude from a paper count that Fire Research had grown at a normal rate for an expanding Science, i.e., doubling every fifteen years.[1] By contrast the area of combustion suppression has remained relatively static over the past decade.

Historically this survey is overlapped by a very capable review on chemical fire extinguishers by Friedman and Levy in 1957 (A*F*–0) and a review of the over-all field of fire research by Berl in 1963 (A*3*–313).

METHODS FOR EVALUATING COMBUSTION SUPPRESSION

To make a meaningful study of fire suppression it is necessary to have techniques for quantitatively evaluating the efficiency of an extinguisher and the techniques for its application. The problem is not straightforward because the types of fires, the extinguishing agents and the techniques vary widely, and there are additional problems connected with specifying the condition and rate of application of the extinguishant.

For economic and scientific reasons, it is desirable to test on a laboratory scale but this introduces problems in scaling results. As an example, one would like to extrapolate results from laboratory pool fires on flames a few centimeters in diameter to gasoline spill fires which may exceed 100 meters across. This is a factor of 10^8 in area and burning rate. Such extrapolations should not be made without consideration of the changes in mechanism which accompany the changes in scale.

Even the simplest case of comparison with a single type of extinguishant involves problems. One must choose between several measures of extinguishing efficiency which, although related, cannot be readily compared. As examples: Should gaseous extinguishers be compared on a mass, volume (molar), or cost basis? In the case of powders, should mass, molar, specific surface, or economic bases be used? The choice depends upon the objective of the study. In the example of powder extinguishers the most meaningful scientific comparison appears to be on the basis of specific powder surface area per unit area of fire while for practical applications an economic comparison is the most useful. Here factors such as ease of application, storage, and cost must be considered. One must be prepared to find results of Fire Research studies expressed in forms which almost preclude quantitative intercomparisons. One goal of such research is to establish parameters which will allow reliable intercomparisons. Unfortunately, this is often not possible with the present state of knowledge.

Extinction

The most straightforward method of evaluating an extinguisher's efficacy is to determine an extinction parameter. The minimum rate of application which will result in the extinguishment of a fire or the time and rate of application required to extinguish a fire are the most common. Extinguishment times vary in a complex manner depending on effective extinguisher concentration. A primitive model

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[1] deSola Price, *Big Science, Little Science*, Columbia University Press, New York, 1963.

would predict that the extinguishing time would be the gas residence time in the flame front and hence be very short. This may be the case for high application rates; but the more usual situation is that an initial application of an extinguisher slows the flame. This increases the residence time of subsequent applications and they are correspondingly more effective. Only after a number of cycles does extinguishment occur.

Specification of the application rate is a complex problem. It is customary to specify mass rate per unit of fire area. Implicitly, this assumes that method of application and its physical state and degree of aggregation are either standardized or unimportant, and that the fire intensity is independent of the size. Neither of these assumptions are justified in practical cases and specification of particle or droplet size, dispersion patterns, and other pertinent physical parameters of the extinguishant and its application are necessary. Further problems are involved in scaling laboratory and field experiments to larger practical fires.

Burning Velocity

Scientists who are somewhat removed from the practical problems of fire fighting, often measure burning velocity of premixed flames and its reduction by extinguishants. These measurements are easy to make. There is little direct practical application of such results; but they have a twofold justification: First, there is a reasonable correlation between flame inhibition effectiveness of an estinguishant (i.e., reduction of burning velocity) and its ability to put out fires. This is not too surprising, but it should be kept in mind that this correlation is empirical and subject to violations because real fires are rarely premixed. Secondly, one may deduce chemical kinetic information from such studies. This is difficult because of the complexity of flames and it is well known that the kinetic constants derived from such "global" reaction assumptions bear little direct relation to the kinetic constants of the true elementary reaction processes in the flame (A8–149 p. 324ff). The application of simple flame theory to burning velocities provides a reasonable method for making empirical correlations, but one should be cautious in extrapolating such results beyond the range of experience.

Flame Strength

With non-premixed systems, the concept of burning velocity becomes hazy and a popular measurement is "Flame Strength." This was introduced by Potter and Butler[2] to describe a flame consisting of two opposed jets of substantially uniform velocity profiles—one of fuel, one of oxidizer. Here flame strength is defined as the maximum flux per unit area of flame front which can be supported before blowout of the flame center. The theory is reasonably well developed. The blowoff flux is proportional to reaction rate, jet diameter, and independent of transport coefficients. This is quite directly related to blowoff limits described below. Diffusion flames are closer to real fires and complications appear beyond the premixed situ-

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[2] A. E. Potter and J. W. Butler, "A Novel Combustion Measurement Based on the Extinction of Diffusion Flames," Am. Rocket Soc. J. *31*, 54 (1959).

ation. The effect of an extinguishant depends on whether it is introduced on the fuel or the oxidizer side. The efficacy of a diluent such as nitrogen is highest when introduced on the fuel side while the efficacy of a chemical inhibitor such as one of the volatile halogen compounds is most effective on the oxidizer side.

Flame Structure

A more sophisticated method of studying flames and flame inhibition is to measure the detailed structure of the flame, i.e., the composition, temperature, and aerodynamic history of a gas element passing through a flame front (A *8*–148; A *8*–149). Interpretations can be made in terms of the elementary physical and chemical processes. The dominant elementary reactions can often be identified and quantitative measurements made of the rates. This is a powerful scientific tool and provides crucial information for any basic theory of flame extinction problems. Several excellent studies (F *4*–6; F *6*–254; F *7*–47; F *7*–93; F *7*–94; F *0*–1) have been made but the information has yet to make practical contributions to fire fighting. The potential of this approach is high, but experimental difficulties have limited the use of the techniques.

Limits

It is common to tabulate results from flame inhibition studies in the form of limits, expressed as a function of the composition of the flame system. Several types of limits are measured: ignition, flammability, blowoff, and detonation. They are related, but in general one cannot be derived from the other.

Ignition Limit—is the limit beyond which it is not possible to ignite a premixed system. Electric sparks are commonly used but pilot flames and hot surface have also been employed. Ignition limits correspond roughly to the flammability limits, because a flame which cannot propagate certainly cannot be ignited. If any method of ignition can be employed then the reverse is obviously true, i.e., any flame which can propagate can be ignited. For a given source and strength of ignition, however, it may be that ignition is not possible, even though flame propagation is. This has practical application in the problem of mine fires.

Flammability Limits—With premixed gaseous systems, this refers to the composition limits beyond which flame propagation does not occur. The flash point of a liquid is the temperature at which its vapor pressure is sufficient to give an ignitable mixture in air. The existance of flammability limits is a much debated question in combustion. Practical limits do exist; but whether fundamental limits exist which depend only on the intensive properties of flame systems is not yet established. Flames with burning velocities below 1 cm/sec usually do not propagate but these limits can be ascribed to quenching because of a too-small burner system, or blowoff due to minor aerodynamic fluctuations. Aside from the question of whether fundamental limits exist the practical utility of the concept is beyond question.

Quenching Limits—If a flame front approaches a solid surface, heat is extracted from the flame front by thermal conduction. The enthalpy and final flame temperature are reduced. As a result the burning velocity of a flame is reduced in the vicinity of a solid heat sink. This has been elegantly studied by Botha and Spalding (E *0*–1) and the structure of a flame in the vicinity of a cooling wall has been studied by Chen and Toong (E *4*–187). Two theories of quenching by heat extraction have been developed (E *1*–123; *1*–125). In practice, when the approach of a flame front to a surface becomes small compared with the normal thickness of the preheat zone the interaction will extinguish the flame. Thus, there is a good correlation between the observed quenching distance (minimum burner diameter or hole through which a flame will propagate) and the flame thickness as measured by Schlieren pictures or other techniques. Since this region is one of pure transport, diffusion and thermal conduction, there is a rough quantitative relation between the pre-reaction flame thickness (A *8*–149 p. 254), the thermal diffusivity (or average molecular diffusivity), and the inverse burning velocity

$$L=(\lambda/\rho_0 v_0 \hat{C})\ \ln[(T-T_0)/(T_i-T_0)]=K/v_0 P \tag{1}$$

where L is the flame pre-reaction zone thickness (cm); $K=2.5(\lambda/\rho_0\hat{C})$ is the average thermal diffusivity (cm²/sec); v_0 is the burning velocity (cm/sec); P is pressure (atm); and T is temperature (°K).

There is also an empirical relation between quenching distance and minimum ignition energy (A *F*–221 p. 361ff); but the theoretical basis for the correlation rests on the concept of excess enthalpy which has not been generally accepted.

Pressure Limits—Pressure limits of combustion are often found in the literature. They represent the pressure dependence of ignition or quenching limits and are expressed in this form because pressure was the experimental variable used in the study.

Blowoff Limits—The interaction between flames and solid surfaces has another important bearing on flame extinction since laminar flames are normally stabilized by a complex interaction between the burner wall involving heat transfer to the wall and the velocity gradient in the boundary layer.

With the common Bunsen burner one might expect stable flames only if the gas velocity exactly balanced the burning velocity of the flame. In practice such flames are actually unstable. Stable burning occurs at stream velocities greater than the burning velocity. The flame assumes a conelike shape with the component of gas velocity normal to the flame front exactly balancing the burning velocity. If it were not for the reduced velocity in the boundary layer of the burner such flames would be blown off. Since the gas velocity approaches zero at the boundary one might expect that laminar flames would be stable irrespective of the stream velocity. This is not the case in practice because, as a flame front approaches the burner surface, heat is extracted by thermal conduction. This reduces the burning velocity. At some distance of approach the two effects may balance and the flame will be stabilized. On the other hand, if burning velocity drops off more rapidly than the flow velocity in the boundary layer, no balance will be reached and the flame will blow off. Thus, blowoff velocity can be correlated with the ratio of boundary layer thickness to flame front thickness. Flame thickness varies inversely with burning velocity (A *8*–149); therefore, the faster the burning velocity the more stable the flame. Since flame front thickness varies inversely with thermal conductivity, a helium diluted flame will be more difficult to stabilize than a corresponding argon diluted flame. Two other factors enter: (1) if the burner is warmed, the heat transfer is reduced and the flame is more easily stabilized, and (2) if diffusion from the surrounding atmosphere tends to increase the burning velocity, the flame will be more easily stabilized. Thus a rich flame will be stabilized by the diffusion of oxygen from a surrounding air atmosphere and will be more stable than a fuel lean flame of the same burning velocity. If the surrounding atmosphere were fuel the reverse would be true. Air flames are stabilized by oxygen atmospheres. Flames can also be stabilized without surface interaction if the stream tubes diverge in such a manner that a balance can be reached between gas velocity and burning velocity. In this case, diffusion of the fuel into the surrounding atmosphere reduces the burning velocity in the boundary, playing a role similar to heat extraction by the burner.

Heat transfer considerations have been developed by Lewis and von Elbe (A *F*–221; A *F*–70 p. 68) into a theory which correlates flame blowoff with a critical boundary layer gradient $g = 4V/(DR^3)$, where V is the average gas velocity (cm/sec), R the tube radius (cm), and D the thermal diffusivity (cm^2/sec), g has the dimensions of seconds and is roughly proportional to and of the order of magnitude of the residence time in the initial flame reaction zone. Agreement with this first order theory is reasonable (within an order of magnitude) and the deviations generally take the directions suggested by the secondary considerations mentioned above. Turbulent flames can be stabilized either by a laminar flame in the boundary layer which continuously reignites the system or by hot reactive gas furnished by a recirculating burning region in the wake of a bluff object (A *F*–70 pp. 21, 40). Turbulent flames show a similar blowoff correlation. The characteristic parameter is the ratio of the stream velocity to the characteristic length of the bluff object stabilizer. This is proportional to residence time in the eddy and it appears obvious that, if this is short compared with the initial flame reaction time, no reservoir of hot reactive gas for igniting the main turbulent stream will exist. Since the main stream velocity far exceeds the burning velocity, blowoff should occur. The characteristic time for blunt objects in turbulent flow is a factor of two or three larger than that for laminar flow, but considering the crudity of the models this indicates that similar factors are operating in blowoff in both cases. A flame can also be destroyed by high turbulence if the shear stresses are strong enough to destroy the reaction zone (A *8*–149 p. 14).

Although more fires are extinguished by blowoff than by all other mechanisms (this is the usual method of extinguishing matches and candles), it is rarely used for practical fire fighting except in oil well fires where dynamite is used to blow out the flame. However, some authorities take the view that flames are ultimately extinguished by the blowoff which follows primary suppression techniques.

Detonation Limits—are analogous to flammability limits. As might be expected, despite similar chemistry the limits of detonation differ from the flammability limits for a system. There are systems which will burn but not detonate and systems which will detonate but possess no stable burning velocity. In the latter cases a transient accelerating flame usually precedes the detonation. An interesting point is that inhibitors for detonations differ from inhibitors for flames even though the same chemical reactions and physical processes must be operating in both cases. The widely different time-temperature histories in detonations and flames makes it likely that different reactions will dominate the two cases. Analogously, differences are found among the chemistries of ignition, slow oxidation, and flames in the same system. Many halogen compounds which inhibit flames appear to be accelerators for detonation (see Section F). On the other hand, many fuels which support combustion such as ethane or ethylene, inhibit the hydrogen-oxygen detonation.

Two important points should be kept in mind in interpreting the literature of combustion suppression. The common measurements fall between direct practical applications and basic studies of the physics and chemistry of the systems. Such laboratory studies should be used to provide a guide line, not hard fast rules. Practical results may be at variance with laboratory studies even though both are correct. The basic physics and chemistry are so complex that the simple interpretations made of the usual combustion and inhibition measurements represent guesses. These guesses should not be confused with the underlying elementary processes which are only slowly being uncovered and understood.

THE LITERATURE OF COMBUSTION SUPPRESSION

The literature of combustion suppression, taken from Section VII of *FRAR* between 1958 and 1966, has been subdivided into nine categories: A, Reviews; B, Gaseous Extinguishers; C, Liquid Extinguishers; D, Reactant Separators; E, Flame Traps; F, Chemical Inhibitors—Homogeneous; G, Chemical Inhibitors—Heterogeneous; H, Mixed Extinguishers; and I, Unusual Fire Systems and Extinguishers. Within each division papers are listed in the order of abstracting. Most of these categories represent fairly well-defined methods for suppressing combustion, but as will develop in the discussion, more than one physical and/or chemical process is often involved and in many cases it is not clear which processes are important.

In the Subject List, abstracts are identified by subsection, volume, and page number in *Fire Research Abstracts and Reviews.* For example, A *1*–12 refers to the article found in section A which was abstracted in Volume 1 on page 12. If more than one abstract appears on a page they are labeled a, b, . . . in the order of appearance. Several titles were derived from Friedman and Levy's survey (A *F*–0). They are labelled *F* in place of the *FRAR* volume number and their sequence number is identical with Friedman and Levy's bibliography. Thus, A *F*–27 refers to the article in section A which is title number 27 in Friedman's bibliography. Miscellaneous references outside *FRAR* are labelled *0.* The authors, title, and source of each article are given followed by key words indicating the subject matter. These subject headings are somewhat more extensive than those of *FRAR.* In general, the original subject headings have been retained with such additions as appeared desirable. Key works include the type of fire or flame studies; the parameters measured; and a list of systems studied (both flame systems and inhibitors). Key words are listed alphabetically and cross-referenced with the section and abstract numbers. The Author List is an alphabetical list of authors with section and abstract numbers.

Reviews

Appendix I-A lists review articles and books on topics related to combustion suppression. Three authors have surveyed the fire extinguishment field as such. The earliest was Bailey (*F*–11) (1937). The most extensive has been the series of articles by Friedman and Levy (A *F*–0; *1*–81; *1*–194; *3*–128) (1958–61) and the latest is covered by Skinner's reports (A *4*–147; *5*–100; (1962–64). The chemistry of flame inhibition was reviewed by Bailey in a book (A *F*–11) (1937) which is unfortunately somewhat dated, after thirty years. A bibliography of the chemistry of suppression was compiled by Murphy (*F*–247) (1955). Research relating to the extinguishment of aircraft fires has been the subject of two government reports by Weiss and Pesman (*F*–334) (1949) and Scull (*F*–287) (1950). Fire research as a whole was reviewed by Berl (A *3*–313) (1961).

Several good general articles on flammability limits have been published by Burgoyne and Williams-Leir (*F*–46) (1949); (*F*–51) (1950); and Mellish and Linnet (A *F*–235) (1953). Sir Alfred Egerton published an excellent article on flame inhibition (*F*–105) (1953).

A number of books and review articles on combustion have sections devoted to flame inhibition. Of particular interest are the book of Jost (A *F*–192) (1946); the review articles and book of Lewis and von Elbe (A *F*–221) (1951). Flame structure and chemistry have been reviewed by Fenimore (A *8*–148) (1964) with a chapter on inhibition; and by Fristrom and Westenberg (A *8*–149) (1965), who offer a critical survey of the kinetics of elementary flame reactions.

Gaseous Extinguishers (CO_2 *and Inert Gas Generators*)

A common method of extinguishing a fire is to blanket it with a stream of inert gas. The commercial CO_2 fire extinguisher and more recently vitiated gas produced by the exhaust of a turbojet engine are examples of this method. There have been proposals to use other inert gases, particularly nitrogen, but the author is unaware of any practical applications beyond occasional emergency laboratory extinguishments by chemists. Inert diluents are important from the scientific point in the study of the inhibition of premixed flames because they provide comparisons which help to separate the physical effects of inhibition from the chemical effects.

As is true with most extinguishment techniques several processes play important roles in the fire suppression and it is often not possible to separate them or isolate the dominant processes which may vary from case to case.

In the case of CO_2 extinguishers, the material is added in the form of low temperature snow and the action can be manifold. The gas will dilute and lower flame temperatures as discussed above. The heat of sublimation of the CO_2 is appreciable and this also results in a lowering of the flame temperature which is added to and comparable with the heat capacity effect discussed above. The solid particles can fall into a burning liquid pool and by producing a froth of cold bubbles reduce the vapor pressure of the liquid through the combined actions of cooling and evaporation and bring the liquid below the flash point. The jet of cold gas may in some cases produce such steep velocity gradients that the fire is blown out. And finally, the gas provides an inert blanket separating the burning fuel from the surrounding oxidizer.

The principle mechanism of the turbojet inert gas generator is the blanketing effect provided by displacement of the atmosphere around a fire with vitiated gas which does not support combustion. Secondary effects are provided by the dilution and the cooling effects of the gas and entrained liquid if foam is generated to help contain the blanket. Blanketing effects are discussed in section D.

In premixed flames a diluent acts in two principal ways*: (1) it lowers the concentration of the reactants and thereby the reaction rate; and (2) because of its heat capacity the diluent which is normally injected at room temperature will reduce the flame temperature. Both of these effects are understood more or less quantitatively. If the flame reaction is a single-step bimolecular reaction the concentration reduction would reduce the rate quadratically. Since burning velocity of such an ideal flame depends quadratically on reaction rate the reduction of burning velocity would depend linearly on dilution (i.e., if an equal volume of diluent were added to a combustible mixture the burning velocity should drop by a factor of two). The second effect, that of reducing flame temperatures, depends exponentially on the temperature drop and this is usually the dominant factor. The effect of heat extraction will be discussed in more detail in the next section.

The best discussions of the role of inert gas diluents in inhibiting premixed flames are probably found in the articles by Burgoyne (A *F*–46), Burgoyne and Williams-Leir (A *F*–51) and Mellish and Linnett (A *F*–235). Creitz (F *4*–141) points out that diluent nitrogen is more effective when injected on the fuel side of a diffusion flame. Two papers (B *3*–87a, b) deal with the development of carbon dioxide extinguishers. The remaining papers (B *6*–172; *6*–274; *6*–275; and *8*–37) discuss the development and testing of an inert gas generator based on an aircraft turbojet engine (B *6*–172; *6*–274; *6*–275) and heat exchange propane burners (B *8*–37). This new development allows the generation of noncombustible gas at such a rate that a building can be flushed free of air in a few minutes. A number of practical problems remain with these devices; but they offer a promising new mode of fire fighting.

Liquid Extinguishers

By far the most common liquid extinguisher is water, although liquid nitrogen has been suggested and in the case of magnesium fires, alcohol has been tried as an initial suppressor. The principal action of a liquid is presumably to extract heat from the fire through its latent heat of vaporization and heat capacity. From this standpoint water is a uniquely suitable liquid, being stable, noncombustible, nontoxic, and having a very high heat of vaporization. Auxiliary effects of these liquids are the diluent and blanket actions. The effects of dilution were discussed in the previous section and blanketing effects will be discussed in the following section. Heat extraction from a flame system reduces flame temperatures. This sharply reduces the reaction rates which depend exponentially on temperature.

In the case of the ideal bimolecular flame, the reduction of rate would be proportional to $\exp(-E/R\delta T)$, where E is the activation energy of the reaction (kcal/mole), R the molar gas constant (kcal/mole°K), and δT the reduction in temperature (°K) in the reaction zone. Experimental flames are more complicated than this simple model since they involve sequences of interacting reactions which do not lend themselves to simple analysis (A *8*–149 p. 323ff). If real flames are forced into the straight jacket of this simple model by assigning an over-all acti-

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* The diffusivity and thermal conductivity are also changed but these are probably minor factors.

vation energy and assuming reaction occurs close to the final flame temperature, a fit can be made over a narrow range and these empirical activation energies lie in the range around 40 kcal/mole. This is higher than the known constituent elementary reactions of flames which lie in the range of 0–20 kcal. This artifact is introduced by the sequence of reactions and because the initial reaction occurs well below the adiabatic flame temperature and with reduced reactant concentrations.

If this analysis is applied to the initial reaction of a sequential flame using measured temperatures and reaction rates the effects of heat extraction provide activation energies for the initial reaction which agree reasonably well with those provided by detailed flame structure analysis (A *8*–149) and other chemical kinetic techniques for studying these elementary reactions.

In practical situations the problem of application can be the factor limiting the efficacy of the water in heat extraction because if the water does not reach the seat of the fire it cannot help extinguish it. This is principally a question of the force and size dispersion of the jet. If the drops are too large only a small fraction will evaporate and be effective and the remainder will run off. On the other hand, if the drops are too small they will have poor carrying power and will not penetrate the fire region and they will also be wasted. The ordinary fire-fighting operation requires 10 to 100 times the minimal amount, assuming perfect application. Thus, there is much room for improvement in sprays, nozzles, and other applicators. Radusch (C *1*–64) has considered the question theoretically assuming that the optimum droplet is that which gives a minimal vaporization time consistent with the required range of the spray. The range in turn is determined by droplet breakup. He points out that the range obtained in practice exceeds that calculated from single droplet viscous drag considerations because entrained air in the jet reduces drag. Rasbash (C *6*–129) analyzes the situation in terms of a dimensionless spray heat transfer number and spray force number which allows the correlation of laboratory and practical fire situations. Malcolm (C *2*–73) has studied spray nozzles and absolute extinction efficiencies. Rasbash and Rogowski (C *1*–15; C *1*–18a) have studied the extinction of pool fires with water sprays and correlated extinction times with the rate of application, droplet size, and the flash point of the liquid. Lode and Dettmar (C *1*–68) have an idealized model for prediction of minimum application rates for water.

Extinction times for practical fire situations have been studied by Rasbash, Thomas and Stark at Boreham Woods (D *2*–135; *2*–136; *2*–137; *4*–198).

Another avenue of research has been the search for additives which will improve the effectiveness of water; Grove, Aidun *et al.* have made a number of studies (C *1*–18b; C *1*–58; C *1*–129; C *2*–71b), and the application to forest fires has been studied by Davis *et al.* and Phillips (C *5*–37b; C *8*–110c; C *8*–114).

Two types of additives are sought: (1) viscosity modifiers which decrease runoff by increasing viscosity; and (2) opacifiers such as aluminum powder which form a reflecting barrier over the burning surface and reduce the radiant heat transfer.

The addition of antifreeze to protect hand water extinguishers has also been studied (C *8*–111a).

Blanket Extinguishers

If a fire is of the nonpremixed type, it can be extinguished by separating the reactants with an inert blanket. This mechanism operates with gas, liquid, and solid extinguishers to a greater or lesser degree; but it is particularly important in the case of foams. The purpose of the foam is to form a relatively long-lived blanket. If air is the foaming gas, then the water film and its additives must be the active agent of suppression; on the other hand, if the foaming gas is noncombustible then the foam film acts as a barrier to retain the blanket of inert gas. It appears obvious and has been confirmed experimentally that inert gas foam is more effective than an air foam. A recent addition to the reactant separator category has been surfactants, that is, surface active agents which form a monomolecular or thicker layer over a burning liquid, reducing its vapor pressure below the flammability limit. The combination of such agent with foam and powder is particularly effective (D *6*–257). This combination is discussed in the section on mixed extinguishers. The surfactant offers an economical type of separator, since theoretically only a monolayer is required. In practice, much more than a single monolayer is required, but the amounts are still small.

The physical chemistry of foams has been the subject of several books and articles (D *2*–139; *3*–87; *5*–193). Foams are also considered useful in aircraft and other gasoline fires (D *2*–75; *3*–49). They have been studied for use in mine fires (D *1*–128; *6*–47; *6*–173; *6*–174; *6*–175; *6*–176).

The important parameters for characterizing a foam are its expansion ratio; i.e., ratio of gas volume to liquid volume. It is desirable that this be as great as possible. The second parameter is the drainage time which controls the lifetime of the foam, and the rate at which it must be replenished. Research in the foam area has centered around a search for agents which will produce foams with desirable expansion ratios and long drainage times (D *3*–87; *3*–90; *3*–216; *4*–152).

A special type of separator is the smoke screen which has been proposed to reduce fires from thermal radiation in case of nuclear explosions (D *6*–37). Timber breaks also function as separators (D *8*–112).

Several special problems have been studied. The use of foams on burning liquids which are miscible with water and destroy the foam requires additives to reduce the foam destruction (D *4*–201a; *6*–143). Glove box fires have also been considered (D *8*–111b).

Extinguishment by Heat Extraction

If heat is extracted from a premixed or other flame by contact with a solid body the flame temperature will be lowered and, as a result, the flame intensity or propagation rate will be reduced. If sufficient heat is extracted, the flame will be extinguished. This can be an important effect in fire extinction by powders, though it is usually of secondary importance compared with chemical effects as discussed in Section G. Heat extraction by powders is limited by their heat capacities and emissivities. In this section we will be principally concerned with the extinction of flames by interaction with massive solid bodies. The effects of the interaction between flames and surfaces have been studied extensively, both theoretically (E *1*–123; E *1*–125) and experimentally (E *0*–1). The general conclusion is that extraction of heat by a solid surface reduces the enthalpy of a flame and hence its mass burning velocity. The limit of this process is the extinction of the flame. This is the principle behind the flame and detonation traps used by Sir Humphry

Davy in his famous mine safety lamp. The usual design consists of screens of honeycombs of metal with a spacing comparable to the pre-reaction, heat transport thickness of the flame. Since this thickness varies inversely with burning velocity, it is found that the faster the flame to be stopped the closer must be the mesh spacing. The mesh must also have sufficient heat capacity to absorb the flame energy, but this is only a limitation with the finest of wire meshes, because gas densities at atmospheric pressure are a thousandfold lower than solids. Practical work on fences has been done in the field (E *8*–113a).

Recent work abstracted in *FRAR* includes a number of studies of quenching by gauzes and other surfaces (E *1*–204; *2*–70; *4*–201b; *5*–38; *6*–142). In addition, Chen and Toong (E *4*–187) have made a very interesting study of the structure of a laminar flame close to a heat sink.

Chemical Inhibitors—Homogeneous

Since the driving force of flames is chemical reaction it is obvious that interfering with critical reaction steps should suppress a fire. These effects have been observed, and they are the basis for the common volatile halide powder extinguishers used on gasoline fires. Such agents also have physical effects. They extract heat and blanket the fuel but inhibition occurs at concentrations so low that the effect must be chemical.

These are two classes: volatile halides from the middle of the periodic table (e.g., carbon and phosphorus) and salts of the alkali metals. The action of the former is in the gas phase and the most popular explanation is that they exchange the reactive flame radicals (H, O, OH) for relatively inert halogen atom radicals. It is noteworthy that the efficacy of a given family of these agents is inversely proportional to the reactivity of the atom (i.e., Br, and I are most effective; F least) and for a given halogen containing compound roughly proportional to the number of halogen atoms in the molecule. This view is discussed in several papers (A *F*–0). Three mechanisms can be visualized: (1) the inhibitor reacts with a radical in the chain branching step, reducing the burning rate; (2) the inhibitor may compete for a crucial radical in a nonbranching chain step; or (3) the inhibitor may increase the three-body recombination of radicals and by this means lower their concentration in the reaction zone. The first would be the most effective; but all of the mechanisms may be important under some conditions. Other views correlate extinguishing power with the electron attachment coefficient (F *4*–141) or the dipole moment (F *3*–214b) but the mechanisms associated with these correlations have not been as completely developed. Powders appear to be heterogeneous in action. The most popular mechanism attributes extinction to the destruction of radicals by recombination on the particle surface. It has also been suggested that the action may be homogeneous and due to volatilization of the particle, its dissociation, and possible radical recombination reactions of the flame radicals with the alkali metal. A third view correlating ionization potential with efficacy has not been systematically developed as a mechanism.

Friedman and Levy's survey (A *F*–0) provides a very good summary of the state and literature of this field through 1959; and an excellent bibliography on "The

Chemistry of Fire Extinguishing" was compiled by Murphy in 1955 (A *F*–247). Since *FRAR* began publishing in 1958, there is probably a satisfactory overlap between these surveys and the present one.

A number of studies have been made of the relation between burning velocity or premixed flames and added inhibitor (F *1*–19; *1*–20b; *1*–62; *1*–195; *4*–143; *4*–145; *5*–192; *6*–141) as well as studies with diffusion flames (F *1*–20a; *4*–141; *5*–101; *6*–39). With diffusion flames it is interesting to note that diluents such as nitrogen are more effective when introduced on the fuel side of the flame while halogenated inhibitors are more effective on the air side. Lask and Wagner (F *8*–196) have studied a number of inhibitors which are more effective than the volatile halides. The most effective appeared to be iron pentacarbonyl. Friedman *et al.* have studied aluminum chloride, sodium amide, and sodium vapor as inhibitors of premixed flames (F *1*–22a; *4*–196; *6*–39).

A number of studies have been made of the structure of inhibited flames—Levy (F *0*–1); Applied Physics Laboratory (F *3*–212; *4*–189; *4*–190; *5*–96); Bonne (F *4*–6; F *6*–254; *7*–93); Fenimore (F *7*–94); Wilson (F *7*–47)—kinetic constants and mechanisms have been derived from these studies for inhibition reactions.

Most of the systems which have been studied involve compounds of carbon and/or hydrogen with oxygen as the oxidizer. These all possess essentially the same chemistry. The best inhibitors are compounds which would be expected to interfere with the branching reaction $H+O_2 \rightarrow OH+O$ by reducing hydrogen atom concentration. This is not universally true of flames, however; for example, when oxides of nitrogen are used as oxidizers conventional inhibitors are ineffective (A *1*–194; F *6*–41b). The flame of boron hydrides with oxygen are also atypical. Another interesting point is the differences between flame inhibitors and detonation inhibitors (F *6*–42; *6*–145). Halogenated compounds appear to promote detonation; iron pentacarbonyl inhibits both flames and detonations. This may be related to the observation by Wilson (F *7*–47) that the operation of halogenated inhibitors is to delay the flame reaction, forcing the initial reaction into a higher temperature range and increasing the local initial rate even though the over-all rate (burning velocity) is decreased.

Skinner and his group have used shock tubes to study inhibition reactions in the hydrogen–oxygen systems (F *5*–99; *5*–101). Van Tiggelen's group at Louvain have made studies of the H_2–O_2–Cl_2 system and developed a simple "global" theory based on chain branching (F *4*–143; *4*–145).

A number of surveys have been made of practical chemical extinguishers (F *1*–21; *1*–60; *1*–132b; *3*–50; *3*–214b). The effect of inhibitors on the slow oxidation has been the subject of a number of interesting studies (F *5*–21; *5*–187; *5*–188; *6*–252; *7*–96). It should be pointed out that the chemistry of ignition and low temperature oxidations appears to be different from that of flames, probably because in the low temperature regime HO_2 is an important radical carrier.

Chemical Inhibitors—Heterogeneous

Powders represent an important class of inhibitors. Salts of the alkali metals are particularly effective. Their effectiveness increases with atomic number (e.g., potassium bicarbonate is more effective than sodium bicarbonate which in turn is more effective than lithium bicarbonate). The anion also has an effect; easily decomposed salts such as carbonates and tartrates are especially effective. The most significant parameter for powder application is the surface area of the applied particles. This would imply that the smaller the particle diameter the more effective it would be since surface to volume ratio increases without limit as particle diameter decreases. In practice, a particle diameter of the order of 20 microns is optimum. Two reasons seem likely: (1) light particles cannot penetrate a fire (see the discussion of Section C, especially C *6*–129); and (2) when the particle becomes small compared with the mean free path of the gas, continuum calculations break down and the finite size of the particle must be considered.

The quantitative correlation between effective particle surface area and extinction capabilities suggests that a surface reaction is involved. One possibility is the three-body recombination of radicals on the surface. Two unexplained factors mar the simple picture: (1) Wise and Rosser (G *6*–45) have pointed out that salts are only effective if they can be expected to volatilize or decompose during their residence in the flame. They suggest that the effective reaction may be three-body recombinations of radicals involving the alkali metal formed by dissociation of the salt. The second disturbing factor is that a calculation of the upper limit for efficiency of such powders, assuming that every molecule which reaches the particle surface recombines, indicated that both laboratory and field practice are more efficient than this theoretical upper limit. The calculation compared theoretical with minimum particle densities effective in quenching flames. The residence times available in the unperturbed flame front and estimated radical diffusion coefficients were used. This indicates that some vital factor has been omitted. Several possibilities exist: (1) the particle may break up in the flame front due to boiling or decomposition so that the available surface area and particle count is much higher than that measured for the particles applied. (2) The residence time may be increased by the thermomechanical effect which can become comparable with flame velocities for small particles (A *8*–149 p. 126). The residence time for extinction may be longer than that estimated from the unperturbed flame, since as a flame is inhibited the burning velocity drops, increasing the residence time for the inhibition. Obviously a more sophisticated model must be used. (3) It may be that inhibition occurs in the gas phase as suggested by Wise and Rosser and the observed dependence on particle surface area comes about because the volatilization will depend directly on the surface area. More basic work is needed in this area.

In addition, it may well be that homogeneous inhibitors such as iron carbonyl (F *4*–6) and lead tetramethyl (G *4*–140) owe their inhibitory effect to fine particles of oxide which appear in flames injected with these compounds.

The studies in this section are divided between suppression of fires and ignition in the laboratory (G *1*–14; *1*–22b; *1*–200; *1*–201; *4*–199; *7*–191; *6*–45), laboratory studies dealing with the suppression of detonation (G *1*–127; *1*–199; *4*–199; *6*–144; *6*–145), and studies of the problems of practical powder extinguishers (G *1*–61; *1*–203; *2*–132; *3*–87a, b, c; *5*–103; *6*–46).

Flame retardants are a special type of heterogeneous inhibitors (G *8*–201). This work is more often discussed under the headings of ignition and pyrolysis.

Mixed Extinguishing Agents

Some studies have been made of the possibilities of combining agents so that weaknesses of one agent will be compensated by another (H *7*–192). Examples are the use of mixed bromotrifluoromethane and water for aircraft crash fires (H *3*–51). In this case the injection of the halogen agent prevents ignition long enough for the water to cool the engine below the ignition point. A second area is the combination of powders, foams, and surfactants by Tuve and his co-workers (H *1*–205; *6*–257). In this case the powder extinguishes the fire; the foam forms a blanket and the surfactant covers the combustible liquid with a film which lowers its free surface and hence vapor production rate. A third area is the absorption of halogenated agents on powders (H *3*–214a). Compatability is often a major problem with mixed extinguishers (A *8*–113b).

Unusual Fire Systems and Extinguishers

As indicated before, most of the extinguishants and techniques have been developed for and studied with relation to the combustion of carbon and hydrogen compounds by oxygen. With a different flame chemistry one would expect other extinguishants and techniques to be required. This is the case. Examples of other chemistries were mentioned in Section E with relation to flames with the oxides of nitrogen as oxidizer (A *F*–0; I *5*–32; *5*–99; *6*–147). An example of a different chemistry is provided by the boron hydrides and alkyl pentaboranes, the so-called HEF fuels (I *2*–138). Here inert foam seems to be the best extinguisher and, due to the toxicity of the material, it is best to allow the fire to go to completion under control rather than to extinguish it and be left with the problem of disposing of a hazardous residue.

Another area is the fires of reactive metals such as magnesium and the alkali metals. These are used in large quantities in space and nuclear applications. The best fire-fighting technique is to cover with an inert blanket of fused salt, graphite, etc. (I *1*–205; *3*–87; *4*–150b; *6*–147; *8*–40). Again control rather than extinction is often the goal of such fire fighting.

SUMMARY

Much effort and ingenuity has gone into fire research, but the basic understanding of the problems is still in a formative stage.

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Subject Heading: ***Fire suppression.***

ABSTRACTS

I. Ignition Phenomena

Adler, J. and Zaturska, M. B. (Imperial College, London, England) "The Dependence of Flame Ignition on Transport Properties and Chemical Kinetic Parameters," *Combustion and Flame* **10**, 273–278 (1966)

Flame ignition from a spherical hot gas pocket has been examined. Critical conditions of ignition are obtained using the temperature profile technique of Spalding.[1] In the general approach of Spalding the temperature is expressed as a simple function containing time-dependent parameters; the function is then substituted into the energy conservation equations which are integrated over the space variable. A set of ordinary different equations is obtained for the parameters.

Some of the essential steps are as follows. The basic equation of energy conservation without heat losses and with spherical symmetry is:

$$c_p\rho(\partial T/\partial t)=\rho(\partial/\partial\psi)[k\rho r^4(\partial T/\partial\psi)]+\dot{q}''', \qquad (1)$$

where r is the radial distance, t the time, ρ the local gas density, c_p the average specific heat at constant pressure, k the local thermal conductivity, T the absolute temperature, $\dot{q}'''$ the volumetric heat release rate due to chemical reaction, and ψ the stream function

$$\int_0^r \rho r^2 dr,$$

with ρ a function of T and

$$r=\left\{3\int_0^\psi \frac{d\psi}{\rho(T)}\right\}^{1/3}.$$

When these parameters are transformed to dimensionless variables, Eq. (1) becomes:

$$\partial\tau/\partial\theta=(\partial/\partial\zeta)[R^4(\partial\tau/\partial\zeta)]+\phi(\tau) \qquad (2)$$

with

dimensionless temperature:

$$\tau=(T-T_u)/(T_b-T_u)$$

dimensionless time θ:

$$d\theta=[\bar{q}'''/c_p\rho_u(T_b-T_u)]dt$$

dimensionless reaction rate:

$$\phi(\tau)=(\rho_u/\rho)(\dot{q}'''/\bar{q}''')$$

dimensionless stream function:

$$d\zeta=(1/\rho_u)\{\bar{q}'''/k_u(T_b-T_u)\}^{3/2}d\psi,$$

where

$$\bar{\dot{q}}''' = \int_0^1 \left(\frac{\rho_u}{\rho}\right) \dot{q}''' d\tau$$

and

$$R = (k\rho/k_u\rho_u)^{1/4} \left\{3 \int_0^\zeta (\rho_u/\rho)\, d\zeta\right\}^{1/3}.$$

The suffixes u and b refer to unburned and burned gases.

Diffusion coefficients of the reactants and products are assumed to be equal to the thermal diffusivity. The temperature dependence of k is given by $k/k_u = \rho_u/\rho = 1+a\tau$. By definition $a = (k_b/k_u) - 1 = (\rho_u/\rho_b) - 1$. The diffusion coefficient becomes

$$D = (k_u/c_s\rho_u)(1+a\tau)^2 \quad \text{and} \quad R = \left\{3 \int_0^\zeta (1+a\tau)\, d\zeta\right\}^{1/3}.$$

Assuming that the flame propagates by means of a first-order, single-step reaction and the reaction rate is temperature-explicit,

$$\phi(\tau) = (n+1)(n+2)(1-\tau)\tau^n, \tag{3}$$

where n depends on the activation energy and the parameter "a". For large activation energies, n is independent of a.

In the profile method of solution, the energy equation is integrated from $\zeta = 0$ to $\zeta = \infty$, resulting in:

$$(d/d\theta) \int_0^\infty \tau\, d\zeta = \int_0^\infty \phi(\tau)\, d\zeta \tag{4}$$

A similar integration from $\zeta = \zeta_i$ to $\zeta = \infty$ (where ζ_i is a function of θ only) results in:

$$(d/d\theta) \int_{\zeta_i}^\infty \tau\, d\zeta + \tau_i (d\zeta_i/d\theta) = -R_i^4 (\partial\tau/\partial\zeta)_{\zeta i} + \int_{\zeta_i}^\infty \phi(\tau)\, d\zeta \tag{5}$$

When $\zeta = \zeta_i$ then $\tau = \tau_i$ and $R = R_i$. To evaluate (4) and (5), the essential profile assumption is made that

$$\tau = \tau_m f(\zeta/\zeta_i), \tag{6}$$

where $f(x)$ is a monotonically decreasing function of x and $f(0) = 1$, $f(\infty) = 0$. τ_m, which is the temperature at the center of the gas pocket and a function of θ, can be found by substituting Eq. (6) into Eqs. (4) and (5).

Numerical solutions are illustrated in graphic form for typical linear profiles of (x). In a plot of τ_m versus ζ_i, the integral curves are flame ignition or extinction types. In flame ignition, τ_m at the center of the gas pocket rises to $\tau_m = 1$ after first falling to a minimum; in flame extinction, τ_m falls continuously. The "radius" of the hot gas pocket at any time, δ, is taken for convenience equal to $2\zeta_i$, since the temperature in a linear profile vanishes where $\zeta = 2\zeta_i$. The critical radius for constant gas properties becomes,

$$r_c^* = (3\delta_c^*)^{1/3} \{k_u (T_b - T_u)/(\bar{\dot{q}}''')^*\}^{1/2}, \tag{7}$$

where * denotes the appropriate variable with $a = 0$.

The authors show how it is possible to obtain ignition criteria based on simple energy balance requirements. For this purpose they use the Peclet group concept,

$$(\mathrm{Pe})_c = 2S_u r_c/D^*,$$

where for large activation energy the flame speed

$$S_u \simeq (1/c_p\rho_u)\{2k_u\bar{\dot{q}}'''/(T_b - T_u)\}^{1/2}.$$

The critical radius for ignition is evaluated from the transformed Peclet number,

$$(\mathrm{Pe})_c = 2\sqrt{2}\{3(1+\tfrac{1}{2}a)\delta_c\}^{1/3}. \tag{8}$$

Comparison of calculated and experimental critical radii of other investigators[2] agree within an order of magnitude.

References

1. Spalding, D. B.: Proc. Roy. Soc. (London) *A245*, 352 (1958).
2. Arnold, J. S. and Sherburne, R. K.: *Fourth Symposium (International) on Combustion*, p. 139, Williams and Wilkins, Baltimore, 1953.

Subject Headings: *Chemical kinetic parameters, effect on ignition; Ignition, dependence on transport and kinetic parameters; Transport properties, effect on ignition.*

J. M. Singer

Bowes, P. C. and Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "Ignition and Extinction Phenomena Accompanying Oxygen-Dependent Self-Heating of Porous Bodies," *Combustion and Flame* **10**, 221–230 (1966)

The ignition and extinction criteria for a porous material undergoing self-heating by an exothermic chemical reaction involving the material itself with oxygen diffusing from the surroundings is considered. A mathematical model based on steady-state heat transfer by conduction, oxygen transfer by diffusion along with heat generation by an exothermic reaction of *n*th order with respect to oxygen partial pressure is developed. An approximate solution to the equations shows that the temperature at any point is given by a cubic equation so that for any given ambient temperature three possible solutions exist. In the region where ignition and extinction are possible all three roots are positive and real. The lowest of these corresponds to chemical reaction control, the middle one is unstable and the highest is in the region of diffusion controlled reaction. A jump from the lowest to the highest corresponds to ignition of the material while the reverse represents extinction. The limits within which these phenomena can occur are investigated in depth.

Some preliminary data on the ambient temperature which will give ignition and extinction of wood sawdust cubes of various sizes (2.5 to 10.2 cm per side) in ambient oxygen concentrations of from 4% to 30% are presented. The data on the ignition temperatures and the temperature rise at ignition agreed qualitatively with the theoretical values, but the ambient temperature required to produce extinguishment calculated on the basis of the ignition properties of the wood sawdust gave a significantly higher value than the measured ones. This was believed to be due to the change in chemical properties of the sawdust following ignition.

Subject Headings: ***Combustion, in porous materials; Extinction, in porous materials; Ignition, in porous materials; Porous materials, combustion in; Porous materials, extinction in; Porous materials, ignition in.***

F. R. Steward

Cullis, C. F., Fish, A., and Gibson, J. F. (Imperial College, London, England) "The Oxidation of Hydrocarbons: Studies of Spontaneous Ignition. I. Ignition Limits in Small Vessels. II. Ignition Limits in Large Vessels," *Proceedings of the Royal Society* **A284**, 108–124 (1965); *Ibid.* **A292**, 575–587 (1966)*

As the authors point out, in spite of the very great importance of hydrocarbon fuel, the variation in limiting ignition pressure with the other parameters of the system is still known only for a few systems. In particular, the effect of the surface of the reaction vessel needed further investigation.

The investigation was carried out in two parts; in the first, small vessels up to 500 cm^3 of various materials and shapes were used while in the second pyrex glass vessels up to 10 liters were used. The system *n*-heptane+oxygen+inert gas mixture was used in all the experiments.

Apart from pyrex glass, vessels made of silica, rough and smooth copper, mild steel, stainless steel, brass, and aluminum-coated stainless steel were also used. The surface to volume ratio varied from 0.61 to 11.0 cm^{-1} in the smaller vessels while with the larger the ratio was varied from 0.22 to 0.77 cm^{-1}. Three of the vessels were packed with Pyrex tubing. A static vacuum system was formed by the reaction vessel, maintained at constant temperature, and connected to both pressure measuring devices and to an approximately 3 liter premixing vessel, kept at 25°C. For the large volume experiments, a 30 liter steel premixing container was used. The required mixtures of *n*-heptane, vapor, oxygen, and inert gas were prepared at ambient temperatures and sub-atmospheric pressure. The mixture was then rapidly shared between the premixing vessel and the reaction vessel by momentarily opening a wide bore tap. The minimum delay between admission and spontaneous ignition was 3 sec so that the measurements refer to static conditions.

Great care was taken in purifying the oxygen and nitrogen used. The *n*-heptane was always better than 98% pure and no detectable difference in the ignition behavior of the various samples was found. The vitreous vessels were rinsed with 40% hydrofluoric acid, water, and acetone before use. The metal vessels were not specially cleaned. In some of the vessels, consistent results could not be obtained until the surface had been thoroughly conditioned by ca 100 ignitions.

In the experiments the limiting total gas pressure for ignition P_I, and the pressure of the fuel and oxygen in the limiting ignition mixture P_T, were measured as the temperature, reaction mixture composition, inert gas concentration, and surface factors were varied.

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* See also *Fire Research Abstracts and Reviews 9*, 69 (1967).

The results showed that in the temperature range 400°–500°C, and at low pressures, slow combustion of *n*-heptane occurs almost isothermally, in the reaction vessels <500 cm^3. At higher pressures there is an initial slow reaction which is accompanied by a pressure increase of 10% of the initial pressure. This increase is followed by transition to spontaneous ignition which, for a given mixture and constant experimental conditions, occurs after a reproducible induction period and leads to a reproducible over-all pressure increase.

Dependence of Limiting Ignition Pressure on Temperature

At about 500°C, P_I decreases sharply with temperature increase. P_I is given approximately by

$$P_I = \text{const.} \times \exp(+E/RT),$$

where $E = 15.3$ kcal mole^{-1}.

Dependence of Limiting Ignition Pressure on Reactant Mixture Composition

When the mole fraction X of fuel in the mixtures is below 0.25, an increase in fuel concentration markedly decreases P_I. As X is further increased, P_I passes through a shallow minimum. Similar-shaped curves were obtained for all the other reaction vessels and could be represented by an equation of the form

$$P_I = AX^{-m} + B(1-X)^{-n},$$

where A, B, m, and n are positive constants. The variation of P_T with X was of the same form. Addition of nitrogen or helium has a promoting effect, the effect of the helium being less pronounced.

Dependence of Limiting Ignition Pressure on the Surface

When P_T was plotted against surface/volume ratio for the vitreous vessels, with the exception of the one with a high surface/volume ratio of 11.0, the results for the unpacked vessels lay close to a straight line. Those for the packed reaction vessels were lower than would be expected simply on the basis of surface volume ratio. By calculating the average distance of a molecule from the surface in all the cases, it was found that P_T and the distance r^*, were correlated by

$$P_T = \text{const.} \times (1/r^*)^{1.3}.$$

No difference in behavior between the silica and Pyrex glass surfaces was found. In the six metal vessels ignition only occurred at considerably higher pressures than in vitreous vessels of a similar size and shape. The pressure/composition ignition profile was, however, also appreciably dependent on the nature of the metal surface. It was found that P_I in the rough copper vessel was gradually displaced toward higher values, the more the vessel was used. Moreover, with alternate oxidation and reduction of the surface at 505°C with oxygen and hydrogen, respectively, both resulted in progressive raising of the limiting ignition pressure.

Some dynamic experiments were made by allowing a given composition to flow into the reaction vessel at various rates. At the lower rates even though the final equilibrium pressure was considerably greater than the value of P_I for the static case, no ignition took place. Increasing the rate of flow eventually led to ignition at a pressure greater than the static limiting ignition pressure.

The authors consider two possible mechanisms for the ignition steps and compare the quantitive predictions with the experimental findings. The isothermal aldehyde model leads to an expression for the net branching factor ϕ. The simplified theory of chain self-ignition describes the ignition limit by equating ϕ to zero. However, this is not a justified assumption in this case, as the dynamic experiments showed. There is a positive critical value, ϕ_c, of the branching factor such that the true criterion for ignition is $\phi > \phi_c$.

Analysis of the aldehyde model leads to predictions which are not in agreement with the experimental results. The second model considered is an olefin mechanism, where hydrogen peroxide is one of the degenerate chain branching agents. This mechanism leads to a prediction for the variation of P_T with temperature, which agrees very well with the results. The markedly different results with vitreous and metallic surfaces are shown to be due to the widely different efficiencies of the surfaces in promoting the hydrogen peroxide termination reaction.

While the simple thermal model was not adequate to explain the results in small vessels, the analysis indicated that thermal factors might become more important in larger vessels. A similar series of experiments was carried out in larger vitreous vessels. Even up to 10 liters, the temperature rise preceding ignition was lower than the limiting rise predicted by Semenov's thermal theory.

For the larger vessels, the isothermal olefin mechanism could explain the results, but the hydrogen peroxide chain termination reaction had to be assumed to be diffusion controlled rather than efficiency controlled. This showed that even where the average distance of a molecule from the surface is considerable, surface reactions can be rate determining.

Subject Headings: ***Ignition, spontaneous, vessel size; Limits of ignition, spontaneous ignition and vessel size.***

M. G. Perry

Friedman, M. H. (Minnesota Mining and Manufacturing Company, St. Paul, Minnesota)* "Shock Tube Measurement of Explosive Sensitivity," *Combustion and Flame* **10**, 112–119 (1966)

The phenomenon of ignition of explosive dusts and sprays is studied with the use of a shock tube. An incident shock wave passes through a sample of explosive powder (particle diameter below 20 microns) supported close to the end plate. In the case of liquids, a sample supported on a coil is shattered by the incident wave, forming a fine spray. The particles of explosive are heated principally by the hot gas which follows the reflected wave. The explosion time (ignition delay) t_e (microseconds) is noted as a function of reflected shock temperature T_S(°K) for four explosives (PETN, hydrazine nitrate, lead azide, and nitroglycerine). The data are correlated by the equation:

$$\ln(t_e/T_S^2) = A + (E/RT_S)$$

Here A is a constant, R the gas constant, and E the activation energy (zero order).

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This equation is the result of an approximate analysis of a model for condensed phase thermal explosion in which heat exchange to the particles occurs by convection and no temperature gradients occur within the particles.

The apparent high temperature activation energies found for PETN and nitroglycerine are 16.4±0.6 and 27.3±1.0 kcal/mole, respectively. These values are significantly less than the published low temperature values 39–52 and 36–50 kcal/mole, which suggests that here high temperature ignitions are preceded by phase changes. Shock tests with PETN give ignition in air (but not in nitrogen) at 990°K after 430 microseconds. This confirms published observations with PETN and nitroglycerine showing a chemical dependence on the gas.

For lead azide, an activation energy of 61±11 kcal/mole is obtained, which is in statistical agreement with the published value of 50 kcal/mole in low temperature kinetic studies. This observation in addition to the noted absence of the effects of pressure (1 atm, 0.5 atm) and gas composition (oxygen, nitrogen, air) suggest that ignition at high temperatures is by the condensed phase mechanism.

It is considered that the process of ignition in impact tests can be simulated in shock tube tests. The explosion time in an impact test is typically about 250 microseconds. Hence the reflected shock temperature at this time delay, T_{250}(°K), which produces explosion should be significant in impact sensitivity.

An analysis of adiabatic gas compression of bubble hot spots produced in an impact tester leads to the following simplified equation:

$$T_{250} - T_0 = Ch^M,$$

where T is temperature (°K), the subscripts 0 and 250 refer to delay time (microseconds), h is the drop height (cm), and C and M are constants. For a series of six different explosives (including PETN, hydrazine nitrate, and lead azide) the shock tube sensitivity, defined as $(T_{250} - T_0)$, correlates well with the impact sensitivity h. In this empirical application (adiabatic compression does not occur in these tests) M has the value of 0.34±0.07. The calculated adiabatic compression ignition temperature for the "hot-spot" bubble for nitroglycerine, lead azide, and PETN in air are 800°, 900°, and 1500°C, respectively. The corresponding values of T_{250} are 480°, 550°, and 800°C.

The shock tube measurement of explosive sensitivity possesses two important advantages: good control necessitating few tests to characterize an explosive, and the requirement of only milligram quantities for a test.

Subject Headings: *Ignition, by shock; Shock ignition, explosives, ignition by shock.*

G. A. Agoston

Kinbara, T. (Sophia University, Tokyo, Japan) and **Kawasaki, A.** (Police Headquarters, Yokama, Japan) "Spontaneous Ignition of Wooden Materials Heated for a Long Time at a Low Temperature," *Bulletin of Fire Prevention Society of Japan* **16,** 9 (1967)

It has been reported at times that fires broke out by the spontaneous ignition of wooden materials contacting for a long time with steam pipes of room-heater. From this, experiments on the spontaneous ignition of a large sawdust ball put into a room of constant temperature was carried out in order to study (1) if the ball, when large enough, ignites spontaneously at a temperature as low as 100°C, and (2) why the temperature rise is so slow that it takes more than 100 hours before ignition occurs.

It has been theoretically well known that whether the temperature of the ball of radius r rises beyond the ambient temperature T_a and catches fire or the temperature rise stops at T_a depends upon the value of a discriminant. This discriminant δ is defined as

$$\delta = (A/k)r^2(E/RT_a^2)\exp(-E/RT_a),$$

where A = the rate of heat generation per unit volume of sawdust when T_a is supposed infinitely high $= 1.46 \times 10^9$ cal/cm^3 sec; E = activation energy = 26.1 kcal/mole; R = gas constant = 2.0 cal/°K; k = conductivity of sawdust $= 1.4 \times 10^{-4}$ cal/cm sec °C. The condition for spontaneous ignition is $\delta > 3.32$ and the larger the radius, the lower is T_a.

The theory has been verified experimentally by many authors, but they have dealt with comparatively small balls which ignite above 180°C. The experiments of the present authors were carried out with a ball of 50 cm diameter. The results showed that the critical temperature was 130°C, which coincides remarkably with the theory. From this it is expected that wooden materials, in favorable conditions, can ignite spontaneously at 100°C when they were piled in a large amount corresponding to a sphere of 80 cm radius.

The time needed for the beginning of ignition sometimes exceeds 240 hours. A thermocouple inserted in the center showed that the temperature was kept at a constant value of 65°C for the most part of this long period. The existence of this stationary state was clarified theoretically with the following assumptions:

(1) Pieces of sawdust contain water and supply vapor to the space between them.

(2) The vapor diffuses through the sawdust with a diffusion coefficient which is ϵ times as large as that through the open air ($=0.25$ cm^2/sec).

(3) In the innermost parts, the vapor is saturated, while on the surface, the vapor pressure is equal to that of outside.

It was revealed that when $\epsilon = 0.5$ the temperature in the innermost parts keeps constant at 65°C, so long as water is contained in the pieces. The theory is applicable to a small ball of 5 cm radius. The stationary temperature is 75°C, which compares with the experimental value.

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

Tosira Kinbara

Slack, C. and Woodhead, D. W. "Correlation of Ignitabilities of Gases and Vapours by a Break Spark and at a Flange Gap," *Proceedings of the Institution of Electrical Engineers* **113**, 297–301 (1966)*

The object of the study was to investigate a possible correlation between the relative ignitabilities of gases and vapours by electric break sparks and at gaps between the flanges of equipment enclosures, and to assess whether the scope of British Standards B.S. 229 (Flameproof enclosure of electrical apparatus) and B.S. 1259 (Intrinsically safe electrical apparatus and circuits) could, in consequence, be extended. Comparisons were therefore made between the minimum igniting currents (M.I.C.) as determined under standardized conditions for the purpose of B.S. 1259, and both the maximum experimental safe gaps (M.E.S.G.) and the statistical maximum safe gaps (S.M.S.G.), as similarly determined for the purpose of B.S. 229. The data used were those for the 25 compounds for which determinations both of M.I.C. and M.E.S.G. had been made, covering the whole range, in ease of ignitability, from acetylene to ammonia. It was found that the relations of both M.E.S.G. and S.M.S.G. with log (M.I.C.) were linear over the range, with highly significant correlation coefficients. An earlier version of this paper was published as E.R.A. Technical Report No. 5042 (see the Annual Report for 1964, p. 67).

Subject Headings: *Ignition, by sparks; Spark ignition.*

Walker, I. K. and Harrison, W. J. (Department of Scientific and Industrial Research, Wellington, New Zealand) "The Exothermic Gaseous Oxidation of Scoured Wool," *New Zealand Journal of Science* **8**, 106–121 (1965)

Because of the widespread disagreement about the reaction of clean, dry wool in an atmosphere of oxygen (or air) at somewhat elevated temperatures, the work reported in this paper was performed. Apparently spontaneous ignition has occurred numerous times in contaminated wool stored for commercial use because of an exothermic reaction with atmospheric oxygen. This work sets out to measure the rate of heat generation of dry wool in gaseous oxygen at temperatures between 90°C and 150°C, using a calorimeter. Pure oxygen was chosen for these experiments to avoid complications due to rate limiting diffusion in the gas phase, or changes of oxygen partial pressure by consumption of oxygen.

Spherical glass flasks of different sizes were used. Water thermostats were employed up to 99°C, and the remaining temperature was covered with a bath of monoethylene glycol. In addition, a cylindrical stainless steel reaction vessel was employed. The two high temperature thermostats were controlled to within 0.05 degrees. In these experiments the wool samples were dried at 120°C in a stream of dry nitrogen. Most of the experiments were performed with a sample of crossbred wool, sheared and scoured commercially about two years previously, and then stored at normal air temperatures.

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* Abstract issued by Safety in Mines Research Establishment, Sheffield, England. Reprinted by permission.

Results are presented in tabular form for peak temperature differences measured between the center and the perimeter of the calorimeter vessels. The volumes and shapes of the vessels are also listed. A second experiment involved the same wool, only this time the sample extracted first with diethyl ether and then with ethyl alcohol. These results are recorded in a second table. Data are shown in a graph for the effect of vessel size on central temperature change, and also for the thermostat temperature effect on the central temperature.

In a rather lengthy discussion, the authors make several attempts to derive a suitable expression for reaction rate of the wool. Reaction rates of scoured wool and of solvent-extracted wool appear to be very similar when plotted against temperature. Conclusions drawn from this study are:

(1) Dry oxygen will react exothermally with the keratin of scoured wool.

(2) For the samples examined, a simple mathematical relationship specifies the rate of heat generation due to reaction between wool and oxygen at temperatures between 90°C and 150°C, at times between 1 hr and 200 hr.

(3) The rate of heat generation is not influenced by fiber diameter of the wool, within the normal commercial range.

Subject Headings: ***Ignition, spontaneous, of wool; Oxidation, of wool; Spontaneous ignition, of wool; Wool, spontaneous ignition of; Wool, oxidation of.***

C. O'Neal, Jr.

II. Thermal Decomposition

Broido, A., Houminer, Y., and Patai, S. (The Hebrew University, Jerusalem, Israel) "Pyrolytic Reactions of Carbohydrates. Part 1. Mutarotation of Molten D-Glucose," *Journal of The Chemical Society, Section B. Physical Organic Chemistry*, Issue No. 5, 411–414 (1966)

The mutarotation of D-glucose in neat samples in the presence of water and of two catalysts was investigated under conditions of little or no intrusion of other reactions. Glucose, perhaps the most widely occurring sugar in nature, either alone or as a basic unit of polysaccharides, on pyrolysis probably yields several decomposition products that are similar or identical to those from the oligo- and polysaccharides derived from it. Hence the choice of D-glucose as a model substance for such practical problems as the decomposition of cellulose in wood, which probably is important in the spread of forest fires, seems justified.

The materials used were α-D-glucose (B.D.H., AnalaR), melting 146°C $[\alpha]_D^{20}$ (in water) $+110.9° \rightarrow +52.5°$ and β-D-glucose (Nutritional Biochemical Co.), melting 150°C $[\alpha]_D^{20} +20.3°C \rightarrow +52.4°$. The α-form contained 0.17% and the β-form 0.15% water. Two-gram samples of α- or β-D-glucose, after preheating (without change) at 135°–140°C in open pyrex tubes in an oven for 15 minutes, were heated at 151°C in an oil-bath for predetermined times, cooled and weighed. Other runs were made at various temperatures around the melting point of glucose; some experiments were made with α-D-glucose containing water, sodium hydrogen carbonate, or boric acid. Specific optical rotation in 0.4 to 0.6 g/ml aqueous solutions was measured at zero time (extrapolated from linear plots of α versus time), $[\alpha]_{D,neat}$, and again 24 hours after dissolving, $[\alpha]_{D,equil.}$. Trimethylsilyl derivatives of the anomers were prepared for gas-liquid chromatographic analysis. Infrared spectra were determined in Nujol.

At 140°C α-D-glucose (still unmelted) showed no immediate and little subsequent change in rotation, less than 0.5% weight loss, and an α/β ratio by gas-liquid chromatography of 4.17, in agreement with the experimental $[\alpha]_{D,neat}$ value. At 151°C samples melted after 2 minutes and turned yellow, then brown in about 2 hours (weight loss about 0.5%). Values of $[\alpha]_{D,neat}$ for the α- and β-forms drew together at about 57°C after about 30 minutes of heating and then declined slightly on further heating; values of $[\alpha]_{D,equil.}$ declined only slightly from the initial 52.5°. Gas-liquid chromatography revealed that the ratio of the two anomers, whether starting from the α- or from the β-anomer, reached 0.802±1 or 2 after 90 minutes, when the total D-glucose ($\alpha+\beta$) remaining was 68% or more. At 165°C α-D-glucose melted in about 1 minute, mutarotation was practically complete after 10 minutes, and the color became yellowish brown with about 0.4% weight loss after 30 minutes. Some decomposition was indicated by $[\alpha]_{D,equil.}$ of 52.5°, 52.5°, 51.8°, and 47.5° at 0, 10, 15, and 30 minutes, respectively.

Infrared spectra of molten equilibrium mixtures were practically identical with spectra of mixtures of the two pure anomers made in the appropriate proportions. The spectra gave additional evidence for the equilibration process but did not exclude the presence of small amounts of 1,6-anhydro-β-D-glucopyranose or of disaccharides.

When 10% of water by weight was added to α-D-glucose the sample melted at 149°C in less than 1 minute and equilibrium in mutarotation was reached in about 10 minutes. Weight loss after 2 hours was about 5.5%, showing that at least 4.5% of water remained in the material. Samples of α-D-glucose were heated at 130°C for 15 minutes in the presence of different amounts of sodium hydrogen carbonate and of boric acid, which did not alter the equilibrium specific optical rotation of the unheated glucose in aqueous solution. In the heated samples both additives strongly catalyzed the mutarotation but boric acid did not catalyze side-reactions whereas the sodium salt did so, strongly.

The results show that, under the conditions used, mutarotation is practically complete before other reactions occur appreciably. The α/β equilibrium is reached in about 15 minutes at 151°C, in about 10 minutes at 165°C while most of the sample is still glucose. Either anomer or any mixture of them may be used to study thermal reactions of glucose at higher temperatures; the same may be true of other sugars. Water enhances mutarotation rates by hastening melting rather than by catalysis.

Proton transfer between two glucose molecules perhaps occurs by loss of the proton of the anomeric hydroxyl group (0–1, the most acidic site of the molecule) and its attachment to the other oxygen (0–5, the most basic site) in a second glucose molecule. The increased ease of anomerization of the 0–5-protonated and the 0–1 deprotonated intermediate is well documented. Other protonated forms may be possible but only the 0–5-protonated form may undergo faster ring-opening than glucopyranose itself. Since mutarotation rates do not change drastically on addition of an equimolecular amount of water it seems that the protonating ability of molten glucose does not differ much from that of water.

The opinion is expressed that mutarotation can occur, at least in part, in the solid state.

Subject Headings: *Carbohydrates, pyrolysis of; Glucose, mutarotation of; Mutarotation, of glucose; Pyrolysis, of carbohydrates.*

F. L. Browne

Fenimore, C. P. and Martin, F. J. (General Electric Research Laboratory, Schenectady, New York) "Flammability of Polymers," *Combustion and Flame* **10,** 135–139 (1966)

The flammability of polymers was measured by determining the oxygen index n (fractional oxygen content) of the atmospheres just capable of burning them. A strip of polymer was suspended in a tube 8.4 cm in diameter, through which flowed upward at atmospheric pressure a metered mixture of air ($n=0.21$) with nitrogen (for $n<0.21$) or with oxygen (for $n>0.21$). The polymer strip was ignited at its upper end and the atmosphere found in which the sample just burned for its entire length. A few tests at reduced pressure were made in a bell jar. Polymers that burned without residue (polyethylene) had steady flames that grew smaller until they extinguished when the oxygen present was just insufficient. Silica-filled silicones gave no flame but a zone of glowing silica worked through the specimen or ceased at extinction. Polymers that charred as they burned (polycarbonates) seemed to smother their flames in char. Some polymers of relatively low molecular weight melted too easily and abstracted more heat from the surrounding diffusion flame than was needed to pyrolyze the polymer, which led to unduly high n. Excessive melting was avoided by using polymers of high molecular weight.

Some values of n reported are: polyoxymethylene 0.148 (at 14 cm Hg pressure 0.190); polyethylene oxide 0.150; kitchen candle 0.16; polymethylmethacrylate 0.173; polypropylene 0.174; polyethylene 0.175 (at 14 cm Hg pressure 0.210); polystyrene 0.183; polybutadiene crosslinked with dicumyl peroxide 0.183; polyvinyl alcohol 0.225; chlorinated polyether 0.232; polycarbonates 0.26 to 0.28; polyphenylene oxide 0.28 to 0.29; graphite (carbon electrode) 0.635 (at 50 cm Hg pressure 0.80, at 24 cm Hg 1.00). Also: "Slow-burning" asbestos-filled polypropylene 0.205; "self-extinguishing" polypropylene (probably contained chlorine and antimony trioxide) 0.282; silica-filled silicone rubber 0.326 (at 14 cm Hg pressure 0.391).

Three commonly used agents for reducing flammability were compared in polyethylene. (A) Admixture of antimony trioxide had negligible inhibitory effect unless the polyethylene was halogenated sufficiently. Maximum effect required about 0.01 antimony atoms per C_2 group in the polyethylene and developed just as well when the chlorine/antimony ratio was 6 as when the ratio was 20. The largest n obtainable with halogen and antimony trioxide was 0.26. Arsenic trioxide, bismuth trioxide, stannic oxide, and lead monoxide were less inhibitive with chlorinated polyethylene than antimony trioxide. (B) Various phosphorus compounds, tricresyl phosphate, triphenyl phosphate, triphenyl phosphite, triphenyl phosphine, phosphonitrilic chloride, were of similar effectiveness per atom of phosphorus added to polyethylene and were less effective than method A. (C) Sufficient substitution of halogen for hydrogen in polyethylene proved more inhibitive than either method A or method B. In the series $\{CH_2CHX\}$ the value of *n* increased as X changed from H to C_6H_5, to OH, or to a halogen. Thus *n* was for polyvinyl fluoride 0.225, for polyvinylidene fluoride 0.44, for Teflon 0.95; and *n* was for chlorinated polyethylene 0.32, for polyvinyl chloride 0.455, for polyvinylidene chloride (Saran) 0.60. Evidently substitution of halogen for hydrogen in polyethylene works mostly by affecting the pyrolysis of the polymer rather than by interfering with gas phase flame reactions because burning polyethylene in atmospheres containing chlorine or hydrogen chloride raised *n* very little.

The oxygen index, *n*, is a useful measure of polymer flammability. Plastics may be "self-extinguishing" if *n* is as small as 0.26 to 0.28 and "slow-burning" if *n* is as large as 0.225.

Subject Headings: *Flammability, of polymers; Polymers, flammability of.*

F. L. Browne

Fenimore, C. P. and Jones, G. W. (General Electric Research and Development Center, Schenectady, New York) "Modes of Inhibiting Polymer Flammability," *Combustion and Flame* **10**, 295–301 (1966)

Within a bell jar, kept at 5 cm Hg pressure and provided with a laminar flow of a mixture of argon with 20% oxygen, a 0.36 cm^2 cross section rod of polymer was mounted vertically on a shaft that could be raised as the polymer burned from its top in order to control the distance between the burning tip and either a fine quartz-coated thermocouple or a quartz probe to sample the gaseous products, which were analyzed spectroscopically.

Polymethylmethacrylate, polyoxymethylene, and probably polyethylene did not react with the gas but merely vaporized in the heat of the surrounding diffusion flames. Then the vaporized products burned in the gas phase.

At 0.1 cm above the burning tip of polymethylmethacrylate 70% of the carbon in the gas was present as monomer, closer to the tip even more. To depolymerize polymethylmethacrylate and heat the product to the surface temperature of the burning tip (850°K) required about 38 kcal per monomer unit. From the limiting temperature gradient measured and the conductivity of the gas a heat supply of 30 kcal per monomer unit burned was calculated which is in reasonable agreement. For polyoxymethylene, the calculated heat input was about 15 kcal and that theoretically expected was 17 kcal per monomer unit for a temperature of 750°K at the burning tip. For polyethylene the composition of the primary products was uncertain. The heat input was about 20 kcal per monomer unit and the temperature at the burning tip 900°K.

Teflon (polytetrafluoroethylene) had to be burned at atmospheric pressure in 95% oxygen. Oxygen was present in samples collected as near the burning surface as possible. The initial products consisted of CO, CF_4, and somewhat less COF_2. Thus burning Teflon probably gasifies by reacting directly with oxygen.

Burning could be inhibited in polymers that gasify by depolymerization either by making the input of heat insufficient or by poisoning the flames.

Substitution of chlorine in polyethylene inhibits by altering the pyrolysis because the nature of the hydrocarbons close to the burning tip is altered greatly, although no chlorinated hydrocarbons appear. Equivalent additions of chlorine or hydrogen chloride to the gas phase fails to inhibit burning of polyethylene, and chlorination inhibits burning in nitrous oxide as well as in oxygen. But bromination of polyethylene is even more effective than chlorination because bromine both alters the pyrolysis and poisons the flame.

Phosphate esters probably inhibit by flame poisoning because they are similarly effective for polymers of different structures and phosphorus appears in the vapors from inhibited specimens.

Antimony trioxide in conjunction with chlorine inhibits by flame poisoning. The burning of chlorinated polyethylene in oxygen is inhibited, but the burning in nitrous oxide is not. The gas above burning specimens has the same composition whether or not antimony is present. When antimony inhibits, much antimony vaporizes, but little vaporizes when it does not inhibit.

Subject Headings: ***Flammability, inhibition in polymers; Inhibition, of flammability, in polymers; Polymers, inhibition of flammability in.***

F. L. Browne

Gregory, D. R. and Littlejohn, R. F. (The British Coal Utilisation Research Association, Surrey, England) "A Survey of Numerical Data on the Thermal Decomposition of Coal," *The British Coal Utilisation Research Association Monthly Bulletin XXIX*, *Review 244*, 173–180 (1965)

This is a review of the stoichiometry and kinetics of the thermal decomposition of coal, with 88 references covering the period 1926–1964.

Subject Headings: ***Coal, thermal decomposition of; Pyrolysis, of coal; Thermal decomposition, of coal.***

R. M. Fristrom

Gugan, K. (Imperial College, London, England) "Natural Smoulder in Cigarettes," *Combustion and Flame* **10**, 161–164 (1966)

The author refers to earlier work[1] which gives results of the influence of puffing parameters on the temperature attained, and the volumes consumed in cigarettes. The present work on natural smoulder is complementary to the above and it reveals that, after an initial (unsteady-state) period, the rate of smoulder becomes constant with time and position.

A theoretical treatment is presented, based on the supposition that the mass rate of consumption must be proportional to the rate of oxygen supply. This supply of oxygen is caused by diffusion and by natural convection. By employing simplifying assumptions, viz., that the burning zone is axially symmetrical, that ash provides a porous sheath about the reaction zone of the same superficial dimensions as those of the cigarette, that gas-phase mass transfer occurs by molecular diffusion, and that the oxygen concentration at the combustion surface is zero, the combustion zone profile is predicted and compared with an actual profile. Fair agreement between the two is obtained. Three sizes of cigarettes were available and volumetric rates of consumption are presented in the interval between puffs and in cigarettes allowed to smoulder without puffing. Rather surprisingly the rates of smoulder are found to be lower between puffs. The reason is that "choking," i.e., the swelling of tobacco filaments on heating and reduction in flow area by condensing tars, occurs at the periphery during the puff by the action of hot product gases on the previously unpyrolized tobacco. This results in a fall in combustion rate due to the air bypassing the combustion zone (by virtue of the porosity of cigarette paper). During the smoulder periods between puffs it is not tobacco of normal consistency or density of packing that is being burnt, but a material of fairly high calorific value, closely packed.

To calculate the combustion temperature in the absence of forced convection, experiments on the heat of combustion of tobacco and on air/tobacco stoichiometry in a bomb calorimeter were performed. These have yielded values of 3760 cal/g and 7.5 g of air required to burn 1 g of tobacco, respectively.

A knowledge of these values enabled the author to calculate the steady-state temperature of combustion (assuming values for the various specific heats), i.e., the smouldering zone temperature. Two calculated temperatures 1200° and 820°C represent the extreme values between which normal smouldering temperature lie. The former corresponds to the radiating area being zero and the latter to the case where all the ash has been removed and the radiating area is taken as that of a whole cone, of height equal to that of the combustion surface, standing on the same base. Experiments indicate that the temperatures lie much closer to the second value, despite the undisturbed layer of ash.

Comparison between the values of stoichiometry for cigarettes during the puff and during natural smoulder indicates that some 90% of tobacco combustibles evade combustion during the puff. This is so since much of the tobacco is distilled ahead of the combustion zone by the hot gases drawn through it in the puff. With truly natural smoulder there is little or no distillation of the volatiles.

Reference

1. Egerton, Sir A. C., Gugan, K., and Weinberg, F. J.: Combustion and Flame 7, 63 (1963).

Subject Headings: ***Cigarette smoulder; Smoulder, of cigarettes.***

R. Long

Keylwerth, R. and Christoph, N. (German Society for Wood Research) "Basic Investigations Concerning the Thermal Decomposition and Ignition of Wood," *Mitt. Deut. Ges. Holzforsch* **50,** 125–137 (1963) In German.

Studies of the ignition of both unprotected and fire-retardant treated woods in a physically well-defined laboratory test which can be translated into a meaningful reproducible routine test for vastly enlarged scales of observation is inherently difficult to achieve. Pilot studies must eventually define the course of test procedures under routine conditions.

Ignition of wood proceeds rapidly after a net rate of heat input has occurred. Of importance is the time rate of heat input. The material subjected to this treatment must be environmentally and physically reproducible if known amounts of heat are injected.

A new thermogravimetric experiment has been designed to import very precisely a known quantity of electrical heat into a wood sample. Resistance wire is inserted into the wood and a measure made of surface temperature and peak local temperature around the wire. Calibration is achieved by imparting an identical electrical pulse into each sample. Thus all differences in dimension or density of each sample can be taken care of initially. A sample is then subjected to a stepwise impulse of electrical energy. A plot is made of temperature of surface versus a time scale showing the variations of temperature of surface after each sharp impulse. Several woods of different density were subjected to this treatment in an effort to obtain a crude differential thermal analysis for each material as a function of the rate of electrical energy input. The evaluation of this thermo-electrical calibration is not complete. A distinction can be detected when comparing treated and untreated wood.

Simple kinetic analysis of the wood burning experiments is not possible. The energies of activation for individual degradations are not in conformity with the over-all general case. It is necessary to obtain disintegration rates under isothermal conditions.

Gas analysis of the products of the thermal degradation of wood has been developed around a dynamic pyrolysis-gas chromatographic technique. A piece of wood was cut into thin slivers by a microtome. The advantage of thin slivers is the possibility of rapid escape of evolving gases and their short time presence in the vicinity of the heated wood. Thus little secondary heterogeneous reaction can occur between the evolved gases and their originator, the hot wood. Oak wood has been treated in this pyrolytic-analytic apparatus. Correlation of type and quantity of gas evolvement with fire-retardant and nontreated oak has been attempted.

A uniform testing procedure is required to permit different laboratories to design an apparatus at low cost with some assurance that the tests are conducted in a reasonably reliable and reproducible manner. The immediate need is to test woods that have been subjected to new fire-retardants and to measure the influence these exert upon the panoply of gases evolved under ignition conditions.

Subject Headings: ***Pyrolysis, of wood; Thermal decomposition, of wood; Wood, pyrolysis of; Ignition, of wood.***

P. Breisacher

Rakowsky, F. W. and Meguerian, G. H. (American Oil Company, Whiting, Indiana) "Precombustion Deposits," *Combustion and Flame* **10,** 182–187 (1966)

According to references quoted, precombustion deposits on burner walls resulting at or near cool flame temperatures (ca 400°C) from hydrocarbon pyrolysis and oxidation exhibit substantially higher molecular weight than the original ingredients. Their formation probably proceeds by a free-radical mechanism. Acetylene and aromatics have been suggested as key intermediates because low hydrogen content enhances carbon to carbon bonding. There are indications that acetylene is not always involved. Evidence for specific activity of benzene has been obtained by Fenimore, Jones, and Moore.[1] Formation of benzene from acetylene was suspected by Gordon, Smith, and McNesby.[2] Van der Held[3] has discussed cracking followed by polymerization.

In the present work, further information was sought by studying deposits at nearly cool flame temperature from pairs of one paraffin and one aromatic compound mixed in varying concentration with nitrogen or air. Combinations were chosen from the following list: *n*-hexane, *n*-actane, *n*-decane, *n*-dodecane, *n*-hexadecane; benzene, toluene, ethylbenzene, cumene, *p*-xylene, mesitylene, 1-methylnaphtalene.

After percolation through silica gel and vaporization, mixtures entered the top of the reactor, a vertical 43 cm long Vycor tube, of 30 mm o.d., in the mid-point of which 10 grams of 4 mm Pyrex glass balls rested on a 18-mesh stainless-steel screen. Wall temperature of the surrounding electric furnace was kept at 400°C from top to bottom. A centrally located thermocouple below the screen measured temperature rises (up to 475°C) due to exothermic reactions, presumably in the gas phase. In all runs a feeding rate of 800 cm^3/min was maintained. The build-up of deposits was followed by weighing them at intervals over periods of hours. Oxygen consumption was determined by chromatographic analysis of exhaust gas.

Experimental Results

1) No deposits from N_2-carried hydrocarbons.
2) With air, practically no deposits either from pure paraffins or from pure aromatic compounds.
3) From mixed paraffin and aromatic compounds, a flat maximum deposit builds up with increasing paraffin concentration.
4) No evidence for involvement of acetylene.
5) Deposit composition changes little with aromatic concentration, the C/H ratio being of the order of twice that of the original.
6) Maximum deposited quantity increases with molecular weight of aromatic compound.
7) Paraffin concentration required for maximum decreases with increase of chain length,
8) but increases with number of α-hydrogens in aromatic compound.
9) Tary carbonaceous material is deposited on walls of exhaust tract.
10) Rate of deposition is described as being influenced by radical absorbent surface, although no distinction between glass and stainless steel is mentioned. A rapid initial weight increase during which the (glass) surface is sparsely covered is followed after less than one hour by a slower but steadily

growing rate which turns out to be proportional to the quantity already deposited: $dD/dt = kD$, where D = weight of deposit at time t, k = a constant factor.

Regarding (10), an explanation is missing. However, most likely, a mechanism involving two-dimensional diffusion of adsorbed molecules[4] accounts for the reported features of the phenomena. This implies that the molecules impinging from the gas phase are only weakly adsorbed on the free glass surface from which they are reflected or soon re-evaporate. The rapid initial deposition corresponds to capillary condensation in the interstices of adjacent Pyrex balls. From the circular meniscus areas, coverage spreads beginning with monolayers of thickness δ. Adsorption on the film surface is much stronger than on glass. Film-adsorbed molecules diffuse towards the film edge, where a fraction f condenses, while the surplus transits to the glass surface. During this period the increase in volume V per unit time is: $dV/dt = k\delta A$, with A = film area at time t. Meanwhile, two-dimensional nucleation[5] leads to the build-up of a second monolayer. At first, its spreading proceeds faster than that of the primary layer, because every secondary film-patch is bilaterally supplied with condensing molecules, i.e., from the top surface and from that of the substrate. Therefore, the edge of a multilayer forms a relatively steep stair. Each of its steps is growing at the same rate as the first layer, provided that f remains constant and much smaller than 1. Hence: the observed growth law. It certainly governs in general the growth of flake-shaped precipitates from the gas phase and also soot particles in flames.

A more elaborate discussion will be published elsewhere.

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4. Volmer, M. and Estermann, I.: "The Mechanism of Molecule Separation in Crystals," Zerts. Physik *7*(1) 13–17 (1921).
5. Volmer, M.: *Kinetik der Phasenbildung*, p. 100 and p. 120, Edwards Brothers, Inc., Ann Arbor, Michigan, 1945.

Subject Headings: ***Deposits, from precombustion reactions; Hydrocarbons, pyrolysis of; Precombustion deposits; Pyrolysis, of hydrocarbons.***

H. M. Cassel

Weatherford, W. D., Jr. and Valtierra, M. L. (Southwest Research Institute, San Antonio, Texas) "Piloted Ignition of Convection-Heated Cellulose Slabs," *Combustion and Flame* **10**, 279–286 (1966)

The ignition of cellulose slabs in the continued presence of both ignition and heat sources has been studied. The slabs were 0.1, 0.3, 1.0, and 3.0 cm thick and of densities 0.2, 0.5, and 0.8 g/cm³. The areas exposed to thermal sources were 15×12 cm. The specimen history was carefully reproduced through identical storage, air exposure time, and humidity control. Air-flow rate was 5 cm/sec and temperatures employed were 127°, 182°, and 237°C with corresponding heat fluxes of 0.06, 0.08, and 0.10 cal/cm^2 sec. These conditions applied to symmetrical heating. The unsymmetrical heating experiment was conducted at 237°C.

The slabs were gold-coated uniformly. About 67% of the incident thermal radiation was transferred to the cellulose. Care was taken to maintain constant emissivities by frequent recoating and cleaning between runs. An auxiliary imbedded electric heater was placed behind the steel plate to assure constant initial surface temperatures.

Time-to-ignition data showed that small changes in bulk density or slab thickness greatly influence the ignition time. It was impossible to obtain a reasonable straight-line plot of ignition time versus thickness or density. Attempts to correlate Nusselt number and Fourier number at ignition times for various densities and thicknesses of slab led to scattered data.

The source temperature was influential in determining the ignition time of all samples. Constant density appeared to correlate well with a calculated uniform fuel-generation rate per unit surface area. Similar criteria can be applied to sample thickness. A fixed flow rate of air will result in a constant fuel-generation rate using one particular heat source. The concentration of fuel in air will be sufficient to support ignition at the ignition time. One-sided heating results in ignition thresholds that are lower in the surface temperature of ignition. Ignition times are longer due to excessive heat loss at the unheated surface. Despite this it is assumed that the relaxed temperatures of the samples subjected to unsymmetrical heating will be as high as symmetrically heated samples. The fuel-generation rate for very thin samples of low density under unsymmetrical or one-sided heating will then be somewhat depleted when ignition finally does occur. Results show many such thin samples would char or disintegrate instead of flame at the ignition point.

Subject Headings: ***Cellulose, ignition of; Convection, heating and ignition; Flame, ignition of cellulose; Ignition, by pilot flames.***

P. Breisacher

III. Heat and Material Transfer

Tyler, B. J. (Manchester College of Science and Technology, Manchester, England) "An Experimental Investigation of Conductive and Convective Heat Transfer during Exothermic Gas Phase Reactions," *Combustion and Flame* **10,** 90–91 (1966). Letter to the Editor.

Current thermal ignition theories do not account for the influence of convection; thermal conduction is, however, incorporated in the theories. To use the theoretical predictions the question of existence of thermal convection must be answered. A criteria for onset of convection is the Rayleigh number.* Frank-Kamenetskii suggests a value of 10^4 for the critical R.

* $R = g\alpha C_p\rho^2\Delta T a^3/k\eta$ where g is the acceleration due to gravity; α the coefficient of expansion; C_p is specific heat capacity; ρ the density; ΔT a characteristic temperature difference; a the vessel radius; k the thermal conductivity; and η the viscosity coefficient.

Experiments were conducted using the reaction of NO with O_2 and covering a wide range of R. The Rayleigh number was varied by changing density and by using gas mixtures to vary k and η. Spherical reaction vessels were used, and temperatures along a vertical diameter were measured by thermocouples.

The data indicate that the critical value of R should be about 600, which is considerably less than 10^4. This critical value should apply to all gaseous systems, be temperature independent, and be relatively insensitive to vessel shape.

The author states that in testing thermal ignition theory the possibility of convection must be excluded. It would seem that thermal convection is an important phenomenon and that the theories should be extended to include this facet.

Subject Headings: ***Conductive heat transfer; Convective heat transfer; Heat transfer, conductive and convective; Ignition theory, effect of thermal convection on.***

A. E. Fuhs

IV. Diffusion Flames

Garside, J. E. (University of Leeds, Leeds, England) "The Combustion of Methane in Diffusion Flames," *Institute of Gas Engineers Journal* **6**, 357–361 and Discussion 362–364 (1966)

This paper is concerned with the utilization of methane for currently existing appliances in England. Although no particular problems exist with burning methane per se, a problem does exist in attempting to do so with the currently existing diffusion burners rather than with an aerated (premixed) burner. Diffusion type flames offer advantages over premixed flames with respect to appearance, compactness, silent operation, and stability as well as ease of maintenance. Information about methane diffusion flames is needed in order to decide whether it will be possible to modify the design of existing burners or to design new burners that will function satisfactorily on methane and similar gases.

The problems associated with methane diffusion flames are discussed and the approach currently being pursued by the University of Leeds is presented. Basically, the difficulty stems from the fact that methane does not produce a stable diffusion flame but rather flames of fluctuating shape and decreased stability. The lower burning velocity and narrower flammability range of methane compared to town gas promote greater instability so that the flames lift from the burner (Bray jet) more readily, while the higher calorific value and greater air requirement of methane influence the flame shape and its sooting propensity. Preliminary observations presented in this paper indicate that the principal factor that causes town gas to burn satisfactorily on Bray jets (whereas methane does not) is the occurrence of reverse air flow (inside the orifice) with the former gas. In the discussion following the paper, disagreement was voiced regarding the validity of the previous statement. The need for further measurements was indicated.

In their fundamental approach to the problem, as compared to the industrial approach, the University of Leeds proposes to study the details of the methane diffusion flame including such phenomena as flame location relative to gas velocity, mixture composition, and temperature. These data will hopefully provide data for the design and manufacture of burners which will allow the diffusion burners to be retained irrespective of the type of distributed gas. Comments made on the presentation showed a wide interest in the problem as well as a fair degree of skepticism regarding the success of a fundamental research study yielding useful design data. The feeling of burner designers and manufacturers appears to be that the empirical approach will yield a successful methane jet design.

Subject Headings: ***Burners, diffusion, for methane; Diffusion burners, for methane; Methane, diffusion burners for.***

L. A. Povinelli

Gordeev, V. E., Komov, V. F., and Troshin, Ya. K. (Institute of Chemical Physics, Academy of Sciences, USSR) "On Detonation Combustion of Heterogeneous Systems," *Doklady Akademii Nauk SSSR* **160**, 853–856 (1965)

The detonation of combustible (oil) films in tubes filled with gaseous oxidizer (air) was studied over a wide variety of conditions. The tube was stainless steel, 22 mm diam and 1.6 m long. It was found that for strong initiation (detonation exploding wire, or strong spark) transition to detonation always occurred providing the oil film thickness exceeded a minimum value of about 32 microns. This corresponded to a loading of 28 g/m^2. If the initiation was a detonation wave of comparable strength to steady state, minimum initiation conditions were reduced an order of magnitude to a film about 2 microns, and loading of 2 g/m^2. These latter conditions corresponded to stoichiometric composition assuming the initially heterogeneous system to be completely mixed.

Subject Headings: ***Detonations, heterogeneous; Films, detonation of; Heterogeneous detonations; Oil films, detonation of.***

R. M. Fristrom

Kirkby, L. L.* and Schmitz, R. A. (University of Illinois, Urbana, Illinois) "An Analytical Study of the Stability of a Laminar Diffusion Flame," *Combustion and Flame*, **10**, 205–220 (1966)

This paper is concerned with a set of numerical computations made in an effort to investigate the effects of Lewis number and heat losses on a laminar diffusion flame. In order to minimize computational difficulties, a simplified model is employed. Thus, the fuel is assumed to be fed into the combustion chamber through a semi-permeable membrane, impervious to oxygen and heat, and to mix with oxygen which diffuses from a gas stream flowing by the top of the chamber. A

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general second-order Arrhenius-type expression is used for the reaction rate and all gas properties are taken to be constant. In most cases, only variations in the fuel injection rate, Lewis number, and heat loss to the surroundings are considered.

Steady-state solutions are presented first, demonstrating the existence of three steady-state solutions, called the burning state, extinguished state, and intermediate state. In addition, it is shown that depending on initial conditions, it is possible to obtain either rich and lean, or only rich extinction limits. Extinction limits are presented for various Lewis numbers, at zero heat loss, and for various values of heat loss, at a Lewis number of unity.

A stability analysis, consisting of a perturbation from steady state, is used to investigate the stability of the various steady-state solutions. It is found that extinguished-state solutions are always stable and intermediate-state solutions are always unstable. However, although burning states have previously been assumed to be stable, it is found that these solutions may be unstable in non-adiabatic systems, or when the Lewis number exceeds unity. Hence, new extinction limit curves are presented and compared with the static extinction limit curves. Finally, the complete transient history of an unstable flame is obtained numerically and presented in graphical form.

Subject Headings: *Diffusion flame, stability of; Extinction, of diffusion flames; Stability, of diffusion flames.*

T. C. Adamson, Jr.

V. Combustion Principles

Adler, J. and Kennerley, J. A. (Imperial College, London, England) "Steady Laminar Flame Propagation with Conductive Heat Losses," *Combustion and Flame* **10**, 191–194 (1966) Letter to the Editor.

This letter consists of an examination and extension of the laminar flame propagation theory of Spalding[1] and Adler.[2] The work reported is complementary to that in Ref. 2, to which the reader must refer in order to properly evaluate (or understand) its significance. The theory under consideration is a one-dimensional model developed by Spalding for laminar flames with distributed conductive heat losses. Adler's subsequent treatment of the theory considers the effects of both upstream and downstream heat losses in the context of a thin-flame assumption, i.e., the single-step reaction representing the combustion process occurs only in a very small region. In the present work the authors attempt to develop an alternative solution for a "normal" (thick) flame and to compare the results thus obtained to those generated via the thin-flame approximation.

In both the present work and the thin-flame approach the conservation equations for chemical reactant and energy, including a term for conductive heat losses, are written, combined, and solved, subject to one of several possible boundary conditions. The results are exhibited in plots of a dimensionless heat-loss parameter, K versus an eigenvalue λ, directly related to the flame propagation velocity. In all cases, it is found that for all values of $K < K_c$, where K_c is a critical heat-loss value, there are two values of λ representing possible modes of steady flame propagation. When $K > K_c$, no solutions exist and flame propagation is impossible. The solutions for K_c are given in Ref. 2 in terms of two flame characterization parameters n and m, the temperature exponents in the expressions for reaction rate and heat loss, respectively. The values for m range from 1 to 5 depending on the mechanism of heat transfer: 1 represents pure conduction; 5, a condition in which radiation is dominant. The parameter n is related to the activation energy of the reactant-consuming chemical process; higher values of n inferring higher activation energy.

In the "normal" flame approximation described in this letter the assumed integrated reaction rate of the "thin-flame" model is replaced by an integral of the rate evaluated over the entire region in which reactant is present. The same activation energy-related n is employed as in Ref. 2 and downstream boundary conditions are assumed to be the same in both cases. The resultant plot of reduced temperature versus concentration, however, reveals a temperature-growth curve different than that assumed in the thin-flame model. If the concentration parameter in a reaction rate-concentration plot generated via this theory is replaced by temperature the function resembles the temperature-reaction rate curve of an adiabatic stoichiometric flame. Indeed, the entire solution reduces as it should, to the adiabatic case when the heat loss parameter K is reduced to zero.

The plots of λ versus K derived from this theory for flame with both upstream and downstream heat losses fall very close to those from the thin-flame theory with *either* upstream *or* downstream losses. Thus, if the heat losses from the thin flame are partially neglected a good approximation to a normal flame is obtained. However, in a real situation there is no way of knowing *a priori* how much to neglect or which of the omissions will be preferable. For a given value of λ, with both losses, K for the normal flame is about twice that of the thin flame. This implies that the critical value of the heat-loss parameter is a normal flame is also twice that for the thin flame. Notably the values of λ and τ (the dimensionless temperature) at the critical point are the same for two theories.

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2. Adler, J.: Combust. Flame *7*, 39 (1963).

Subject Headings: ***Conduction, losses in flame; Flame propagation, conduction losses.***

W. J. Miller

Affens, W. A. (U. S. Naval Research Laboratory, Washington, D. C.) "Flammability Properties of Hydrocarbon Fuels—Interrelations of Flammability Properties of *n*-Alkanes in Air," *Journal of Chemical and Engineering Data* **11**, 197–202 (1966)

By a systematic study of literature data, mathematical equations have been derived which describe the interrelationships of flammability and other related properties of the *n*-alkanes. The properties which have been correlated are: lower and upper flammability limits, flash point, vapor pressure (at the flash point), boiling point, stoichiometric concentration, heat of combustion, molecular weight, and carbon number. Good agreement was found between average literature data and values calculated by the derived equations. From a given flammability property, by use of the derived equations, it is possible to predict the other properties, as well as the relative magnitudes of changes in these properties as a result of a change in the given property.

Subject Headings: *Correlation of flammability, of hydrocarbons; Flammability, of hydrocarbons; Hydrocarbons, flammability.*

Author's Abstract

Campbell, E. S., Heinen, F. J.,* and Schalit, L. M.** (New York University, University Heights, New York) "A Theoretical Study of Flame Properties as a Function of the Characteristics of Flame Gases," *Royal Society Philosophical Transactions* 259. A.1101, 355–389 (1966)

This paper presents results of a continuation of Campbell's studies concerning the structures and burning rates of one-dimensional, adiabatic, laminar flames with various model kinetics. The article is divided into two parts. In the first part, the authors develop the scheme of numerical integration that they used for solving the flame equations under conditions such that the steady-state approximation of chemical kinetics is approximately but not exactly applicable for the reaction intermediaries. In the second part, a detailed discussion is given of the results obtained by this technique for the model chain reaction

$$X+A\rightleftarrows X+B \qquad (1)$$

$$B+A\rightleftarrows B+C \qquad (2)$$

in which X stands for any molecule, A is the reactant, B the chain carrier, and C the reaction product. Step (1) is taken to be endothermic and (2) exothermic, and results are given only for cases in which the heat of reaction is the same for each step, the activation energy in the exothermic direction is zero for each step, and the frequency factor for each forward reaction is the same as that for the corresponding reverse reaction. Attention is focused on effects of varying the Lewis numbers (three choices are considered, one with each $Le<1$, one with each $Le=1$, and one with each $Le>1$) and on effects of varying the relative rates of steps (1) and (2) by varying the ratio of frequency factors, $\omega\equiv A_2/A_1$. Results give flame speeds and give profiles of concentration, production rate and mass flow rate for reaction intermediaries, profiles of ratio of convection to heat conduction terms in the energy equation, profiles of ratio of diffusion to heat conduction terms in the energy equation, profiles of temperature gradient, profiles of the net rates of reaction steps (1) and (2), and profiles of the ratio of the rate of heat release by step (1) to the total rate of heat release. Numerous peripheral discussions are given in the text and in eight appendixes concerning numerical techniques and the validity of

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many different approximations that simplify the equations. The conclusions that can be drawn from the results are too involved to be discussed properly in a review of the present length.

The journal (*Phil. Trans.*), with its liberal space limitations, offers a nearly unique opportunity for a somewhat discursive and pedagogic presentation of material. Unfortunately, the authors did not avail themselves of this opportunity. The paper is written as obscurely as earlier papers in the series, and the average reader will find it appreciably more difficult to read the paper than to read the first paragraph of this review. No section on conclusions is given in the paper. Moreover, there are many possibilities for misinterpretation. For example, from one sentence [that containing Eq. (9.3)], the ingenue might well conclude that the Arrhenius reaction rate law was invented by Campbell and Fristrom in 1958, an interpretation that certainly was not intended. Furthermore, the work on flame theory, quoted in the references, is confined almost exclusively to that of Hirschfelder's group and its offshoots, even though there are now many other important contributions to the theory of flames with complex kinetics. This is disconcerting for a number of reasons. One is that some of the material (e.g., the demonstration that the viscous term is negligible in the energy equation) is already available elsewhere, even in textbooks. Another is that a great deal of work has been done recently on the solution of singular perturbation problems, including useful numerical approaches [e.g., G. Moretti, "A New Technique for the Numerical Analysis of Nonequilibrium Flows," *AIAA J. 3*, 223 (1965)], for problems that exhibit many similarities to the one attacked in Part I of this paper. One wonders whether the authors might have been able to make use of some of this recent work for alleviating the difficulties that arise in flames that begin to depart from the kinetic steady-state approximation.

Subject Headings: *Flame, theory; Flame, properties.*

F. A. Williams

Craven, A. D. and Foster, M. G. (ICI Fibres Ltd, Harrogate, Yorkshire, England) "The Limits of Flammability of Ethylene in Oxygen, Air and Air-Nitrogen Mixtures at Elevated Temperatures and Pressures," *Combustion and Flame* **10**, 95–100 (1966)

This paper presents the limits of flammability of ethylene in oxygen, air, and air–nitrogen mixtures measured in a three liter spherical chamber with heating or fusing a wire positioned in the center of the chamber as the ignition source. The limits in oxygen were determined at 80°, 120°, and 150°C over the pressure range from 135 to 515 psia. The limits in air and air–nitrogen mixtures were determined at 20° and 250°C under three different pressures, atmospheric pressure, 45 and 135 psia. The results were discussed and compared with the available data of previous works.

Subject Headings: *Combustion, of ethylene; Ethylene, flammability and combustion of; Flammability, of ethylene.*

S. J. Ying

Cullis, C. F., Fish, A., and Pollard, R. T. (Imperial College, London, England) "The Slow Combustion of Aluminium Trimethyl," *Proceedings of the Royal Society* **A288**, 123–132 (1965)

Previous kinetic studies of the gaseous oxidation reactions of the metal alkyls, namely, boron, indium, and zinc, have shown a variety of rate-controlling mechanisms. The authors have extended their oxidative reaction studies to include aluminum trimethyl, which is of particular interest because it is the most electron deficient group III alkyl, is a dimer in the vapor phase, and will ignite spontaneously in air, thus having potential applications for certain air-breathing combustion engines. The purpose of their investigations was to examine the kinetics of the gaseous oxidation of trimethyl aluminum (TMA) to establish, by comparison with other metal alkyls, a general mechanism for their oxidation. By studying the slow oxidation, the authors hoped to arrive at some insight into the mechanism for spontaneous autoignition in air.

Kinetic and analytical studies of trimethyl aluminum were undertaken at temperatures and pressures below those required to produce spontaneous combustion. In contrast to studies made with boron and indium, no peroxides were detected and no volatile oxygenated organic compounds were found. The only products detected were methane, hydrogen, and a solid methoxymethyl aluminum compound.

The experiments were conducted in a spherical pyrex vessel in which pure trimethylaluminum was introduced. At a known pressure into the center of the vessel, oxygen was introduced through a capillary. A cinephotographic record of a glass spiral gauge was used to measure changes in pressure as the reaction took place. Known volume samples of the gaseous product were withdrawn and analyzed by various techniques; gas chromatographic for gases; iodometric for detection of solid peroxides; infrared spectrophotometric for other solids.

The results indicated that slow oxidation invariably produced a decrease in total pressure of the system. The over-all order of the reaction was determined by plotting the log of the initial pressure exponential decay curve and approximating the rate expression by the equation: $dp/dt = -kp_1p_2^2$, where p_1 is the initial pressure of trimethylaluminum, p_2 the initial pressure of the oxygen, and k the experimental rate constant.

Analysis showed only CH_4 and H_2 within the gas products. The amount of methane found corresponded closely to the conversion of one of the six methyl groups of the gaseous dimer, Al_2Me_6. No HCHO or CO was detected. A white, opaque, smoke solid was formed, condensed upon the walls of the vessel. This solid contained no peroxides and from the IR spectrum it was concluded that the solid was dimethoxymethylaluminum, $(MeO)_2AlMe$. The reaction rates were little affected by temperature or by the addition of an inert gas, but were affected by the surface/volume ratio and by accumulation of solid products on the surface of the vessel.

The authors conclude that the reaction occurs by a free-radical chain mechanism and therefore they propose a series of chain-branching steps. Postulating chain-branching termination at the vessel walls, these reaction equations account for methane and hydrogen in the gas phase, the presence of dimethoxymethylaluminum at the chamber walls, and the scheme seems reasonably consistent with the observed kinetics.

Subject Headings: ***Aluminum trimethyl, combustion of; Combustion, of aluminum trimethyl.***

D. Dembrow

Halpern, C. (National Bureau of Standards, Washington, D. C.) "Effects of Some Halogenated Hydrocarbons on the Flame Speed of Methane," *Journal of Research of the National Bureau of Standards* **70A**, 133–141 (1966)

The effects of five halogenated hydrocarbons on the flame speed of methane have been studied. Bromides are more effective in reducing flame speeds than are chlorides and the reduction in flame speed is proportional to the amount of inhibitor added.

Subject Headings: *Burning velocity, of methane, effect of halogen compounds on; Flame speed (see Burning velocity), methane burning velocity, effect of halogen compounds on; Halogen compounds, effect on burning velocity of methane.*

Author's Abstract

Howard, J. B. (Massachusetts Institute of Technology, Cambridge, Massachusetts) and **Essenhigh, R. H.** (Pennsylvania State University, University Park, Pennsylvania) "Combustion Mechanism in Pulverized Coal Flames," *Combustion and Flame* **10**, 92–93 (1966). Letter to the Editor.

Analysis of data obtained from measurements of a one-dimensional pulverized bituminous coal flame, which had indicated that ignition occurred on the solid surface of the particle and not in the volatile pyrolysis products, has been extended to consider the combustion process.

It is concluded that for larger particles, greater than 65 microns, the heterogeneous reaction would be quenched at the onset of the devolatilization, because the volatiles sweep away and use up the oxygen diffusing to the particle surface. It is suggested that particles smaller than 65 microns are incapable of generating a sufficiently concentrated screen of volatiles; only a fraction of the oxygen is used up by the volatiles, the rest are able to migrate to the solid surface to maintain the heterogeneous reaction. The proportion of volatiles reaction to heterogeneous reaction decreases as the particle size drops and, at 15 microns or less, the reaction is apparently all heterogeneous with no discrete volatile flamelet around the particle.

The evidence for this hypothesis is a consideration of all possible mechanisms and the progressive elimination of all but one by the method of disproof. The salient points of the argument are as follows.

If the heterogeneous reaction were completely quenched at the onset of devolatilization there would be no loss of fixed carbon until pyrolysis stopped. In fact the fixed carbon did not remain constant but dropped during pyrolysis from 90% to 50% or 60%. To establish what particle size was affected by the continued heterogeneous reaction, the authors had previously shown that the pyrolysis was a first-order volumetric process and hence the devolatilization time would be independent of particle size below 100 microns. Thus, the surface flux of volatiles must increase with particle size.

Using oil drop theory, it follows that volatile generation rates above some critical value can maintain a flamelet at a discrete distance from the particle surface. The flamelet consumes all the oxygen and forms a protective screen around the particle.

Below the critical generation rate there is excess oxygen available for the continuation of the heterogeneous reaction. Knowing the volatiles generation rate for different sizes of particles, the critical diameter (the original text says "radius" but presumably this is a misprint and diameter was intended) was calculated to be 29 microns. This is in fair agreement with the experimental value of 15 microns when it is realized that this value is obtained by splitting the total volatile loss between (a) pyrolysis and gas phase combustion and (b) the heterogeneous combustion of "volatiles" in the whole coal in the particle before pyrolysis. This latter is a measure of the coal contained in particles below the critical size and may be used in conjunction with the size distribution of the coal.

The data has also provided information about the activation energy of the heterogeneous reaction. Comparison of the activation energy in the tail of the flame with that in the pyrolysis zone suggests this latter energy is an adsorption activation energy due to the greatly reduced oxygen partial pressure at the solid surface following the incomplete volatiles reaction.

Subject Headings: ***Coal particles, combustion of; Combustion, of coal particles; Heterogeneous combustion, of coal particles; Particles of coal, combustion of.***

G. L. Isles

Johnson, J. E. and Woods F. J. (Naval Research Laboratory, Washington, D. C.) "Flammability in Unusual Atmospheres. Part 1. Preliminary Studies of Materials in Hyperbaric Atmospheres containing Oxygen, Nitrogen, and/or Helium," *NRL Report 6470* (October 31, 1966)

This study was undertaken following a fire that occurred in the decompression chamber at the Navy Experimental Diving Unit of the Washington Navy Yard, February 1, 1965,[1] resulting in the death of two occupants. Investigation revealed a paucity of information concerning ignition and combustion in nonterrestrial, hyperbaric atmospheres. As a consequence, the experiments described in this report were undertaken.

In the literature the authors found only two earlier works dealing with flammability of materials in hyperbaric atmospheres, and only one of them reported effects in oxygen-enriched atmospheres.[2,3]

In the experiment the authors used two chambers, each with a viewing port or window, for their ignition and flame spread rate determinations. One chamber, 12.6 liters volume, was used for normal atmospheric pressure determinations (i.e., ca 1 bar, where 1 bar equals 100,000 newtons per square meter). The second chamber was a hyperbaric chamber having a volume of 142 liters and an upper working pressure of 5.2 bars absolute (75 psia). The smaller chamber could be evacuated so that the desired mixture of gases could then be charged. The larger chamber required purging with the desired mixture to obtain the desired atmospheric composition, since this chamber was not equipped for evacuation.

The tests consisted essentially of exposing test specimens to a "hot wire" igniter, noting the ignition delay time, and observing the rate of flame spread on the sample. The igniter used a 25 gauge nichrome wire, wound on a 0.635x2.22 cm form. The igniter was energized in most trials at 18 volts, giving a current of 4.0 amperes. Test samples 10.2 cm long and 0.635, 0.953, or 1.27 cm wide were used. The standard paper samples, which were prepared from resin impregnated filter paper, 5 micron pore size, from the Skinner Purifier Division of the Bendix Aviation Corporation meeting specification MIL-F-5504B, "Filters and Filter Elements, Fluid Pressure, Hydraulic, Micronic Type", were either 0.635 or 1.27 cm wide, and the other material samples were 0.935 cm wide.

The test sample was mounted so that one end of the sample contacted the igniter coil and the other end was restrained by a clamp. Temperature measurements over the sample surfaces were made by means of 3 iron-constantan thermocouples spaced 2.54 cm apart along the length of the sample. The rate of flame propagation could be ascertained either by visual observation or analysis of the thermocouple recording charts. The samples could be mounted in either a vertical or horizontal position. Cloth samples were supported by threading a length of nichrome wire through the length of the fabric so that either a vertical or horizontal position could be maintained. For the most part samples were stored at 50% relative humidity prior to tests.

Table 1 shows results in the flammability tests using the standard resin impregnated filter paper samples, untreated terry cloth, and treated terry cloth samples. The treated terry cloth samples were impregnated with tetrakis (hydroxymethyl) phosphonium chloride, $(HOCH_2)_4PCl$, i.e., commercial Roxel-treatment. Table 1 shows higher flame spread rates for vertically mounted samples than for corresponding horizontally mounted samples, and that, in general, the burning rate was markedly increased with increase in the oxygen content of the atmosphere. For example, the filter paper samples under both 1 and 2.1 bars pressure burned approximately twice as fast with the oxygen concentration at 31% by volume than at 21% by volume in oxygen-nitrogen atmospheres. The effect of pressure on combustion rate was not as marked. However, in some cases (Table 1), ignition was at the highest test pressure, 5.2 bars (75 psia), where, all other test conditions being the same, no ignitions were observed at the lower pressures.

The authors pointed out the comparative behavior of the combustibles tested in nitrogen and helium atmospheres. The greater ignition delay and otherwise greater difficulty for ignition in helium–oxygen atmospheres than in nitrogen–oxygen atmospheres was explained on the basis of greater thermal conductivity of helium with respect to nitrogen. For example, Fig. 1 shows the effect ot the atmospheric composition on the nichrome wire igniter temperature.

The following effects were also investigated:

1) The effects on ignition delay and burning rate of relative humidity in preconditioning storage of standard paper samples, igniter temperature (i.e., electric current in the igniter wire), and oil impregnation of the standard paper samples.
2) Flame resistance of selected materials at 3 different concentrations of oxygen in nitrogen–oxygen atmospheres and at normal atmospheric pressure. The selected materials included treated and untreated cotton fabrics, a treated foamed elastomer, and flame resistant greases.

The authors report no significant differences in burning rates of standard paper samples attributable to either preignition storage for 24 hr at 50% or 100% relative humidity, or in atmospheres of different oxygen concentrations, and only two

TABLE 1

Combustion of the standard paper, a terry cloth, and a terry cloth treated with a fire retardant

Atmosphere	Pressure		Paper		Terry cloth		Treated terry cloth			
			Horizontal position		Horizontal position		Horizontal position		Vertical position	
	(bars)	(psia)	Ign. delay (sec)	Burn rate (cm/sec)	Ign. delay (sec)	Burn rate (cm/sec)	Ign. delay (sec)	Burn rate (cm/sec)	Ign. delay (sec)	Burn rate (cm/sec)
O_2/N_2 (21/79)	1.0	15	6.5	0.23	8.4	0.20	NI†	NI	NI	NI
	2.1	30	6.0	0.25	6.6	0.61	NI	NI	9.6	*
	3.1	45	7.2	0.30	—	—	NI	NI	7.2	0.13§
	4.1	60	6.0	0.30	4.8	1.17	NI	NI	6.6	0.31§
	5.2	75	4.8	0.28	4.9	0.89	5.0	0.03‡	—	—
O_2/He (21/79)	1.0	15	NI	NI	—	—	—	—	—	—
	2.1	30	NI	NI	—	—	—	—	—	—
	3.1	45	NI	NI	—	—	—	—	—	—
	4.1	60	NI	NI	—	—	—	—	—	—
	5.2	75	18.0	0.48	18.0	0.40	NI	NI	*	*
O_2/N_2 (31/69)	1.0	15	6.0	0.43	—	—	18.0	§	*	*
	2.1	30	5.7	0.47	—	—	7.2	0.23	6.3	2.61
	3.1	45	6.0	0.45	—	—	—	—	—	—
	4.1	60	4.8	0.53	—	—	—	—	—	—
	5.2	75	5.4	0.53	—	—	—	—	—	—
O_2/He (31/69)	1.0	15	17.0	0.76	22.5	1.27	NI	NI	—	—
	2.1	30	14.3	0.69	27.0	1.02	NI	NI	—	—
	3.1	45	8.1	0.70	—	—	NI	NI	—	—
	4.1	60	7.5	0.76	—	—	NI	NI	—	—
	5.2	75	7.5	0.86	—	—	§	0.05	§	§

$O_2/N_2/He$: (31/34.5/34.5)	1.0	15	10.2	0.61	10.8	0.94	NI	NI	—	—
	2.1	30	11.1	0.67	10.2	1.70	NI	NI	§	§
	3.1	45	8.4	0.56	—	—	9.0	0.38	7.2	2.54
	4.1	60	6.6	0.56	—	—	—	—	—	—
	5.2	75	5.4	0.68	—	—	—	—	—	—

† NI denotes no ignition under the test conditions.

‡ Flamed momentarily, then smoldered for entire length of cloth strip.

§ Did not flame, but smoldered for entire length of cloth strip.

* Burned or charred about one-half length of test strip.

Although ignition was more difficult in the helium atmosphere than the nitrogen atmosphere of the same oxygen concentration, once ignited the flame spread on the test samples was more rapid, as seen in Table 1. These results are corroborated in other studies (Ref. 4).

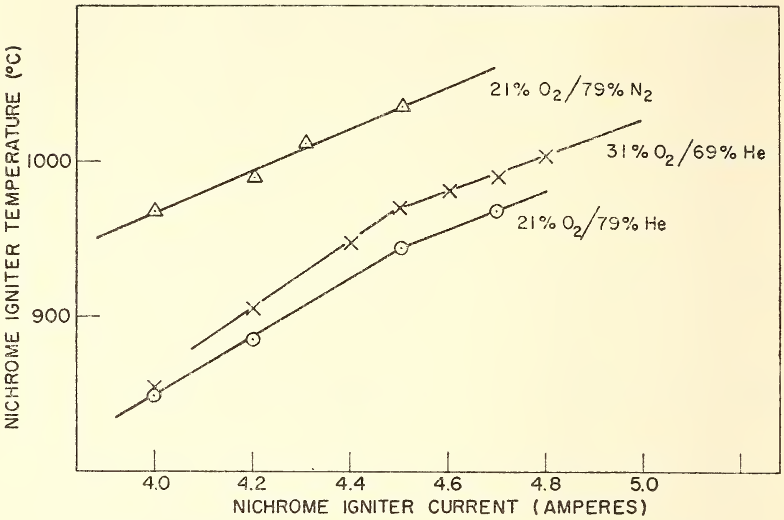

Fig. 1. Effect of different atmospheres on igniter temperature.

materials tested in the 41% oxygen concentration in the nitrogen–oxygen atmosphere did not ignite, namely Teflon and glass.

Though results clearly indicate increased flammability of materials with increase in atmospheric oxygen concentration, and to a lesser extent increased flammability with increased pressure, the authors conclude that no simple multiplying factor can be applied in predicting flammabilities in nonterrestrial atmospheres based on data obtained under terrestrial conditions.

The study is part of a continuing study, and conditions proposed for further investigation include atmospheric pressures less than 1 bar (i.e., under normal atmospheric pressure), pressures up to 20 bars (300 psia), and wider ranges of oxygen concentrations, especially in helium–oxygen atmospheres.

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Subject Headings: *Combustion, in hyperbaric atmospheres; Flammability, in hyperbaric atmospheres; Hyperbaric atmospheres, combustion and ignition in; Ignition, in hyperbaric atmospheres; Oxygen atmospheres, combustion and ignition in.*

J. E. Malcolm

Michaud, M., Mondain-Monval, G., Accorsi, R., and Ivernel, A. (De la Société l'Air Liquide, France) "Oxygen and Combustion—Theoretical and Experimental Fundamentals," *Revue Generale de Thermique* 4, 527–551 (1965)

Part I. Theoretical Considerations on the Thermodynamics of Combustion—G. Mondain-Monval

This study is a three-part series intended for various engineering purposes dealing with the production and application of high temperatures, using hydrocarbon fuels as the source of energy, and combustion as the process for liberating that energy. The three papers of the study are divided into separate topics; the first deals with thermodynamic equilibrium, the second with mechanisms of combustion in flames, and the third with heat transfer.

In the first paper the author is concerned with fundamentals of thermodynamics and methods for performing theoretical calculations of combustion equilibrium. The author notes that the production, application, and understanding of high temperature phenomena are the objectives of numerous researches in the domains of chemistry, metallurgy, aerodynamics, propulsion, plasma physics, etc. He suggests that a better comprehension of thermodynamics, energetics, and the physical and chemical characteristics of gases at high temperature is needed, but for the practical thermal engineer's needs, the use of existing thermodynamic laws is quite adequate. Of the numerous methods of predicting high temperature equilibria, the author selected the method of enthalpy–entropy as conceived by LeChatelier and developed by Ribaud and Manson. This method, if performed manually for complex gas mixtures, is laborious and tedious. However, the use of automatic computers which have been developed during the past few years has removed the labor and tedium and permits results of highest precision. The basic hypothesis for one's undertaking a calculation of the combustion process is that a chemical reaction of combustible and oxidizer proceeds until thermodynamic equilibrium is attained.

The author treats the initial combustible mixture as a physicochemical system in metastable equilibrium in which a small disturbance such as a localized flame can transform the mixture into a burnt gaseous system in stable equilibrium corresponding to a minimum thermodynamic potential. For those people who are concerned with the combustion process proper, the thermodynamics furnishes several important results, three of which are generally needed by the thermal engineer: (1) quantity of heat released, (2) temperature at which the heat is released, and (3) chemical composition of the heated, combusted gas.

The author then considers isobaric combustion and shows how the principle of conservation of energy permits one to calculate the quantity of heat liberated by a combustible mixture, given the initial conditions, the final conditions, and knowledge of the reacting materials. As an example, a stoichiometric mixture of methane and air is taken. Having found the heat liberated, the author proceeds to obtain the final temperature. He shows that it is necessary to know not only the heat released by the chemical reaction, but also the enthalpy of the combustion products as a function of temperature. Thermodynamic principles are now applied, permitting calculation of the enthalpies of the combustion gases in thermodynamic equilibrium as a function of temperature for given pressures. Account must be taken of the dissociation which occurs as the equilibrium shifts when the temperature is raised. As an example, the enthalpy–temperature diagram of a stoichiometric mixture of methane and air combustion over a range of 1 to 10 atm is given. The author lists five principal parameters for detailed examination in the determination of both isobaric and adiabatic temperatures of combustion: (1) nature of the combustible, (2) nature of the oxidant, (3) ratio of combustible to oxidant, (4) combustion pressure, and (5) enthalpy of the combustible mixture. He then displays a graph of enthalpy–temperature for a range of hydrocarbons burning with air or oxygen.

The non-adiabatic, isobaric combustion temperature is shown to be lower than the adiabatic and the author proposes an analogy between an electrical generator and a thermal generator to elucidate this distinction. In this analogy, the *flame temperature* corresponds to *voltage*, the *releasable heat* corresponds to *current*. The *adiabatic temperature* corresponds to the *peak voltage* when the electrical generator delivers no current, there being an infinite electrical resistance. The *releasable quantity of heat* from a thermal generator corresponds to the *current* from a short-circuited electrical generator. A graph of *temperature* versus *heat released* and a similar graph of *voltage* versus *current* shows how the analogy between a thermal and an electrical generator is helpful to the practicing thermal engineer. An interesting new term, "exergy" is described to represent the thermal energy, $\mathcal{Q}$, times the Carnot ratio $(T-T_0)/T$. "Exergy" is zero at the adiabatic combustion temperature where $(T-T_0)/T$ is a maximum but $\mathcal{Q}$ is zero, and at ambient temperature where $\mathcal{Q}$ is a maximum but $(T-T_0)/T$ is zero. The author has calculated these variables for a methane–air and oxygenated air thermal generator showing both the temperature attainable and the heat realizable. Further graphs are given to show the effect of preheating the combustible gas mixture, the effects of varying the stoichiometry, and the effect of augmenting air with oxygen. The use of these graphs permits determination of the final temperature and pressure based upon a knowledge of the combustible system and the initial conditions. The remaining problem is determination of the final chemical composition, and the author shows how the laws of physicochemical equilibrium are applied. A graph of stoichiometric methane–oxygen composition versus temperature is given. At low temperature, the composition of the combustion products would consist essentially of carbon dioxide and water vapor. At a temperature of 1500°K, dissociation into carbon monoxide and hydrogen becomes appreciable. Above 2500°K, dissociation into atomic hydrogen, atomic oxygen, and the hydroxyl radical (OH) becomes noticeable.

The first part of this series can be summarized as a presentation of a means to enable the practicing thermal engineer to determine (1) the external characteristics of a thermal generator from thermodynamic principles, and (2) the products of combustion from the physical chemistry of a hydrocarbon combustion system reaching equilibrium. Graphs are provided which can be applied, assuming the postulation of thermodynamic equilibrium is met; they do not apply to those systems which are governed by chemical kinetics. If the reaction time is insufficient, the chemical system cannot attain the equilibrium fixed by local conditions of pressure and temperature. In such circumstances, one must study intermediate species in the reactions taking place and the process of interrupting the reactions, freezing the composition.

Part II. Mechanisms of Combustion in Flames—R. Accorsi

In the second paper the author is concerned with the physical and chemical mechanisms of combustion in flames. He divides the combustion process into two subordinate and distinct phenomena which invariably occur between a combustible and an oxidizer: (1) the mixing of combustible with air and (2) the combustion proper, namely, the chemical combination of the combustible with the oxygen in the air. These two phenomena, although they take place successively, have to be distinguished, and in so doing, one divides the various flames into several classes. If the mixing process occurs well ahead of the flame front, this is the premixed flame, generally of gaseous combustibles. If the mixing process and the combustion process occur almost simultaneously, the combustion can take place as rapidly and at the same time as the mixing is effected; then the speed of the mixing process limits the over-all process, and one has a diffusion flame. The diffusion flames can be further subdivided depending upon the nature and phase of the combustibles, into gaseous or liquids, both volatile and nonvolatile, and solids, as for example powdered coal.

Of the numerous combinations, two schemes are considered by the author: (1) reactions in the gas phase and (2) reactions of a heterogeneous phase mixture as between liquid or solid combustible and gaseous oxidizer.

The author then presents a general description of the mechanisms of the various flames ranging from the premixed gas flames to diffusion flames, all of which utilize the air as the oxidizer. He treats the nitrogen in air as taking only the part of a diluent in the combustion reaction, but he also shows the effect on the mechanism if oxygen is used in place of air.

The author next treats of the detailed combustion mechanisms within premixed gaseous mixtures. He divides the total combustion phenomenon into two aspects: (1) inflammation and (2) propagation. The inflammation of a gaseous mixture can be obtained by various methods, the classic one being to elevate the temperature rapidly. The inflammation temperature is the temperature to which the mixture must be raised for it to self sustain the reaction (500° to 700°K for most hydrocarbons). Note that the ignition temperature is not a physical constant, since it depends upon the method used to determine its value. Two interpretations have been used to explain the act of inflammation: (1) LeChatelier's, a thermal interpretation which depends upon the hypothesis that the speed of the oxidation behaves exponentially with temperature, and (2) the more modern interpretation in which the speed of the reaction depends upon chain-making or -breaking reactions in which free radicals or active centers intervene as intermediate species in the over-all process. The author points out that, whereas the flame temperature depends upon the initial gas mixture, the pressure depends upon the degree of confinement. Furthermore, the pressure can also depend upon the final gaseous composition which in turn can be modified by the presence or absence of catalysis or inhibitors which play a role in the rate of the reaction process.

Next the author turns to flame propagation and he discusses the limits of inflammability. His discussion covers two major aspects of flame propagation—namely, *deflagration* wherein the flame speed is of the order of meters/second and *detonation*, of the order of kilometers/second. Propagation by detonation is practically never observed in the absence of a shock wave and the flame front coincides with the advance of the pressure wave. The transmission of flame by detonation is shown to be effected by pressure and not by transmission of heat. Propagation of a deflagration, on the other hand, shows a high degree of variability, depending on the characteristics of the gas and also upon the form and dimensions of the container and the direction in which the propagation is effected. The mechanism of transmission of the inflammation may be interpreted by either theory cited above and in fact the two phenomena of active center diffusion and heat transfer superimpose on one another, but active center diffusion appears to play the essential role.

The author next treats of the energetic aspect of combustion. He notes that the combination of combustible with air and the liberation of caloric energy takes place within a narrow zone (0.1 to 0.2 mm thick) within premixed flames. If oxygen is in excess, the combustion process leads to a mixture of carbon dioxide and water vapor, but if the temperature is high these two species become partially dissociated into carbon monoxide and hydrogen. If the oxygen is insufficient, the combustion leads to carbon monoxide, hydrogen, and water with possible formation of carbon soot. The general rule is that the oxygen unites first with carbon to produce carbon monoxide. The energy liberated is contained within the burnt gases, which are thus carried to a high temperature. In reality, a part of this energy is lost by radiation and convection and the theoretical temperature calculated on the basis of the assumption of thermodynamic equilibrium for an adiabatic combustion process represents an upper temperature limit.

The author provides graphs showing the flame speeds for premixed flames as a function of proportion of combustible to oxygen for various gases, such as hydrogen, acetylene, methane, propane, city gas, and water gas. He also shows the effect of oxygen enrichment on flame speed.

Next the author covers the combustion of carbon particles suspended in air. He notes that for carbon particles larger than 300 microns the flame speed is controlled by diffusion, and he gives the governing equations and compares them with those generated for small particles (0.4 micron) and intermediate size particles (88% less than 66 microns) from experimental data at IJmuiden, France, and Sheffield, England, respectively.

Diffusion flames are discussed from a similar mechanism viewpoint, namely, (1) the process of mixing, (2) the influence of fluid flow or movement, (3) the phenomena of recirculation, and (4) the effect of oxygen augmentation on diffusion flames. Graphs are shown of repartition of CO and O_2 from a typical burner and of the variation in emissivity constant as a factor of C/H ratio. This study includes a consideration of the flow lines behind a stabilizing disk used for a flameholder and it shows the effects of air-enrichment on various burners and furnaces, emphasizing the effect of oxygen directed into the injectors.

The second part of this series can be summarized as (1) providing a general background for the various mechanisms that enter into the combustion reaction for different types of flames, and (2) supplying information concerning both premixed and diffusion flames, indicating the mechanisms involved for (a) initiation and (b) stabilization of flames, (c) the process of mixing the combustible with the oxidizer, and (d) the factors governing the flame speed itself, and the over-all combustion rate.

Part III. Heat Transmission—A. Ivernel

The third paper of this series concerns itself with heat transmission in general and with the specific problem of oxygen augmentation and its effect upon radiation, free convection, and forced convection in practical furnace applications.

In dealing with the heat radiated, the author points out that there is some compromise point between the decrease in emissivity and the increase in temperature by the admixture of oxygen. If one agitates a flame containing soot, for example, its emissivity increases in the process, and augmentation of oxygen has a double effect. On the other hand, the presence of cracked by-products which had contributed strongly to giving a flame a high emissive constant may disappear almost completely so that a typical fuel oil flame to which oxygen has been added may appear transparent. At the same time, the temperature of the flame increases, and thus it is necessary to find the point where the gain of T^4 more than compensates for the decrease in the emissivity constant. Consider for example a methane–air gas flame or natural gas–air flame where cracking occurs. The emissivity constant is due almost entirely to CO and H_2O, and it reaches a maximum value of 0.15 blackbody. With pure oxygen the emissivity constant diminishes slightly and the temperature rises. A simple calculation shows that, whereas a methane–air flame reaches a temperature of 1870°K, with pure oxygen a value of 2520°K is reached so that the total radiative value ($\epsilon\sigma T^4$) is multiplied by about 3 or 4.

In free convection the classical formulas apply, the important and controlling term being ($T_g - T_s$), which is the difference in temperature between gas and wall surface. Under turbulent conditions, the heat transfer coefficient is modified by a suitable correction factor. In forced convection a similar form of expression is used, the appropriate terms being modified to account for the effect of convective flow.

The remaining portion of the heat transmission study deals with results of experimental studies made at IJmuiden. Those experiments were conducted in an instrumented experimental furnace in which both localized heat flux and over-all heat flow were measured. Curves showing experimental versus theoretical increases in heat flow as a function of increased oxygen augmentation are shown. Curves of wall temperature, gas temperature, heat transfer coefficient, radiation, and heat flow for various flow rates of oxygen and at various distances from the injection point are shown. To summarize the IJmuiden experiments, the author has furnished both theoretical considerations and experimental results aimed at providing a better means of predicting both qualitative and quantitative estimates for the use of oxygen augmentation for numerous practical applications where heat from combustion is required, such as steelmaking, cementmaking, greeneries, etc.

Conclusions

This series of articles provides an excellent survey of French activities in the field of hydrocarbon combustion research. It covers a wide range of investigations from theoretical to experimental, from premixed gas systems to diffusion flames. It shows certain areas of specific French emphasis, as in combustion of carbon soot and oxygen augmentation studies for furnace operation. It is recommended as an introduction for thermal engineers requiring a practical and comprehensive treatment of the combustion process as well as a review for those actively pursuing flame studies or combustion research.

Subject Headings: ***Combustion, thermodynamics of; Equilibria, in flames; Heat transfer, in combustion; Thermodynamics, of combustion.***

D. Dembrow

Plückebaum, J. W., Strauss, W. A., and Edse, R. (The Ohio State University, Columbus, Ohio) "Propagation of Spherical Combustion Waves," *ARL 63-101 Contract AF33(616)-8129 Aeronautical Research Laboratories, Wright-Patterson Air Force Base, Ohio* (June 1963)

Measurements were made of propagation rates of spherical combustion waves in gaseous explosive mixtures, in 65 cm diameter thin-walled rubber balloons and in a 40 cm diameter steel bomb. The propagation rates of stabilized spherical detonation waves were determined for acetylene–oxygen, hydrogen–oxygen, hydrogen–nitrous oxide, and methane–oxygen mixtures. Acetylene–oxygen mixtures were studied in detail with particular attention given to the effect of ignition energy on the propagation rates. A high speed strip film camera was used to record the propagation of the combustion wave front. In all experiments the explosive gas mixtures were initially at atmospheric pressure and room temperatures.

Subject Headings: ***Burning velocity, propagation of spherical combustion waves.***

Authors' Abstract

Rosser, W. A., Jr. (Stanford Research Institute, Menlo Park, California) and **Peskin, R. L.** (Rutgers University, New Brunswick, New Jersey) "A Study of Decomposition Burning," *Combustion and Flame* **10**, 152–160 (1966)

The mass burning rate $\dot{m}$ of liquid hydrazine (N_2H_4) decomposition flames saw investigated both experimentally and mathematically. The droplet diameter ranged from 0.3 to 1.3 cm. The objective was to find the dependence of $\dot{m}$ versus droplet size and pressure, and a mathematical model describing the experimental result.

The experimental setup consisted of the porous aluminum oxide sphere connected to the regulated N_2H_4 supply by a stainless-steel feed line and the enclosing, vacuum-tight chamber, for which the pressures of N_2 and O_2 could be regulated.

The burning rate was determined by exactly feeding N_2H_4 at such a rate that the thickness of the N_2H_4 film covering the aluminum oxide sphere did not change with time. Decomposition flames of these simulated drops of the used N_2H_4 containing about 1 wt % of aniline and of water were difficult to stabilize without the presence of oxygen. Therefore, at least 10% of O_2 were normally used during the experiment. Fortunately, increasing amounts of O_2 only increased $\dot{m}$ but did not change the observed relationship:

$$\dot{m} \sim d_l^2,$$

where $\dot{m}$ = mass burning rate in g/sec, and d_l = liquid drop diameter in cm. This result implies that, in the case of free burning droplets and because of $\dot{m} \equiv (d/dt) \times (\rho \pi d_l^3/6)$, the rate of decrease of droplet diameter with time t would be constant, i.e., $dd_l/dt = \text{const}$ or $t \sim d_l$.

This result, on one hand, is the same as corresponding to the familiar reaction rate controlled burning of premixed flames stabilized on porous spheres, porous flat flame burners, etc., with a constant $dd_l/d_l = S_u$, or burning velocity; on the other hand, it is very different from results obtained with conventional diffusion-limited burning of fuel droplets which conform to relationships $\dot{m} \sim d_l$ and $t \sim d_l^2$. In order to get a better feeling for the meaning of this relationship, one might remember that the length L of a laminar diffusion flame is approximately given by a similar relationship $\dot{m} \sim L$, independent of burner diameter or flow velocity. A further outcome of the reported experiments is the linear dependence on pressure p:

$$\dot{m} \sim p.$$

Because of the general relationship $\dot{m} \sim p^{n/2}$, this pressure dependence indicates an over-all reaction order of $n = 2$.

Compared with a gaseous N_2H_4 decomposition flame burning with a velocity S_u of about 120 cm/sec and a maximum flame temperature of 1900°K, the measured rate of liquid consumption was about 0.02 cm/sec, corresponding to a gaseous burning velocity of $S_u = 20$ cm/sec; the maximum flame temperature being about 1450°K. The measured liquid hydrazine surface temperature was 94±2°C, at 1 atm pressure, corresponding to a vapor pressure of 0.51 atm.

In order to accommodate these experimental data into a mathematical model, the authors solved the system of two linear differential equations corresponding to the conservation of mass and energy with the following assumptions:

Spherical symmetry,
Lewis number equal to 1,
Temperature independent reaction rate,
Simplified N_2H_4 decomposition mechanism according to N_2H_4 products,
Boundary conditions: (a) at infinite distance from the droplet: N_2H_4 concentration and flame temperature equal to zero; (b) at the droplet surface: all the heat transferred to the liquid is used for N_2H_4 vaporization, the reaction product convection and diffusion are equal and the total net mass flux is that of the reactants.

An approximate analytical solution was found which is valid for not too small droplet diameters. The corresponding curves of fuel vapor concentration and temperature versus distance from the drop surface follow qualitatively the expected profile but are stretched out too far; the calculation yielded a maximum temperature and a reduction to 10% of the initial N_2H_4 concentration at a distance of two droplet radii from the surface. This is compared to an observed position of the maximum optical emission zone of only 0.066 cm away from the droplet surface. Very probably, this error is caused by the assumed small first-order reaction-rate constant, which, in the one example given, is much smaller than values found in the literature (see e.g., Ref. 1). However, the reaction-rate-controlled decomposition or premixed flame model which was used, faithfully reproduces the expected and experimentally found relationship of $\dot{m} \sim d^2$ even for the smallest droplet used, 0.3 cm.

Reference

1. Michel, K. W. and Wagner, H. Gg.: *Tenth Symposium (International) on Combustion*, p. 353, The Combustion Institute, Pittsburgh, Penna., 1965.

Subject Headings: ***Decomposition, in flames; Flame, theory.***

U. Bonne

Takeyama, T. and Miyama, H. "Rate of Ammonia Consumption in the Ammonia Oxidation in Shock Waves," *Bulletin of the Chemical Society, Japan* **39,** 2352–2355 (1966)*

An investigation was made of ammonia oxidation in shock waves over the range of conditions $2100 \leq 2600°K$, $2.1 \leq 5.4$ atm, $0.5 \leq [NH_3]/[O_2] \leq 2$, and $1.0 \times 10^{-4} \leq [O_2]$, $[NH_3] \leq 4.1 \times 10^{-4}$ mole/liter, by monitoring the ultraviolet absorption of ammonia at 2245 Å. The absorption coefficient of ammonia was measured at various temperatures; the rate constant of the decomposition reaction at higher temperatures with a mixture of 1% NH_3 and 99% Ar was found to be in good agreement with the results of other studies. By using several mixtures of ammonia and oxygen highly diluted with argon, the rate of ammonia consumption immediately after an induction period was found to be expressed by

$$-(d[NH_3]/dt)_0 = k_0[NH_3]^{1.5}[O_2]^{0.5}[Ar]^{0.5},$$

where $\log k_0\,(\text{liter}^{1.5}\,\text{mole}^{-1.5}\,\text{sec}^{-1}) = 12.77 \pm 0.10 + (-8488 \pm 573)/T$. This corresponds to an apparent activation energy of 38.8 ± 2.6 kcal/mole. In order to explain the above rate expression, the following mechanism having R_1 radical as a chain-carrier was considered.

$$NH_3 + O_2 \rightleftarrows [NH_3 \cdots O_2]$$

$$[NH_3 \cdots O_2] + Ar \rightarrow R_1$$

$$R_1 + NH_3 \rightleftarrows [R_2 + \cdots] \rightleftarrows R_1 + \cdots$$

$$R_1 + R_1 \rightarrow \text{stable products.}$$

Subject Headings: ***Ammonia, oxidation in shock waves; Oxidation, of ammonia, in shock waves; Shock waves, oxidation of ammonia in.***

Tosiro Kinbara

* Contribution to *Fire Research Abstracts and Reviews* from Tosiro Kinbara.

Tingey, G. L. (Battelle Memorial Institute, Pacific Northwest Laboratory, Richland, Washington) "Kinetics of the Water–Gas Equilibrium Reaction. I. The Reaction of Carbon Dioxide with Hydrogen," *The Journal of Physical Chemistry* **70,** 1406–1412 (1966)

Commercially pure CO_2, H_2, and CO, diluted with helium were mixed in known proportions and passed over copper turnings at 300°C to remove traces of oxygen. Water vapor could be added to the mixture from a humidifier containing degassed distilled water. Gas chromatography was used to analyze the mixture, while moisture and low oxygen concentrations were determined by sensitive electrolytic analyzers.

The experiments were conducted using a static technique for temperature between 400° and 660°C and a flow technique for temperatures in excess of 580°C. In the static system the mixture was sealed into Pyrex ampoules before heating, whereas in the second technique, the mixture was passed directly into a heated reaction chamber. The chamber was arranged to have a uniform temperature along its length and the effects of a velocity gradient across the gas flow (a wide scatter among the experimental results) were substantially reduced by placing a quartz cylinder axially along the furnace, creating an annular gap 0.5 cm wide. The linear velocity of 10 cm/sec prevented back diffusion. Experiments were designed to provide information on reaction rate, order of reaction, the Arrhenius parameters, and the effect of a graphite surface on the reaction rate.

The reaction time used in the evaluation of the results was the difference between the total time in the reaction chamber and a measured induction period for the particular reaction chamber used. It was shown that above 800°C the rate exhibited a first-order dependence on CO_2 concentration in the range 50 to 500 Torr and a one-half-order dependence on H_2 in the range 4 to 500 Torr. There was an initial inhibition by CO causing a 15% decrease in rate when the CO pressure was 40 Torr but no further decrease in rate as the CO pressure increased. At 775°C, the order with respect to CO_2 and the CO inhibition were unchanged, while the order with respect to H_2 was one-third. The reaction was shown to proceed simultaneously by two paths. One, referred to as Mechanism I, activation energy 39.2 kcal mole^{-1}, frequency factor $7.6\times 10^4\ M^{-1/3}$ sec^{-1} predominates below 800°C, while Mechanism II, with an activation energy 78.0 kcal mole^{-1} and frequency factor $1.2\times 10^{13}\ M^{-1/2}$ sec^{-1} is predominant above 800°C. A nuclear grade graphite surface had a negligible effect on the reaction rate, provided no surface contamination had taken place.

The rate for the total reaction may be considered to be the sum of the following equations:

$$d[CO]/dt = d[H_2O]/dt = 7.6\times 10^4 \exp(-39{,}200/RT)[H_2]^{1/3}[CO_2],$$

$$d[CO]/dt = d[H_2O]/dt = 1.2\times 10^{13} \exp(-78{,}000/RT)[H_2]^{1/2}[CO_2].$$

Using a four-step process to describe the total reaction, the activation energy and frequency factor ($E=80.6$ kcal mole^{-1} and $5\times 10^{12}\ M^{-1/2}$ sec^{-1}) calculated from data on the four steps are close to the measured values. It is probable that there might be a different initiation reaction involved rather than the dissociation of H_2 at the vessel surface, which was assumed for the prediction.

The low temperature mechanism has not been investigated in sufficient detail, but it is known that even trace quantities of oxygen can have an enormous influence on the high temperature reaction and, despite the experimental precautions, oxygen might have affected the low temperature results.

Subject Headings: *Carbon dioxide, hydrogen reaction; Hydrogen, carbon dioxide reaction; Water gas equilibria.*

P. L. Start

VI. Radiation

Krakow, B. (The Warner & Swasey Company, Control Instrument Division, Flushing, New York) "Spectroscopic Temperature Profile Measurements in Inhomogeneous Hot Gases," *Applied Optics* 5, 201–209 (1966)

This paper represents part of a program of spectroscopic temperature determinations in hot gases, initiated by R. H. Tourin.[1] Objective of the work reported is the determination of temperature profiles of combustion products issuing from flames.

Experimental

Emission and absorption of hot CO_2 at several frequencies in the region of the fundamental vibration (4.3) were measured. Each sample was produced by burning CO with O_2 on a flat flame burner and adding controlled amounts of cold CO_2 to regulate the flame temperature without causing any large changes in composition. Flame propagation rates were controlled by small doses of H_2. The O_2 contents were those needed for stoichiometric conversion of all the CO and H_2 to CO_2 and H_2O. It was assured that C and O combined according to the equilibrium constants given by Lewis and von Elbe.[2] Each sample was flanked by guard flames of H_2 having the sample temperature, so that it was isothermal within the optical path. A three-burner assembly of 5x5 cm zones, each flanked by a pair of 1.3x5 cm guard burners, faced the spectrometer housing through an atmosphere of pure N_2.

Transmittance data were obtained from measurements of single zones at five temperatures between 1450° and 2800°K. Wavelengths 4.555, 4.696, 4.865 were used in the "weak-line" regions, 4.179 in a "strong-line" region of the hot CO_2 spectrum. Two-zone and three-zone radiance data, given in tables, were measured both ways, with the first zone nearest to and farthest from the detector. In the three-zone experiments monotonous temperature profiles as well as a maximum in the center were investigated.

Procedure of evaluation

Disregarding scattering, the spectral irradiance by a one-dimensional, monochromatic beam through a section of hot gas in thermodynamic equilibrium varies according to the "transfer equation"[1]

$$dH(\lambda, x) = k(\lambda, x)\{H(\lambda, x) - P(\lambda, T_x)\}, \qquad (1)$$

where H = measured irradiance, k = absorptivity, P = Planck blackbody radiance function. Hence, by integration,

$$H(\lambda, 0) = P(\lambda, T_x)\{1 - \exp[Lk(\lambda)]\}, \tag{2}$$

where the exponential = the transmittance $\tau(\lambda)$ through thickness L. For n adjacent, nonisothermal zones one obtains

$$H(\lambda_j, 0) = \sum_{i=1}^{n} P(\lambda_j, T_i)\{[1 - \tau_i(\lambda_j)] \prod_{h=0}^{n-1} \tau_h(\lambda_j)\}. \tag{3}$$

In applying (3), spectral emittances are measured at n different wavelengths for n different sets of τ_h values. This yields n independent equations for n values of Planck functions, from which the n temperatures T_i are evaluated.

The infrared transmittances are themselves temperature dependent. In general, direct measurement can be made only of the total transmittance but not of individual or a small group of zones. Therefore, a certain *a priori* knowledge of transmittances is required. This permits the solution of the n equations by an iterative procedure. For a rough estimate of the temperature profile approximate transmittance values and measured spectral radiances are used to calculate a set of Planck functions from which a better estimate of temperatures is derived. Better transmittances can then be computed. The procedure is repeated until the calculated thermal structure stops changing appreciably.

Temperature profiles thus obtained agreed well with predetermined structures.

References

1. Tourin, R. H. and Karkow, B.: Appl. Optics *4*, 237 (1965).
2. Lewis, B. and von Elbe, G.: Combustion, Flames and Explosions of Gases, p. 680, Academic Press, 1961.

Subject Headings: ***Temperature, measurement, in inhomogeneous flame gases; Spectroscopic temperature measurements.***

H. M. Cassel

Pich, R. (Walther and Cie A. G. Köln-Dellbrück, Germany) "Simplified Calculation of the Wall Temperatures of Furnace Tubes Subjected to Radiation from One Side," *Brennstoff-Wärme-Kraft* **17**, 298–304 (1965) In German.

For the correct design of boiler tubes, a detailed knowledge of the temperature profile over the tube cross section is required. Of particular importance are the mean total cross section temperature θ_m (for the calculation of the thermal stresses in the tube wall) and the maximum and mean wall temperature at the tube's vertex facing the flame radiation (for selection of the proper material, its thickness and lifetime considerations).

In order to protect the firebox walls from excessive thermal stresses, in modern boilers the separation of the tubes has been decreasing to the point where $t/D_a = 1$,*

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* In order to avoid repetition and for the reader's convenience, the meaning of the used symbols is tabulated at the end of the abstract.

i.e., where they form a continuous wall. It is specially in these cases where the resulting uneven heating leads to uneven temperature distributions within the tube cross section. Since the exact calculation of the tube's vertex temperatures is very complicated, the author derived approximate equations for the calculation of the inner, mean, and outer vertex wall temperatures of the tube.

In older approximations the assumption had been made that $\partial\theta/\partial\gamma=0$, i.e., the tangential heat transfer in the tube wall had been neglected. Therefore, the vertex temperatures obtained by this method had always been too high. With the present approximation, instead of using a γ-independent $q_a\approx\text{const}=q_0'$, $q_a(\gamma)\approx q_{a1}$ is used, which happens to be very close to $q_a(\gamma)$ for $t/D_a=1.7$. The smallest error with this approximation is thus encountered for boilers with $t/D_a=1.7$, while it is larger for $t/D_a<1.7$. For these, however, the error is on the safe side since the approximation still furnishes vertex temperatures that are too large.

The author calculated numerical data for the comparison between two of the three solutions of the stationary, source-free temperature field $\nabla^2\theta=0$ perpendicular to the tube axis, z, discussed so far:

(G_0) Exact solution, with

$$\partial\theta/\partial z=0 \qquad \text{and} \qquad q_a=q_{am}+\sum_{n=1}^{\infty} a_n \cos(n\gamma)$$

as given by Eq. (25) in the author's paper;

(G) The author's approximation, using G_0 but with the simplification

$$q_a\approx q_{a1}=\tfrac{1}{2}q_0'(1+\cos\gamma)$$

given in Eqs. (54) and (55); and

(N) The rough approximation with

$$\partial\theta/\partial\gamma=0 \qquad \text{and} \qquad q_a=q_0',$$

which strictly is only valid for $t/D_a=\infty$ and leads to [Eq. (32)]

$$\theta-\theta_d=q_a[(u/\alpha_i)+(r_a/\lambda)\ \ln(r/r_i)].$$

Part of the numerical data is presented in the form of ratios of temperature differences

$$f_{ta}=(\theta_a-\theta_d)_G/(\theta_a-\theta_d)_N$$

and

$$f_{ti}=(\theta_i-\theta_d)_G/(\theta_i-\theta_d)_N.$$

Both for $t/D_a=\infty$ and for $u=1, f_{ta}=f_{ti}=1$ since then, at $\gamma=0$,

$$G_0=G=N \text{ (no tangential heat transfer)}.$$

Furthermore, the absolute temperature differences $\theta_a-\theta_d$ and $\theta_i-\theta_d$ are also given. Since these temperatures refer to the vertex of the tube ($\gamma=0$) and since $q_{a2}\ll q_{a1}$ and the radiative heat transfer inside the tube can be neglected ($\alpha_{sn}\ll\alpha_i$), the equations for the temperature differences only depend on q_0', α_i and $\tau_{a,i}$:

$$\theta_a-\theta_d=(q_0'/\alpha_i)\tau_a,$$

and

$$\theta_i-\theta_d=(q_0'/\alpha_i)\tau_i,$$

where $\tau_{a,i}$ is a tabulated function of m and u only; the mean vertex wall temperature is obtained with good approximation as the arithmetic mean between θ_a and θ_i.

Two examples illustrate the achievements or engineering value of the approximation:

1. For a tube of natural convection boiler with $D_a = 57$ mm, $t = 75$ mm, $s = 5$ mm, $\lambda = 33$ kcal/(mh°C) and $\alpha_i = 18{,}000$ kcal/(m^{2}h°C), corresponding to $t/D_a = 1.3$ and $u = 1.21$, the author obtains, with $m = 2.73$, $f_{ta} = 0.99$ and $f_{ti} = 0.98$.
2. For a super heater tube in a forced flow boiler with $D_a = 26.9$ mm, $t = 37.5$ mm, $s = 5.6$ mm, $\lambda = 32$ kcal/(mh°C), and $\alpha_i = 2000$ kcal/(m^{2}h°C), corresponding to $t/D_a = 1.4$, $u = 1.71$, and $m = 0.35$, $f_{ta} = 0.75$ and $f_{ti} = 0.72$ is obtained.

From these examples it can be seen that in applications with large heat transfer coefficients α_i, the tangential heat flow is relatively negligible as compared to the radial heat flow. The significance and usefulness of the approximation becomes evident, however, in superheater tube application, where the α_i are relatively small but the temperatures are high and more critical with regards to the proper selection of materials and dimensions.

List of Symbols

D_a = outer tube diameter
D_i = inner tube diameter
f_{ta} = ratio of temperature difference between steam and outer vertex temperature
f_{ti} = ratio of temperature difference between steam and inner vertex temperature
m = $\alpha_i s/\lambda$
q_a = total heat radiated to the tube per unit surface; $q_a = q_{a1} + q_{a2}$; $q_a = q_0'$ at $\gamma = 0$
q_{a1} = heat radiated from the flame front
q_{a2} = heat radiated to the tube from its adjacent firebox wall, $q_{a2} = 0$ for $t/D_a = 1$
$\overline{q_{a1}} = q_{a1}$ for $t/D_a = \infty$ i.e., for one isolated tube heated by an infinite flame front
q_0' = maximum of $q_a (= q_{a1}$ for $\gamma = 0)$
r = radius of the tube
r_a = outer radius
r_i = inner radius
s = $\frac{1}{2}(D_a - D_i)$ tube wall thickness
t = center to center separation of the tubes; $1 \leq t/D_a \leq \infty$
u = D_a/D_i, i.e., the diameter ratio of the tubes o.d./i.d.
α_i = heat transfer coefficient in kcal/(m^{2}h°C)
α_{sn} = heat transfer coefficient describing radiation inside the tube
γ = angular coordinate of tube cross section; $\gamma = 0$ at vertex
θ = temperature
θ_m = mean temperature of the total tube cross section
θ_a = outer wall temperature at the vertex of the tube
θ_i = inner wall temperature at the vertex $(\gamma = 0)$ of the tube
θ_d = steam temperature, assumed to be uniform inside the tube
λ = heat conductivity in kcal/(mh°C)

Subject Headings: *Furnace wall temperatures; Radiative transfer, in furnaces; Wall temperatures, in furnaces.*

U. Bonne

Staackmann, M., Baker, R. L., Colvin, C. B., Goodale, T. C., and Hawkins, M. B. (URS Corporation, Burlingame, California) "Final Results of Smoke Screen System Development," *Final Report prepared for Office of Civil Defense under Contract No. OCD-PS-64-63* (June 1966)

The basic objective of this study was to develop radiation-attenuation systems utilizing ground-level, wind-dispersed smoke screens for the protection of large areas from the thermal radiation of nuclear weapon detonations. The approach taken has incorporated two separate but closely related objectives:

1. Develop an interim smoke screening system to the point that prototype designs can be made.
2. Develop improved or second-generation smoke screening systems through the design feasibility stage.

The scope of work included the following: (1) evaluation of liquid-fuel and solid-fuel smoke generators; (2) a theoretical-computational study concerned with determination of the optimum particle size distribution of various smokes; (3) conceptual designs of control, initiation, and installation components for smoke screening systems; (4) investigations concerning promising smoke-producing materials and reactions for application in second-generation generators; (5) predictions of the cost and effectiveness of interim systems.

Smoke screen system considerations included attention to meteorological factors, warning time, and the thermal threat from nuclear weapons.

Significant findings are:

1. On a pound-for-pound basis, the liquid-fuel generators produced smoke which is more effective for attenuation of thermal radiation than the smoke from solid-fuel generators.
2. The improved effectiveness of the smoke from liquid-fuel generators over that from solid-fuel generators is primarily due to the higher percentage of carbon present in the smoke.
3. Optimum carbon particle size (diameter) for use in smoke screens was found to be approximately 0.25 μ, with the efficiency being fairly insensitive to particle size over the range 0.2 to 0.3 μ diameter.
4. It was found that catalysts could be used to greatly increase the smoke production from liquid fuels.
5. Smoke screen systems costs were estimated for solid-fuel generators at upwards of $180,000 per square mile of protected area and for liquid-fuel generators at upwards of $50,000 per square mile.
6. The cost-effectiveness study indicated that the costs per added survivor (for a basic thermal countermeasure system costing $100,000 per square mile) ranged from $33 to $500.

Subject Headings: *Smoke screens; Thermal radiation.*

Excerpts from Authors' Summary

VII Suppression of Combustion

Baldwin, R. R., Simmons, R. F., and Walker, R. W. (The University, Hull, England) "Inhibition of Hydrogen+Oxygen Reaction by Ethylene. Part 1. Kinetic Results. Part 2. Discussion and Evaluation of Velocity Constants," *Transactions of The Faraday Society* **62**, 2476–2498 (1966)

These two papers are the latest in a series by the authors on the inhibition of the hydrogen–oxygen reaction by various hydrocarbons. Prior papers have described studies of inhibition by CH_4, C_2H_6, C_3H_8, C_4H_{10}, and neo-C_5H_{12}. The publications cited in the title serve to expand the list to include C_2H_4.

The same experimental technique has been employed in all cases, viz., the determination of the inhibiting effect of the above hydrocarbons at the first and second explosion limits for various $H_2/O_2/N_2$ mixtures. The inhibition was evaluated experimentally in KCl-coated vessels by a measurement of the change in explosion pressure induced by the addition of hydrocarbon. The experimental variables include: (1) vessel diameter, (2) $H_2/O_2/N_2$ mixture ratios, (3) hydrocarbon partial pressure, and (4) initial reactor pressure.

Previous studies on the inhibition by CH_4 and neo-C_5H_{12} have been interpreted to indicate that inhibition is provided by a chain-terminating reaction involving an oxygenated hydrocarbon species. These two compounds, however, apparently reduce the explosion pressure through a different mechanism than do C_2H_6, C_3H_8, and C_4H_{10}. The kinetic results obtained from the C_2H_4 inhibition study are very similar to those previously reported for C_2H_6, C_3H_8, and C_4H_{10}; the efficiencies of these compounds in suppressing explosion pressures are also very nearly the same. Moreover, careful attempts by the authors to detect oxygenated hydrocarbons in the products of a C_2H_4-inhibited system were unsuccessful. It has therefore been concluded that C_2H_4 inhibits the hydrogen–oxygen reaction in a manner closely akin to that of C_2H_6, etc.

The mechanism suggested for the inhibition by C_2H_6 at the second limit is

$$H+C_2H_6=C_2H_5+H_2 \qquad (14b)$$

$$C_2H_5^*+O_2=C_2H_4+HO_2. \qquad (20)$$

[The authors' numbering system is retained throughout this abstract.] This, of course, is to be superimposed onto the over-all H_2/O_2 second limit reaction scheme:

$$H_2+OH=H_2O+H \qquad (1)$$

$$H+O_2=OH+O \qquad (2)$$

$$O+H_2=OH+H \qquad (3)$$

$$H+O_2+M=HO_2+M \qquad (4)$$

$$HO_2\overset{\text{surface}}{=}0.5\ H_2O+0.75\ O_2 \qquad (5)$$

In the case of C_2H_4 inhibition, the formation of ethyl radicals and their subsequent reaction is again the indicated path to chain termination. The ethyl radicals now are formed via

$$H+C_2H_4=C_2H_5^*. \qquad (14)$$

Since the ethyl radicals formed in Reaction (14) contain some 38 kcal of energy they may decompose [Reaction (D)] unless collisionally stabilized [Reaction (S)],

$$C_2H_5^* = C_2H_4 + H \tag{D}$$

$$C_2H_5^* + M = C_2H_5 + M^*. \tag{S}$$

The competition between Reactions (S) and (D) results in a decrease in C_2H_4 inhibition efficiency with decreasing reaction pressure. At low pressures the C_2H_4 reacts according to Reactions (14a) and (15a) rather than by the inhibition mechanism above.

$$H + C_2H_4 = H_2 + C_2H_3 \tag{14a}$$

$$OH + C_2H_4 = H_2O + C_2H_3. \tag{15a}$$

The authors' derivation of the reaction mechanism is thorough and painstaking. Many possible alternatives to the reactions above have been considered and either rejected as inconsistent with the data or far less likely than those comprising the scheme presented. For example, at the second limit, under a stationary-state assumption the mechanism given yields the following relationship:

$$P_2^0 - P = k_{14} i P_2^0 \mathcal{Q} / 2k_2 y,$$

where P_2^0 and P are the uninhibited and inhibited second-limit explosion pressures, respectively, i is the inhibitor mole fraction, y the O_2 mole fraction, and $\mathcal{Q}$ the fraction of C_2H_5 radicals undergoing termination reactions. k_{14} and k_2 are the rate constants for the reactions indicated by the subscripts. The mole fraction of inhibitor required to reduce the explosion pressure to one-half its original (uninhibited) value is denoted by $i_{1/2}$, and is given by

$$i_{1/2} = k_2 y / k_{14} \mathcal{Q}.$$

This expression predicts a direct linear dependence of $i_{1/2}$ on y at constant $\mathcal{Q}$, in direct agreement with the experimental observations. Similar treatments involving termination reactions between O or OH and C_2H_4 do not yield predictions in accord with the observations.

In the second paper the authors have attempted to extract rate constants from the experimental data. Although the technique is adequate for evaluating the relative magnitudes of the constants involved, other measurements must be invoked to arrive at absolute values.

The method employed for the determination of k_{14} yields a value for the ratio $k_{14}/k_2 = 466$. k_2 has been taken from the work of Baldwin and Melvin[1] as 7.5×10^6 liter mole^{-1} sec^{-1} at 813°C. Thus, at this temperature $k_{14} = 3.5 \times 10^9$ liter mole^{-1} sec^{-1}. The variations in experimental data in this case are much smaller than the uncertainty in k_2 ($\pm 50\%$).

k_D is much more difficult to evaluate than other rate constants involved in this mechanism. The expression upon which the calculation of k_D depends includes the ratio $k_D/k_s M'$, where k_s is the rate constant for the collisional stabilization of $C_2H_5^*$ and M', is a modified third-body concentration parameter involving both the partial pressure of a third body and its estimated collisional stabilization efficiency. The authors have used their experimental results and comparisons-of-literature values for deactivation cross sections to derive a k_D, which falls reasonably close to a value extrapolated from existing low-temperature data. It is equally as instructive to use the extrapolated value to derive information about the deactivation efficiencies of the species present.

k_{14a} and k_{15a} are calculated relative to k_2 and k_1, respectively, and as in the case of k_{14} these computations are only as good as the reference rate constant. k_2 has already been discussed; k_1 has been taken from Kaufman and Del Greco's[2] determination of 1.65×10^9 liter mole^{-1} sec^{-1}. In all cases, the authors have plotted their data together with that already present in the literature to arrive at Arrhenius parameters for the reactions involved. Table I summarizes their results.

TABLE I

Rate constants and Arrhenius parameters

Reaction	Number	$k_{813°K}$	E, kcal/mole	log A, liter mole^{-1} sec^{-1}
$H+C_2H_4=C_2H_5^*$	(14)	3.5×10^9	3.18	10.47
$C_2H_5^*=C_2H_4+H$	(D)	3.3×10^8	2.20	8.97
$H+C_2H_4=H_2+C_2H_3$	(14a)	2.5×10^8	9.8	11.0
$OH+C_2H_4=H_2O+C_2H_3$	(15a)	1.1×10^{10}	3.5	11.0

References

1. Baldwin, R. R. and Melvin, A.: J. Chem. Soc. *1964*, 1785.
2. Kaufman, F. and Del Greco, F. P.: *Ninth Symposium (International) on Combustion*, p. 659, Academic Press, 1963.

Subject Headings: ***Explosion limits, of hydrogen-oxygen inhibited by ethylene; Ethylene, inhibition of hydrogen-oxygen explosion by; Hydrogen-oxygen, explosion limits; Inhibition, of hydrogen-oxygen explosion limits; Oxygen-hydrogen, explosion limits.***

W. J. Miller

Rosser, W. A., Jr., Inami, S. H., and Wise, H. (Stanford Research Institute, Menlo Park, California) "The Quenching of Premixed Flames by Volatile Inhibitors," *Combustion and Flame* **10**, 287–294 (1966)

Quenching of premixed fuel-oxidizer flames by volatile additives was studied; the change in quenching diameter with inhibitor concentration was used to measure inhibitor effectiveness. The fuel-oxidizer combinations studied comprised methane–air, methane–nitrogen dioxide, methane–nitrogen dioxide–air and methane–nitric oxide.

Methane–Air Flames

The effect of methyl bromide, hydrogen bromide, and bromotrifluoromethane on the quenching distances of methane–air mixtures was studied. When either methyl bromide or hydrogen bromide is added to a given fuel–air composition, the reciprocal of quenching diameter decreases linearly with the mole fraction of inhibitor in the mixture. When bromotrifluoremethane is added to a fuel–air mixture, the quenching diameter increases linearly with mole fraction of inhibitor.

Other compounds tested for inhibition effectiveness were: sulphur hexafluoride, boron trichloride, boron trifluoride, boron tribromide, phosphorus trichloride, and phosphorus oxychloride. The first three were much less effective than the last three. For near-stoichiometric methane–air flames the addition of a few tenths of a mole per cent of sulfur hexafluoride, or boron trichloride, or boron trifluoride to the combustible mixture increased quenching diameter to some extent. With boron trichloride and boron trifluoride the observed effectiveness indicated some chemical interference with the combustion process.

The compounds boron tribromide, phosphorus trichloride, and phosphorus oxychloride were found to be very effective inhibitors. Quenching diameter was observed to increase linearly with mole fraction of inhibitor. These compounds are comparable in effectiveness and are three to four times as effective as hydrogen bromide.

While most quenching measurements involved methane–air flames, some attention was devoted to the effect of oxygen concentration on the ability of hydrogen bromide to quench other methane–oxygen–nitrogen flames. The measurements revealed that the quenching effectiveness of hydrogen bromide decreases rapidly with increasing concentration of oxygen. It may be concluded that an increase in flame temperature seriously reduces the sensitivity of a methane–oxygen–nitrogen flame to chemical inhibition.

Methane–Nitrogen Dioxide Flames

Quenching diameters of various methane–nitrogen dioxide mixtures were measured. Neither methyl bromide nor bromotrifluoromethane inhibits methane–nitrogen dioxide combustion to a significant extent. The addition of nitrogen or of carbon dioxide to a methane–nitrogen dioxide mixture increases quenching distance more than does a similar addition of bromotrifluoromethane. For all three additives the quenching diameter increased linearly with additive concentration (0 to 20% additive).

Methane–Air–Nitrogen Dioxide

The progressive substitution of nitrogen dioxide for air in a stoichiometric methane–air mixture increases quenching diameter and decreases the sensitivity of the system to inhibition by bromotrifluoromethane. The quenching diameter of the uninhibited mixtures increases from 3.3 mm for no added nitrogen dioxide to 5.0 mm for $NO_2/(NO_2+\text{air})=0.54$, the highest concentration of nitrogen dioxide used. Over the same range of nitrogen dioxide concentrations, the quenching diameter of a given composition increases linearly with the mole fraction of added bromotrifluoromethane.

Methane–Nitric Oxide Flames

The effect of four additives, bromotrifluoromethane, hydrogen bromide, nitrogen, and hydrogen chloride on quenching diameter was determined. For all four additives the quenching diameter increases linearly with the concentration of additive (0 to

10%). It may be concluded that methane–nitric oxide combustion is not sensitive to chemical inhibition. A few quenching measurements with ammonia–nitric oxide mixtures indicate that these flames too are not sensitive to chemical inhibition.

In summary, (a) the experimental results indicate that the nature of the oxidizer is the most important single factor in determining sensitivity to chemical inhibition, and (b) flames involving oxygen as the oxidizer seem to be susceptible to chemical inhibition.

Subject Headings: *Boron trichloride; Boron trifluoride; Bromotrifluoromethane; Hydrogen bromide; Inhibition, of methane flames; Methyl bromide; Quenching diameters; Phosphorus oxychloride; Phosphorus trichloride; Sulfur hexafluoride.*

E. C. Woodward, Jr.

VIII. Model Studies and Scaling Laws

Byram, G. M., Clements, H. B., Bishop, M. E., and Nelson, R. M., Jr. (Southern Forest Fire Laboratory, U. S. Forest Service, Macon, Georgia) "Project Fire Model. An Experimental Study of Model Fires," *Final Report Office of Civil Defense Contract OCD-PS-65-40 through National Bureau of Standards* (June 1, 1966)

After decades of research, the laws governing free-burning fires and their spread still remain to be defined. Part of the problem lies in an inexact understanding of the basic mechanisms and the relative importance of the numerous variables germane to these types of fires.

To study these variables and mechanisms on a convenient and practical basis, scale modeling appears promising. However, scaling laws must be developed to make such tests meaningful. This report concerns efforts to use model crib and pool fires to reveal their physical characteristics and the relationships of wind speed, surface slope, and moisture content to the rate of fire spread.

Thus, the major significance of this report lies not in its specific quantitative findings, but rather in the observed trends which can become so useful in establishing modeling dimensionless groupings for scaling future tests. Some discussion also is included about thermocouple corrections when measuring small laboratory fires where flame radiation effects are comparatively negligible.

Some of the significant findings of this test program, using ethanol pool fires and white fir wood cribs, are summarized below. In calm air, pool flames tend to tilt toward the center of the fire. In even a light wind, however, the flame becomes elongated so as to remain in contact with the horizontal surface in a downwind direction. As the wind speed or pool width increases, the scorch distance resulting from this elongation increases. Pool flames also are displaced upslope on non-horizontal surfaces, in calm air. The buoyant action of the flames thus appears to play a more important role than thermal radiation in spreading the fire.

Crib fires advancing with the wind (headfires) seem to follow a nonlinear increase in spread rate with increasing wind speed, between 2 and 12 ft/sec, depending on crib and fuel bed structure. However, backfires exhibit a rate of spread that is insensitive to wind speed. Thus, radiative and conductive heat transfer to the unburned solid fuel must control the spreading process.

The burnout time τ, or residence time t_r, of crib fires appear to be little affected by wind. Consequently, other basic variables of fire spread such as the average rate of loss of mass G, and the average rate of convective heat output I_a, may similarly be expected to be independent of wind. Tests to confirm these conclusions show that G is a maximum of about the same magnitude at the same position in the burning zone regardless of wind speed. However, the burning zone width becomes greater for a fire exposed to wind.

In calm air, fire spreads at increasingly greater rates for upslopes greater than about 20 degrees, whereas the downslope rate remains substantially constant. At a slope approaching 60 degrees, the front rate of spread becomes twice the rearward one.

Under controlled calm air conditions, the rate of fire spread has a dependency on fuel moisture content M of the form

$$R = -K \log(M/M_{\mathrm{cr}}),$$

where the constant K varies between 0.70 and 0.90 in./min depending on fuel density, and the critical moisture where fire spread ceases varies between 78% and 84%.

In summary, it is found that slope and wind have only minor influence on fuel burning parameters such as residence time or burning rate, although obviously affecting the fire spread rate. Fuel bed geometry, fuel moisture, and other fuel properties appear to influence mass burning rate and burnout time and if subsequent tests show this to hold true for other types of fuels, simplifications in fire modeling laws could result.

Nondimensional relations are derived for scaling future model fires having either a strip or area heat source. It is also suggested that larger dimensioned fires may be needed to reveal whether viscous effects are important in these types of crib fires.

Subject Headings: ***Fire, crib; Fire, pool; Model fires; Modeling, of fires; Scaling, of fires.***

K. M. Foreman

IX. Atomization of Liquids

Benarie, M. M. "A New Method of Measuring Particle Size by Microscopic Examination," *Staub* **26**(5), 207–210 (1966)* (In German)

A new method for particle size analysis is proposed which is based on the use of an optical "sieve" obtained by microscopic examination varying the numerical aperture. This method gives accurate results in the particle size range between 0.5 and 2 μ in the same time required for microscopic examination using an eyepiece grid. This method should, therefore, be preferred to microscopic examination using

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grids. In addition, this method is less tiring for the person carrying out the examination, since he does not compare the particle sizes any more, but only decides whether a picture appears. Finally, the new method eliminates the main sources of errors occurring in the case of optical microscopy which is unsuitable in the range below 2 μ.

Subject Headings: *Microscopic determination, particle size; Particles, size, determination by microscope.*

Eisenklam, P. and Arunachalam, S. A. (Imperial College, London, England) "The Drag Resistance of Burning Drops," *Combustion and Flame* **10,** 171–181 (1966)

The effects of evaporation and combustion should produce drag coefficients for burning liquid fuel drops which are smaller than standard values applicable to smooth inert spheres in steady motion. The film drag will be lessened by an increase in the boundary layer thickness and a reduction of the velocity gradient on account of bulk flow from the surface. The form drag should be reduced by combustion "filling-in" the low pressure region in the wake.

Theoretically, the solution of the equation of motion of the drop with appropriate boundary conditions, coupled with due allowance for heat transfer, mass transfer, and chemical reaction, is intractable. Simplified approaches to the modification of drag coefficients by evaporation have been made for a flat plate and a sphere, and both have been used to suggest significant reduction of drag coefficient below the standard value.

A limited amount of experimental work that supports the theoretical predictions has been carried out, but differences in experimental techniques and the types of flames produced prevent satisfactory correlation of results.

The authors decided to investigate the drag forces acting on single drops of *iso*-pentane, *n*-heptane, and benzene, falling freely in cold oxygen-rich atmospheres. Generally the drop size was less than 2 mm diam and the investigation was carried out with Reynolds numbers between 90 and 400. Drops, produced by a microburette were allowed to fall singly through a gas igniter into the combustion chamber. Their trajectory and size history were recorded by a photographic procedure, in which a stroboscopic flash unit was arranged to produce a series of shadow images of the drop on a photographic plate. The accuracy of the measurement of the time interval between flashes, and hence images, was ensured by tape recording signals initiated by the flash tube. Initially the drag coefficient was calculated from the expression

$$C_d = \tfrac{4}{3}(\rho_l/\rho_g)\, D\, \frac{g[1-(\rho_g/\rho_l)]-a}{V^2} \qquad (1)$$

and Reynolds number was expressed as

$$\mathrm{Re} = DV\rho_g/\eta_g,$$

in which C_d = drag coefficient (dimensionless)
ρ_l = density of liquid (ml^{-3})
ρ_g = density of gas (ml^{-3})
D = drop diameter (length)
g = acceleration due to gravity ($\text{length}\cdot\text{time}^{-2}$)
a = acceleration of drop ($\text{length}\cdot\text{time}^{-2}$)
V = velocity ($\text{length}\cdot\text{time}^{-1}$)
η_g = absolute viscosity ($ml^{-1}\,t^{-1}$).

All physical properties involved were included at atmospheric temperature, i.e., approach conditions.

Two types of flames were detected. Envelope flames were initiated by a prolonged ignition treatment and completely surrounded the drop. Comparatively short ignition led to "side" flames being set-up downstream from the forward stagnation point. Such flames were often unstable and they altered during flight.

Experimental drag coefficients for nonburning drops agreed with the expected standard curve and, while the results for burning pentane drops with envelope flames in varying oxygen concentrations were in similar agreement with the standard curve, those for heptane and benzene in pure oxygen were higher than the standard curve. Drag coefficients for drops of all three fuels burning with side flames in widely differing oxygen atmospheres were less than the standard values.

The deviations measured suggested that mean values of the physical properties involved in Eq. (1) should be used. The results were recalculated using a weighted mean of the properties at the drop surface, at the flame front at an adiabatic flame temperature 3180°K, and for cold approach conditions in the ratio 1:2:1, and the recalculated drag coefficients were 80% lower than the standard values. For Reynolds numbers ranging from 2 to 15, the drag coefficient is approximately 1.0.

Using an approximate theoretical approach, the drag coefficient may be considered to be the difference of two terms. C_d' is the coefficient due to the forces on the control surface, and C_d'' is the coefficient due to vapor momentum leaving the surface, so that

$$C_d' = C_d + C_d''.$$

Comparison of standard values with C_d' and C_d evaluated with mean physical properties suggested that three-quarters of the reduction from the standard drag coefficient is due to flame alone and one-quarter due to the efflux of vapor.

Subject Headings: ***Drag resistance, of burning droplets; Droplets, drag of.***

P. L. Start

Helwig, N. (Experimental Section of the Mining Union, Dortmund-Derne, Germany) "Investigations on the Influence of Particle Size on the Progress of Coal-Dust Explosions," *Staub* **26**, (2), 25–31 (1966)

To investigate the influence of physical and chemical factors on the development of coal dust explosions, the phenomena determining the propagation of an explosion are defined as the specific explosion capacity. An explosion chamber was developed to evaluate this capacity. By varying the diameter of particles and keeping the other factors constant, it is possible to understand the phenomena occurring during explosions on and in coal particles. There are interrelationships showing that, as a function of chemical structure, a solid material reaction develops on the surface which has been changed during explosion. This result is confirmed by rapid pyrolysis tests carried out with coal dust in an inert atmosphere. These tests allow visual observation of surface changes as a function of particle diameter.

Subject Headings: ***Coal dust, explosions; Dust, explosions, of coal; Explosions, of coal dust; Particles, sizes and explosions of.***

Author's Summary

Kallend, A. S. and Nettleton, M. A. (Central Electrical Research Laboratory, Leatherhead, England) "Combustion of Single Coal Particles: Volatile Burning," *Sixth International Conference on Coal Science, Münster* (June 1965)*

Measurements of the surface and central temperatures of captive coal particles during volatile burning have been made. These show that the surface temperature remains more or less constant at around 400°C while the central temperature rises only slowly reaching 400°C just at the end of the volatile burning. It is suggested that heat conduction largely determines the burning time for this type of coal.

Subject Headings: ***Burning, volatile, of coal; Coal, particle combustion; Particles, coal, combustion of.***

X. Meteorological Interactions

Murgai, M. P., Varma, R. K., and Bahl, S. K. (Defence Science Laboratory, Delhi, India) "Natural Convection above Two Axi-Symmetric Fires," *Combustion and Flame* **10**, 240–245 (1966)

This paper treats the interaction between two axi-symmetric turbulent fires in a calm, neutral atmosphere. The paper utilizes the sink-distribution technique as used by Murgai and Emmons[1] for a single turbulent fire. Utilizing a number of approximations, the effect of the interaction between the two fires is obtained. The authors find that the plumes from the two fires tilt toward each other and eventually merge into a single plume.

Reference

1. Murgai, M. P. and Emmons, H. W.: J. Fluid Mechanics *8*, 611 (1960).

Subject Headings: Convection, above fires; Fires, merging of; Plumes.

D. L. Turcotte

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Fosberg, M. A., O'Dell, C. A., and Schroeder, M. J. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service, Berkeley, California) "Some Characteristics of the Three-Dimensional Structure of Santa Ana Winds," *U. S. Forest Service Research Paper PSW-30* (1966)

Foehn winds in southern California, locally known as Santa Anas, are a critical fire weather pattern. They are related primarily to the synoptic-scale pattern, but small variations in the synoptic pattern produce large changes in the mesoscale Santa Ana characteristics. The behavior of large wildland fires is affected by variations in the mesoscale Santa Ana of such features as foehn islands, surfacing, and intensity of outflow. Such variations would similarly affect mass fires resulting from nuclear attack.

The purpose of this study was to determine the three-dimensional structure of the Santa Ana so that its mesoscale morphological behavior could be understood. Data were collected from two Santa Ana events. These data consisted of aircraft traverses and soundings along the air flow path through Cajon and San Gorgonio Passes. Cajon Pass is parallel to the upper flow and San Gorgonio Pass is perpendicular to the upper flow. Wind structures along these cross sections were determined by pilot-balloon soundings and radar-tracked balloons, both for soundings and for trajectories. Radiosonde and rawinsonde observations were obtained at all existing observation locations in the Pacific Southwest. Surface data collected consisted primarily of measurements of winds and temperatures of three networks. The three groups of stations used were the regular Weather Bureau and Federal Aviation Agency, the Los Angeles and Riverside Air Pollution District stations, and a temporary network of stations set up for this study by the Forest Service.

Data were analyzed at the local scale to obtain detailed information of local outflow, and at the mesoscale to determine the three-dimensional structure and the interaction with underlying surface and the synoptic scale features. These analyses were of vertical cross sections and horizontal charts.

The significant features of the Santa Ana, as determined by these two case studies, other less detailed studies of the Santa Ana, and comparison with the data and conclusions from studies in Europe, are:

1. The foehn process is exclusively an isentropic process, except in the lower boundary layer where interaction with local flows, Ekman spiral effects, and barrier effects are important.
2. There is a bispectral distribution of gravity waves. The dominant wave is of the order of 300 km and is produced by the conservation of potential vorticity. The second wave fundamentally a simple lee wave, is of the order of 6–10 km.
3. The long wave, or lee trough, is responsible for the foehn islands on the plain. Minor topographic obstacles intersect the flow in the upper portion of the planetary boundary layer.
4. Foehn surfacing on the plain is related to the intensity of the foehn and to the behavior of the Ekman spiral in the planetary boundary layer. The foehn surfacing along the lee slope of the mountain is primarily produced by suitable wave length and amplitude of the short mountain waves.
5. The intensity of the foehn appears to be related to the gradient of the

Montgomery stream function on an isentropic surface. This surface is in the transition layer between the synoptic-scale flow and the local flow.

6. The release of latent heat, an important aspect of the European foehn but absent in the Santa Ana, appears to influence only the temperature of the outflow.

These features were synthesized into a descriptive model of the Santa Ana.

The most profitable study of the Santa Ana foehn appears to be along two lines, both of which are planned for the near future. Numerical analysis of potential and kinetic energy appears to be the best approach to understanding the intensity of the foehn. The study must recognize the importance of vertical stretching between the isentropic surfaces and the gradient of the Montgomery stream function. The second approach will be a detailed investigation of the local wind interaction with the Santa Ana. Both are planned for the near future.

Subject Headings: *Foehn winds; Santa Ana winds; Winds, Santa Ana, foehn structure.*

Authors' Summary

XI. Operational Research Principles Applied to Fire Research

Broido, A., McConnen, R. J., and O'Regan, W. G. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service, Berkeley, California) "Some Operations Research Applications in the Conservation of Wildland Resources," *Management Science* **11**, 802–814 (1965)

The need for quantitative solutions to the complex problems encountered in the conservation of resources has given rise to the utilization of operations research (O/R) techniques. Examples cited demonstrate the superiority of O/R methods over conventional "rule-of-thumb" wisdom, although the utility of the standard procedure was confirmed in at least one case. Difficulties in applying O/R techniques to conservation problems arose from the implied requirement for establishment of values in common units for all products.

Minimization of Wildland Fire Costs was effected by consideration of three cost categories: (1) losses sustained by fire, (2) fire suppression costs; and (3) presuppression costs. In a recent analysis, Parks[1] concluded that the conventional policy of increased initial attack can decrease total fire costs, a conclusion that was confirmed by the results of a 5-year experiment in which manning was increased on eight National Forests.[2]

Insect Pest Control by Chemical Methods was analyzed by Watt,[3] and others, who developed a computer simulation program for the evaluation of candidate strategies. Based on insect population data from Magdeburg, Germany, a regression analysis indicated that changes in insect population from year $t-1$ to t were better correlated with populations at $t-2$ than at $t-1$. Relative effects of the following strategies were evaluated: (1) Maximum possible chemical control, (2) Optimum strategy from dynamic programming, and (3) Optimum strategy from two-stage look ahead programming. Depending on the structure of the specific problem (i.e., weather

Plant for fully regulated forest by end of transition period			1/	Clear-cut improved stands						Single stand improvement practice 2/3/				Clear-cut unimproved stands						Constraints 4/	
X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	X_{12}	X_{13}	X_{14}	X_{15}	X_{16}	X_{17}	X_{18}	X_{19}	X_{20}		
1	1		1	-1			-1							-1		-1		-1		$\leq$	$A_1 = 0$
		1	-1		-1	-1		-1	-1						1		-1		-1	$\leq$	$A_2 = 0$
				1	1					-1										$\leq$	$B_{1,1} = 0$
						1					-1									$\leq$	$B_{1,2} = 0$
							1	1				-1								$\leq$	$B_{3,1} = 0$
									1				-1							$\leq$	$B_{3,2} = 0$
										1	1			1	1					$\leq$	K_1 = acres
																1	1			$\leq$	K_2 = acres
												1	1					1	1	$\leq$	K_3 = acres
1																				$\geq$	D_1 = acres
	1	1																		$\geq$	D_2 = acres
				$1^b{}_{1,1}$			$1^b{}_{3,1}$							$1^k{}_1$		$1^k{}_2$		$1^k{}_3$		$\geq$	E_1 = volume
			$2^a{}_1$		$2^b{}_{1,1}$	$2^b{}_{1,2}$		$2^b{}_{3,1}$	$2^b{}_{3,2}$						$2^k{}_1$		$2^k{}_2$		$2^k{}_3$	$\geq$	E_2 = volume
c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9	c_{10}	c_{11}	c_{12}	c_{13}	c_{14}	c_{15}	c_{16}	c_{17}	c_{18}	c_{19}	c_{20}		Z (min.)

1/ Plant during interval 1 and clear cut during interval 2 of transition period. It is not meaningful to define activities which would permit planting and harvesting the same interval.

2/ No stand improvement work is considered feasible for the second type of stand constraint K_2.

3/ If the stand improvement practice were partial cutting, some contribution might be made toward satisfying the required harvest schedule.

4/ The 5 constraint classes are defined as:

A_t	Nonstocked acres which become available for planting in time interval t
$B_{i,t}$	Forest stand i modified in time interval t, available for either harvest or further modification
K_i	Existing acres by ith category of forest stand (given age and type of trees), i = 1, 2, 3, available for either harvest or modification
E_t	Required timber harvest for each time interval t.
D_t	Acres required to be planted in period t. The D_t's are a specified age distribution of forest stands at end of transition period of length T

FIG. 1 Timber management as a linear progaming problem: a simple case involving two time intervals and three types of existing forest stands

and ecological responses, increased vigor of the surviving insects), Watts concluded that either of the programming strategies may prove superior. However, in no case was the conventional "maximum control" technique recommended.

A third example was *A Linear Approach to Forest Management*, which provides an operational method for optimizing the multiple use of wildlands by developing an acceptable distribution of forest types to satisfy a specified timber harvest schedule. Format for simplified application to forest management solely for timber production is presented in Fig. 1, which identifies dynamic formulation of a linear programming problem, subject to five major classes of constraints. Extension of this technique to multiple-use management of a given wildland area requires establishment of policy goals and evaluation criteria for each usage; e.g., man-days of use for recreational areas, monthly variation of availability for water supplies. Once formulated, solutions will permit ready evaluation of administrative policies with respect to forest lands. Limited empirical work at the Pacific Southwest Forest and Range Experiment Station indicates that conventional techniques are frequently the least optimum of alternative procedures.

Simulation Techniques in Wildland Management included two examples:

1. Simulation of *Tree Farm Management* involves simulation of the production of a single class of timber as a function of time for a thousand acres of uniform site and specified acreage distribution of initial age classes of trees. Initial results

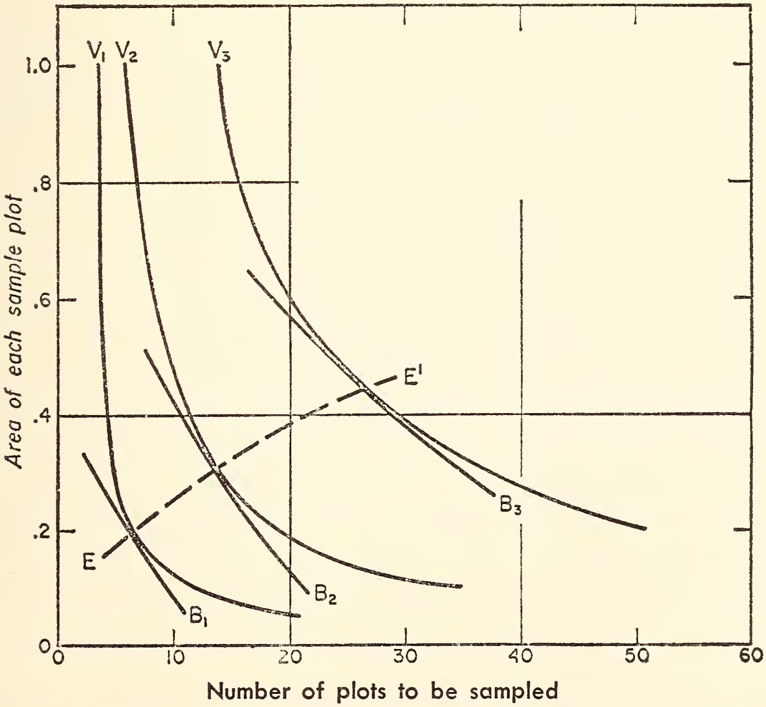

FIG. 2. Schematic relationship between sample plot size and number, confidence interval half-widths (V), budgets (B), and line of efficient sampling rules (EE^1).

demonstrate the importance of recognizing and allowing for the elements of uncertainty in the decision-making process.

2. *Computer Model for Sampling Studies* provides a sampling plan which defines the fundamental probability set. Empirical work related area of sample plot to number of plots to be supplied for each of several confidence levels (V), and identified minimum cost (B) with each confidence level curve. As shown in Fig. 2, the optimum sampling plan is represented by the curve $E-E'$, i.e., the locus of all points of tangency between corresponding V and B curves.

References

1. Parks, G. M. and Jewell, W. S.: "The Development and Application of an Analytical Model for Initial Attack of Wildland Fires," *Res. Rept. ORC 64-8*, University of California Operations Research Center, Berkeley, California, 1964.
2. U.S. Forest Service: "Increased Manning Experiment" (C.Y. 1955–59 and F.Y. 1956–60).
3. Watt, K. E. F.: Can. Entomologist *95*, 525 (1963).

Subject Headings: *Chemical control, of insects; Conservation, of wildlands; Forest management; Insect control, by chemicals; Wildlands, conservation of; Wildlands, fire in and management of.*

C. C. Miesse

Mikelonis, E. C., Shearer, R. P., and Duguay, G. L. (HRB-Singer, Inc., State College, Pennsylvania) "Preliminary Infrared Fire Mapping Systems Analysis," *Final Report under Contract OCD-PS-65-6 Office of Civil Defense through U. S. Naval Radiological Defense Laboratory* (November 1965)

The problems of detecting and monitoring fires that would result from a nuclear attack on the continental United States have been analyzed in order to determine the necessary characteristics for an airborne infrared fire mapping system. Although local units would fight local fires as they occur, a coordinated fire-fighting effort which commits extensive fire-fighting resources must be based upon a coherent plan established by analyzing information about distinctive fire characteristics, local environment conditions, and terrain features. The use of infrared mapping systems for this information appears to offer superior intelligence information because of the ability to see through haze, smoke, and other suspended particles. The Air Force has the responsibility for high altitude post attack damage assessment within an hour to provide the initial information for national policy decisions. However, this data will be inadequate for the operational aspect of our survival and recovery programs on the state or local level. A 5000 to 15,000 feet infrared survey would, however, provide imagery of reasonable resolution quality at three to six hour intervals in order to minimize loss of life and resources. The essential components of the instrumentation would be an airborne platform, a detector-scanner-recorder package, and a processer.

Military aircraft, in addition to being targets themselves, will be, to a large extent, committed to military missions. Considerations of the available personnel, deployment of aircraft, esprit de corps of alternative organizations, and similar factors show that the Civil Air Patrol is the outstanding civilian organization capable of post-attack fire mapping. Of course, in practice, each state would probably determine an optimum blend of business, private, Forest Service, CAP, military, and other available aircraft.

The critical areas that may be attacked have been defined on the following basis:

Military Targets—An area containing retaliatory forces and hardware or directly supporting a retaliatory effort. This would include all SAC missile and air bases, certain Naval installations, and their headquarters. Also included are Air Defense bases and their headquarters.

Economic—Political Targets—An area that has value added by manufacturing of $150 million; or a value added by manufacturing of $75 million and containing a State Capital; or a value added by manufacturing of $50 million and by being the manufacturing center of important military products.

Miscellaneous Targets—Dams which generate more than 300 MW, locks, and manufacturing centers of nuclear weapons.

The surveillance zones that would be covered by the IR mapping would include all economic-political targets in their entirety and, in addition, the 320 square miles surrounding any Standard Metropolitan Statistical Area, any city of greater than 25,000 population, and any State Capital contained within, overlapped by, or in the close proximity to any military and/or miscellaneous target area. Thus there would be 124 economic-political targets, 85 military targets, and 18 miscellaneous targets. The surveillance zones would include 60.5% of the population and 75.2% of the total value added by manufacturing in the United States but would comprise only 5.2% of the land area.

In order to implement such a plan at least three aircraft must be assigned to each mapping system to assure a high probability of having one aircraft survive the attack. The missions should be controlled by state level Civilian Defense officials since they are in the best position to coordinate the survival and recovery operations within their own states. Some incentive, at least in the form of reimbursement of expenses, will be required to persuade aircraft owners to modify their aircraft and to accomplish the required training in order to be in a position to perform the mapping missions. The IR units should be stored in a hardened shelter except when in use for training or actual mission performance (declassification of the unit would greatly simplify the problems of storage, control, and use of this equipment). With the type of aircraft that would be available, all the critical areas in the United States could be mapped in less than 3 hours with 149 IR units, in less than 6 hours with 94 IR units, and in less than 12 hours with 63 IR units.

Subject Headings: ***Fire mapping, by infrared; Infrared, fire mapping; Mapping of fires, by infrared.***

T. P. Anderson

XII. Instrumentation

McCarter, R. J. and Broido, A. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service, Berkeley, California) "A Calorimeter for Determining Radiation and Convection in Small-Scale Combustions," *Paper Presented a Spring Meeting of the Western States Section of The Combustion Institute, Denver, Colorado* (April 1966); *Pyrodynamics* **4**, 191–203 (1966)

A "bench-top" calorimeter (Fig. 1, p. 223) was constructed to determine the radiation–convection partition of energy released in the burning of fuel. Samples of 1 to 2 g, no larger than 4 cm in horizontal dimension, and with flame height less than 15 cm can be accommodated. The apparatus functions by (1) absorbing radiant energy from the burning fuel in an insulated thin aluminum shell whose temperature rise is recorded by a series of imbedded thermocouples, and (2) measuring convective energy by recording the electric power required to heat an air stream so that it just balances the flow rate and temperature of gases convected from the combustion zone. The apparatus can be used with both liquid and solid fuels and for both glowing and flaming modes of combustion.

Subject Headings: *Calorimeter, for radiation and convection; Combustion calorimeter, for radiation and combustion.*

Authors' Abstract

Wilson, R. A. and Noste, N. V. (Intermountain Forest and Range Experiment Station, U. S. Forest Service, Missoula, Montana) "Project Fire Scan Fire Detection Interim Report, April 1962 to December 1964," *U. S. Forest Service Research Paper INT-25* (1966)

The objective of this study is to develop improved means of fire detection, fire mapping, and the measuring of rates of fire spread based on infrared surveillance. This report covers three phases of investigation.

The first phase was exploratory in nature and was to assess the type and difficulty of the technical problems inherent in airborne infrared fire detection. An infrared optico-mechanical receiver was installed in a modified Beechcraft AT–11 aircraft, having a 12.7 cm diameter cathode tube rendering map-like imagery of 4 milliradian resolution. Continuous strip photo recordings were made of the cathode tube readout. Simulated fire "targets" were produced using 35.5 cm diameter buckets, 22.8 cm deep, partially filled with sand and containing initially 4.54 kg of charcoal as the burning medium. Aerial fire spotting was attempted during both night and day using the infrared detection system over forested test areas in which the fire "targets" had been placed. Problems encountered included the following:

Navigation was difficult and unsatisfactory using the cathode scope only. Use of known check points and dead reckoning were required to assure proper identification of location.

Daytime detection was difficult. Best daytime observations were made with an indium antimonide detector with a 4.5 to 5.5 micron wavelength filter, but the

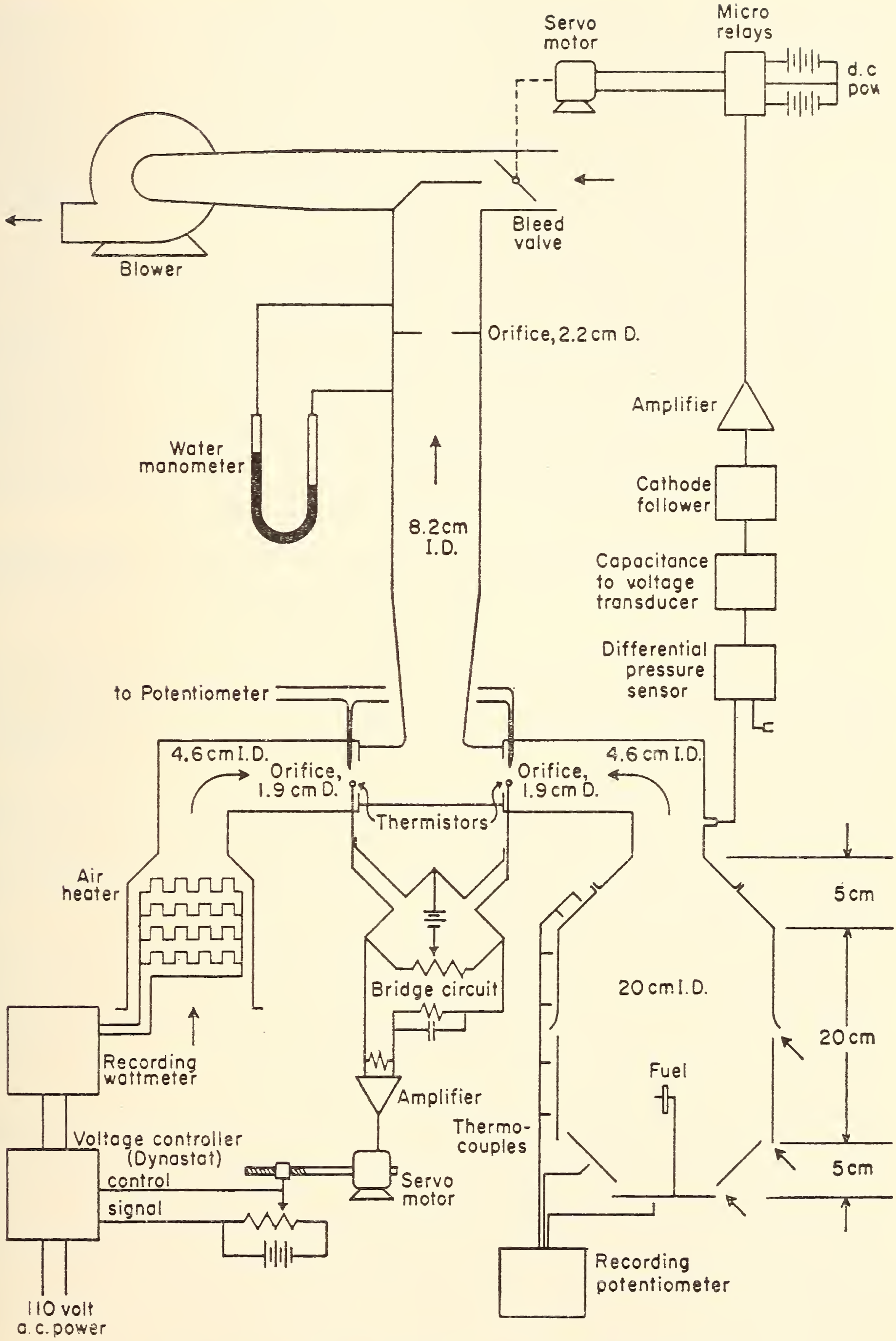

FIG. 1. Schematic diagram of calorimeter controls and air flow.

results were still marginal, to the extent that daylight detection trials were discontinued. [*Since daylight is rich in infrared radiation of the wavelengths to which the detectors evaluated in this study are sensitive, daylight interference poses a problem. Earlier studies conducted by the Walter Kidde and Co. for the Engineer Research and Development Laboratories, U.S. Army, indicated some promise for fire detection in daylight detector and filter combinations sensitive only in wave bands of the infrared corresponding to water and carbon dioxide absorption in the earth's atmosphere.*—Abstracter's Note] Night-time detection was accomplished using lead sulfide or indium antimonide detectors without filters.

The photo-recorded imagery required considerable judgment in extracting data, and its value was often questioned because of improper film exposure.

Based on the test results of this phase, the authors concluded that the detection probability was a function of forest type, stand density, vertical angle (angle between the line of sight from detector to target and zenith), and horizontal ground distance. In addition, based on one test flight they concluded that a scanning system of 2 milliradian resolution (such as used in that one flight) would achieve better results than the 4 milliradian resolution system, particularly in denser stands. The authors noted that, although this study phase was essentially exploratory in nature, it provided orientation in problems of airborne experimentation.

In the Phase II, test areas were selected for diversity, stand density, and form. A target array of five 0.093 square meter area buckets placed on a radius of ca 1, 2, 3, 4, or 5 m was used in lieu of a single fire target. Film recording of the cathode scope was discontinued.

Data indicating detection probability were developed for four representative coniferous timber types, and a positive correlation was observed between the fire target pattern radius and the detection probability up to a radius of from 3 to 4 meters. Detection of targets viewed at angles greater than 50 degrees from the vertical was unsatisfactory.

Problems unsolved at the end of the second phase concerned inadequate sensitivity of the test system, limitations of the test aircraft (the same as used in the first phase) with respect to altitude and navigational capabilities, inability to evaluate timber obscuration factors from the flight path, and lack of rapid photographic recording of the cathode scope readout.

The phase III program based on the results obtained in Phase II was conducted in two parts. In the first part, on U.S. Air Force Convair T–29 aircraft was used equipped with a Doppler radar navigation aid, a new infrared scanning and image system with a higher resolution cathode tube, and a continuous strip photographic readout. A pulse-height discrimination circuit was incorporated in the detection system.

In the fire patrol mission flown in August 1964 two flight passes were made. The results were not considered satisfactory and it was decided to continue the Phase III study from a fixed mountaintop test site. A suitable mountaintop site was selected, and the video electronics used during the flight part of the program were discarded and an oscilliscope was substituted with supporting circuitry to give a "pulse" readout. As a signal readout, notation was made of the pulse height response to the target signal, or a photograph record was made of the trace. The scanner azimuth was precisely controlled enabling detailed observation of individual optical sweeps of the scanner. Also by back sighting from the fire target areas on a

100 watt incandescent lamp located adjacent to the detector the test personnel could estimate the extent of foliage obscuration along the scanning line of sight.

The objectives of this part of the program were to determine detection probabilities at view angles of over 50 degrees; study in greater detail the effects of obscuring factors, sizes, types of canopy, etc.; determine the effects of background temperature, target emissive area, and scanner field of view on the signal to noise ratio and the detection probability.

Based on the results the authors present a discussion of the data obtained and an analysis of the apparent sensitivity of the detection system (output voltage response to the watt per sterradian effective target emission). They state, however, that the results of this first mountaintop series of tests should be regarded as inconclusive, since difficulty was encountered in characterizing the target area timber stands, the sampling of percentages of detection versus vertical angle was poor (indicating a requirement for larger test plots than those used), and the electronic equipment was limited in dynamic range and linearity.

In this report, 33 figures are included showing test configurations and the correlations of results. Five appendices are included presenting test area descriptions, and problems associated with radiation detection, including atmospheric absorption.

Subject Headings: *Fire, detection, by infrared; Infrared, fire detection.*

J. E. Malcolm

Hayhurst, A. N. and Sugden, T. M.* (University of Cambridge, Cambridge, England) "Mass Spectrometry of Flames," *Proceedings of the Royal Society* **A293,** 36–50 (1966)

The ionization of Na, K, and Li in an enriched H_2–O_2 flame has been studied from the standpoint of actual ion-concentration profiles and the determination of the origin of each of the ions detected. The detector used was a quadrupole mass spectrometer mounted directly above the flame holder. The flame itself was directed onto the apex of a thin 60° angle cone with orifice openings of 0.002 to 0.006 in. Flow rates through the orifice were determined to run from 0.5 to 2.4 cm^3/sec at S.T.P. A 6 in. diffusion pump kept the pressure down in the interim chamber between the orifice and the quadrupole housing. An interspersed hollow conical electrode is maintained at a negative potential so that negative ions can be rejected and positive ions separated from the main body of neutrals before entering the analyzer tube. The pressure inside the latter tube is maintained at $<10^{-5}$ mm by additional pumps and cryogenic traps. The housing itself is at 200 V during positive ion analysis. The R.F. quadrupole supply is capable of an output of 450 W at 2.8 Mc/sec. The mass spectrum is scanned manually by varying the output of the generator while holding the pole plate voltage ratios constant. Each mass number was resolved by a specific value for the plate potentials and transmitter frequencies.

The ion collecting efficiency of the system is claimed to be only around 2%. This is principally due to ion–molecule reactions or collisions occurring in the interim

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* T. M. Sugden now at Thornton Research Centre, "Shell" Research Ltd., Chester, England.

chamber. The detector is a Faraday cup (−50 V) connected to a vibrating reed electrometer. Calibration of the mass scale is accomplished by putting known metal ion generators into the flame. The base detectability of the instrument is 10^5 ions cm^{-3}.

The flame mixtures used were 4:1:4 and 3:5:1:3 by volume $H_2:O_2:N_2$. Temperatures were measured by Na D-line reversal. Calculation of the equilibrium concentrations of H_2O, H_2, H, OH, and N_2 for both of these flames showed that in actuality the concentration of OH and H are usually much greater than the equilibrium value. The entrainment of sheath air prevents accurate composition analysis of the flame more than 2 cm from the hot reaction zone.

No negative ions were detected when flames were burnt without additives. Many varieties of negative ions are found in the cool outer areas of the flame. Only OH^- and Cl^- were found in the hot region of the flame. K^+ is the principal positive ion found.

The route toward negative ion formation is through dissociative attachment

$$HCl + e^- \rightarrow Cl^- + H$$

$$HOH + e^- \rightarrow OH^- + H$$

based on the observed and calculated values of Cl^- and OH^- and the values of $H = 7H_e$ equilibrium 1 cm from the reaction zone. The rates of production of the Cl^- by three-body reaction is smaller by a factor of 4 than that observed. The OH^- rate of formation observed is not in perfect agreement with that predicted by the dissociative attachment mechanism. Much better agreement would be obtained if the electron affinity of the OH radical was about 33% lower.

Positive ions detected after addition of the respective metal halides were A^+ and the monohydrate A^+H_2O. The H_3O^+ ion is present with no halide addition and is observed to drop very rapidly upon addition of NaCl to the flame. Na^+ and Na^+H_2O concentrations rise very rapidly within the reaction zone. The ratio of Na^+/Na^+H_2O rises very fast until it decays toward an equilibrium value. This suggests the possibility that equilibrium is attained,

$$A^+ \cdot H_2O \rightleftarrows A^+ + H_2O$$

The disappearance of H_3O^+ is first order in (H_3O^+). The mechanism fitting the data for $(Na^+ \cdot H_2O)$ and (H_3O^+) as a function of distance from the flame reaction zone suggest the exchange reaction of

$$H_3O^+Na \rightarrow H + Na^+ \cdot H_2O$$

or the ion–molecule reaction

$$H_3O^+ + Na \rightarrow H_2O + H + Na^+$$

It is not possible to distinguish the reaction mechanism in the current system.

Hydrocarbon impurities in the gases are thought to influence greatly the high rate of ionization of Na in the flame zone. Electrons are produced by the reaction of CH radicals which react with O atoms.

$$CH + O \rightarrow CHO^+ + e^-$$

These electrons are "hot" in the sense that thermal equilibration of the former is delayed by interaction with molecules with a small vibrational disequilibrium.

Sodium D-line reversal temperatures did not show high flame zone temperatures. Some question still remains on the suggested mechanism,

$$Na+e^- \rightarrow Na^+ + 2e^-$$

Subject Headings: *Flame, mass spectrometry of; Mass spectrometry, of flame.*

P. Breisacher

XIII. Fire-Fighting Techniques, Equipment

Kollmann, I. F. and Teichgräber, R. "New Test Procedures for the Determination of the Inflammability and Fire Retardant Properties of Woods and Laminated Woods," *Mitt. Deut. Ges. Holzforsch* **50**, 186–194 (1963)

A comparison of the fire-retardant properties of wood when the procedural tests have been conducted by one of many different methods is difficult. To evaluate these tests on the same material, it was necessary to build or purchase the equipment for the most commonly employed procedures used up to 1959: (1) Firetube (Truax-Harrison); (2) Firescale (Seekamp); (3) Fire Chimney; (4) Fire Chamber (Brauns); (5) English Procedure; (6) Inclined Panel.

The reduction in weight of a laminated or layered wood sample as a function of temperature rise was determined by methods (2), (4), and (6). The results were so greatly different that they cast doubt about all of the procedures. The physical situation shows that loss of weight occurs slowly until the flash point is reached. The measurement of this temperature is subject to great differences by various test procedures. In procedure (2) a determination of the side flared by the flame and the unexposed side is made simultaneously. Procedure (6) measures only the unexposed side temperature. Results of comparison tests show greatly varying values for the flash point.

The loss of weight is a function of the retardant treatment history of the sample. This is especially true of the laminated woods. One thing is clear, the greater the weight loss rate the more vigorously the burning rate.

Tests on fir oak, plywood, wood fiber, and laminated slab samples showed that the sizing or gluing of these materials must be done in conjunction with fire-retardant impregnation procedures; otherwise, the properties of an identical sample will vary greatly under even the same test procedure. The change in the air temperature above a test sample as a function of test time will also serve to determine the differences in fire protection afforded untreated and treated woods and wood laminates.

Subject Headings: *Fire retardants, tests for; Flammability, of wood; Wood, flammability and fire retardance in.*

P. Breisacher

Marcy, J. F. (Federal Aviation Agency's National Aviation Facilities Experimental Center, Atlantic City, New Jersey) "Interior Material Finishes," *Fire Technology* **2,** 321 (1966)*

Passenger cabins of modern transport airplanes are vulnerable to accidental fires. There is difficulty in extinguishing latex foam fires. Polyurethane foam burns more rapidly than the vinyl or latex foams, but unlike the latex does not smolder. Only vinyl foam cannot be ignited to a self-sustaining fire in the seat cushions. Fiberglass covering prevents flame and fresh air from reaching the flammable foam padding. Once the covering material is destroyed, the foam padding burns rapidly.

Subject Headings: *Aircraft, interior materials, Fire, in latex foam, vinyl foam, and urethane foam.*

Nash, P. (Joint Fire Research Organization, Boreham Wood, England) "Fire Protection in Factories," *The Plant Engineer* **10,** 36–42 (1966)

This paper, originally presented at a meeting of the British Institution of Plant Engineers, deals with a survey of fire costs and fire prevention, detection, and extinction as practiced in Great Britain.

During 1964 and 1965 fire losses in Great Britain were over $200 million compared to $180 million in 1963 and $150 million in 1962. About half of these losses were due to a small number of large industrial and commercial fires.

In considering a fire prevention system, in order to provide appropriate response mechanisms to the threat of fire, it is necessary to understand all parameters that can affect safe operation within suitable limits.

Two safety devices which are being used to combat the spread of fires due to combustion of gas and vapors in industrial plants are the flame arrestor and the explosion relief vent. Flame arrestors quench the flame of an explosion and prevent its propagation. They do not primarily lower the explosion pressure. The explosion relief vent complements the flame arrestor because it lowers explosion pressure, although it does not prevent flame propagation.

Fire detection is commonly based on either the heat sensing principle or the smoke sensing principle. Other methods such as infrared and ultraviolet radiation emission and ultrasonic techniques are now receiving attention for fire situations requiring high sensitivity. The heat-sensitive fire detection system, which is operated by hot gases rising from a fire, is the one most commonly used in enclosed areas. The convective heat transfer from the hot gases to the sensing head raises the temperature of a sensing element, which results in a change in its physical properties. An alarm circuit is triggered when a predetermined change has occurred. Typical heat-sensing elements include fusible links, bimetallic strips, thermocouples, fluid-filled tubes, and electrical conductors.

The response time of a heat-sensitive system depends on several factors including the rate of growth of the heat output from the fire, the area and thermal capacity of the element, the temperature setting of the detector, and usually the height of the ceiling in the area in which the detector is mounted.

* Abstract by Editor of *Fire Technology*. Reprinted by permission.

Smoke detection systems are of two types: the ionization chamber type and the optical type. The ionization chamber operates on the principle that smoke will absorb or deflect ionizing particles, thus causing a change in an otherwise constant ionization current. The optical detection system depends on a change of intensity of a light beam which is scattered or absorbed by smoke particles in its path.

The agents available for fighting industrial fires include water, foam, dry powders, vaporizing liquids, inerting gases, inert gas foams, and high expansion foams. Automatic water spray systems can be used to extinguish flammable liquid fires and for cooling and extinguishing mixed fires of flammable liquid and hot metal. Spray droplet size is critical in the control of flammable liquid fires. Protein based foams extinguish flammable liquid fires by forming a protective blanket which starves the flame zone of oxygen. Dry powders are very effective on flammable liquid fires because of their fast action. They have higher effectiveness on a weight basis than foam. Dry powders lack the capability for post extinction protection. Under windy conditions their performance is reduced. Inert gases extinguish fires by oxygen dilution down to a level of 5% to 14% oxygen. Oxygen removal can be accomplished using a gas turbine inert gas generator. The inert gas generator can also be used to produce high expansion foam. The foam prevents loss of inert gas when filling large volumes of a building on fire. Gaseous carbon dioxide continues to be the classic inerting agent. It has been used many years to protect manufacturing processes. Liquid nitrogen has not come into general use because of handling problems. Vaporizing liquid agents have not come into general use because of toxicity problems.

Subject Headings: ***Fire, detection, extinction, prevention, protection, in factories; Factories, fire prevention in.***

A. L. Goldstein

Nash, P. (Joint Fire Research Organization, Boreham Wood, England) "Fire-Resistant Lifeboats for Oil Tankers," *The Engineer* **221**, 508–510 (1966)

This article specifies the basic requirements for the survival of lifeboats and crews of oil tankers, and examines solutions to some practical problems. The suggested main design requirements are:

(1) Air temperature in a lifeboat should not exceed 70°C after five minutes exposure;
(2) Oxygen concentration should be at least 19% by volume during the five-minute period;
(3) The CO concentration should be such that the product of time in hours and concentration in ppm should not exceed 300.

One of the simplest ways of providing a protected enclosure is to cover the accommodation space of a lifeboat by a rigid canopy and maintain a water film on the canopy and hull. For a 24 ft to 26 ft lifeboat of 8 ft to 10 ft beam, the total exposed surface of hull and canopy will be about 400 ft^2. The water film required to absorb all the heat radiation from a large spill fire of oil which corresponds to about 3 cal cm^{-2} s^{-1} could theoretically be provided by a uniformly distributed flow of about

22 gal/min. The air withdrawn from within the canopy by an internal combustion propulsion engine, and the air converted to carbon dioxide by breathing, must be replaced by fresh air from a compressed air supply.

Several types of lifeboats with canopies, protected by water sprays, were tested by subjecting them to fire involving 500 gal of kerosine in a tank 35 ft by 50 ft. The boats tested included one with a steel hull and asbestos canopy, a steel hull with treated fabric canopy, an aluminum hull with untreated canvas canopy and a glass-reinforced plastic hull and sectional canopy of the same material. The protective film was created by pumping water at 120 gal/min through distribution pipes.

Two other methods of protection were described. One method which avoids the distribution difficulty of the water-wetted canopy is to cover the exposed area of hull and canopy with a rigid heat-insulating material. Another method would be to construct the hull and canopy as a water jacket. Water from the sea, below the oil layer, would be pumped into the water jackets at the lowest points and allowed to spill out at the top of the outer skin of the jacket.

Subject Headings: *Fire-resistant life boats; Life boats, fire-resistant.*

K. Sumi

Rasbash, D. J. and Langford, B. (Joint Fire Research Organization, Boreham Wood, England) "The Use of Nets as Barriers for Retaining High Expansion Foam," *Fire Technology* 2, 321 (1966)*

In a fire situation in a large compartment, barrier nets can be lowered to retain high expansion foam in the subdivision involved. The hole areas of the test nets vary from 0.0031 sq in. for a nylon net to 0.42 sq in. for an asbestos net. There is no substantial difference between the materials used. Foam heights up to 30 ft can be maintained. For a nonflammable fabric, asbestos or ordinary string net treated with a fire retardant is used. The nets drape around the floor objects, thus confining the foam to the subdivision.

Subject Headings: *Foam, net barriers for; Net barriers, for foam.*

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XIV. Miscellaneous

"National Gypsum's Creative Research and Testing Center," *Fire Technology* **2**, 322 (1966)*

The newly expanded sound and fire testing facilities of the National Gypsum Company's Creative Research and Testing Center in Buffalo, N.Y., has facilities for research and development involving interior and exterior building materials including gypsum, asbestos, cement, lime, wood fiber, paper, metal, paint, plastic, acoustical and joint material. The fire test laboratory includes a tunnel furnace, a wall furnace, and a floor–ceiling furnace designed to duplicate similar equipment of the Underwriters' Laboratories. The possibility of improving and expanding present test methods to permit correlation of the results with field results is to be explored.

Subject Headings: *National Gypsum's Creative Research and Testing Center; Testing Center; Research Center.*

Malhotra, H. L. (Joint Fire Research Organization, Boreham Wood, England) "Fire-Resistance of Brick and Block Walls," *Joint Fire Research Organization Fire Note No. 6* (1966)

Consolidated data are presented on fire-resistance tests performed on brick and block walls at the Fire Research Station. The tests were conducted on loadbearing and non-loadbearing constructions of various types of bricks, concrete blocks made with dense and lightweight aggregates in both solid and hollow form, aerated concrete blocks and cavity walls. An attempt has been made to indicate the thickness of various materials necessary to satisfy the fire-resistance requirements for different grades. There is need for further investigations to fill in the gaps in the existing information and to make some of the data more precise.

The following table gives the resistance grading for loadbearing and non-loadbearing walls for various materials.

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TABLE 1

National fire-resistance gradings

Construction	Loadbearing							Non-loadbearing						
	Thickness (in)							Thickness (in)						
	6	4	3	2	1½	1	½	6	4	3	2	1½	1	½
Bricks* of fired clay, concrete or calcium silicate unreinforced, unplastered or with C/S† or S/G‡	8	8	8	4	4	4	4	8	6¾	6¾	4	4	3	3
V/G§	8	4	4	4	4	4	4	4	4	4	4	4	3	3
Concrete blocks—Class 1—solid—unplastered	6	6	6	4	4	4	4	6	6	5	3	3	3	2
C/S† or S/G‡	6	6	6	4	4	4	4	6	4	4	3	3	3	2
V/G§	6	4	4	4	4	4	4	4	3	3	3	2½	2	2
Concrete blocks—Class 2—solid—unplastered	—	—	—	4	4	4	4	8	6	6	4	4	3	2
C/S† or S/G‡	—	—	—	4	4	4	4	6	6	4	4	4	3	2
V/G§	—	4	4	4	4	4	4	5	4	4	3	3	3	2
Aerated concrere blocks density 30–75 lb/ft^3—unplastered	9	7	6	4	4	4	4	6	4	3	2½	2½	2	2
Concrete blocks—Class 1—hollow—unplastered	—	—	—	4	4	4	4	8½	6	6	4	4	4	3
C/S† or S/G‡	—	—	—	4	4	4	4	6	6	6	4	3	3	3
V/G§	—	—	—	4	4	4	4	6	4	4	3	3	2½	2½
Concrete blocks—Class 2—hollow—unplastered	—	—	—	—	—	—	—	8½	6	6	6	5	5	5
C/S† or S/G‡	—	—	—	—	—	—	—	6	6	6	6	5	5	4
V/G§	—	—	—	—	—	—	—	6	5	5	4	4	4	3
Perforated fired clay bricks 40–50 per cent solid unplastered, C/S† or S/G‡	—	—	—	—	—	8½	8½	—	—	—	—	—	8½	8½
—50 per cent solid C/S† or S/G‡	—	—	—	8½	8½	8½	8½	—	—	—	8½	8½	8½	8½
—50 per cent solid V/G§	—	8½	8½	8½	8½	8½	8½	—	8½	8½	8½	8½	8½	8½
Fired clay blocks (Outer skin not less than ½ in)														
One cell ≮50 per cent solid C/S† or S/G‡	—	—	—	—	—	—	—	—	—	—	—	—	4	3
One cell ≮30 per cent solid C/S† or S/G‡	—	—	—	—	—	—	—	—	—	—	—	—	6	6
Two cells ≮70 per cent solid C/S† or S/G‡	—	—	—	4	4	4	4	—	—	—	4	4	4	3
Two cells ≮45 per cent solid C/S† or S/G‡	—	—	—	—	—	—	—	—	—	—	9	9	6	6
Three cells ≮70 per cent solid C/S† or S/G‡	—	6	6	6	6	6	6	—	6	6	6	6	6	6

TABLE 1—*Continued*
National fire-resistance gradings

Construction	Loadbearing							Non-loadbearing						
	Thickness (in)							Thickness (in)						
	6	4	3	2	1½	1	½	6	4	3	2	1½	1	½
Cavity wall construction solid—2-in air gap‖														
Outer leaf 4-in brick, or block of fired clay or concrete or calcium silicate														
Inner leaf solid bricks of clay, concrete or calcium silicate, no finish	4	4	4	4	4	4	4	4	3	3	3	3	3	3
Inner leaf Class 1 concrete block (solid) no finish	4	4	4	4	4	4	4	4	3	3	3	3	3	2
Inner leaf Class I concrete block (hollow) no finish	—	4	4	4	4	4	4	4	4	3	3	3	3	2½
Inner leaf Class 2 concrete block (solid) no finish	—	—	—	4	4	4	4	4	3	3	3	3	3	2
Inner leaf aerated concrete blocks—no finish	9	6	6	4	4	4	4	4	3	3	2½	2½	2	2

Class 1 concrete blocks mean those made with foamed or expanded slag, sintered pulverized fuel ash crushed brick, expanded clay or shale, well-burnt clinker and pumice

Class 2 concrere blocks mean those made with flint, gravel, granite and all crushed natural stones

* Bricks are assumed to be solid except for the presence of frogs. Coatings are not less than ½ in thick including the finish coat.

† C/S means cement/sand rendering.

‡ S/G means sanded/gypsum plaster.

§ V/G means vermiculite/gypsum plaster of a mix in the range 1½ to 2:1 by volume. (For clay bricks and other materials with similar surfaces perlite/gypsum plaster may be substituted.)

‖ For loadbearing walls the load is assumed to be shared by both leaves except for fire-resistance periods of 2 h or less.

Subject Headings: *Block walls, fire resistance of; Brick walls, fire resistance of; Fire resistance, of block and brick walls; Walls, block and brick, fire resistance of.*

Author's Summary

Schaffer, E. L. (Forest Products Laboratory, U. S. Forest Service, Madison, Wisconsin) "Effect of Panel Thickness and Noncombustible Inserts on Surface Flammability of Plywood," *U. S. Forest Service Research Note FPL-0152* (January 1967)

Abstract

Douglas-fir plywood in 0.25 to 1 in. thicknesses was evaluated for flame-spread resistance in the 8-ft-tunnel furnace test, corner-wall test, and mild Schlyter test. Under these methods no significant effect on flamespread resistance was obtained by varying panel thickness. Work with noncombustible inserts showed that 1/32 in. asbestos or aluminum sheets employed with thin face veneers in panel constructions could significantly reduce surface flammability.

Conclusions

It can be concluded from this work that:

1. No increase or decrease in surface flammability as measured by three test methods can be attributed to changes in plywood panel thickness.
2. The 1/32 in. asbestos or aluminum sheet inserts when employed with thin face veneers in panel constructions will provide construction resistant to flame spread.
3. Aluminum foil (1/1000 in. thick), when used as a noncombustible insert beneath a thin veneer surface, is not sufficiently durable to resist puncture during fire exposure by the liberated volatiles from the plywood core. This behavior limits the effectiveness of the insert as a flame-spread inhibitor.

Subject Headings: *Flammability, of plywood; Plywood, flammability of.*

Author's Abstract and Conclusions

Steen, H. K. (Pacific Northwest Forest and Range Experiment Station, Portland Oregon) "Vegetation Following Slash Fires in One Western Oregon Locality,' *Northwest Science* **40,** 113–120 (1966)

Frequent examinations of thirteen pairs of plots near Oakridge, Oregon, during the first 11 to 16 years following slash burning, showed some effects of burning logging slash. Significantly more conifer reproduction was found on unburned plots for the first 6 years following slash burning. However, by 7 years, there was no longer a significant difference between conifer stocking on burned and unburned plots.

Significantly more brush covered unburned plots than burned plots for only the first 5 years following burning; by 7 years the differences in brush cover were no longer significant. Snowbrush and varnishleaf ceanothus created dense shade on burned but very little on unburned plots. Total amount of cover of herbaceous plants was similar for both burned and unburned plots, but species composition differed. American twinflower covered much of the unburned area, but little of the burned. Trailing blackberry shaded more of the burned than the unburned area.

Subject Headings: *Slash fires, vegetation following; Vegetation, following slash fires.*

Author's Summary

Wass, C. A. A. "Coal-Mine Explosions and their Prevention: A Review of Recent Researches," *Paper Presented to a Symposium at Imperial College, London, England, 19–21 April 1966. Vol. 2: Shock and Vibration 1966 London: Society of Environmental Engineers.**

This paper describes Safety in Mines Research Establishment's research on the causes, the mechanism, and the means of prevention of explosions. The research is divided into three main parts. First, there is a study of the mechanism of explosion, which includes theoretical work together with experiments on a small scale in a shock tube and at full scale in a new explosion gallery 400 yards long; and coupled with the studies of mechanism are the studies of preventive measures. The second part of the work is the study of the occurrence and behavior of firedamp, particularly the problems of detecting the firedamp and achieving satisfactory dilution with the ventilating air. The third part is the study of possible igniting sources. These include electric sparks and arcs; sparks and heated surfaces caused by frictional effects; and hot products from the discharge of explosives. Studies of the mechanism of ignition by these various means are coupled with studies of ways of preventing such ignitions occurring in coal mines.

Subject Headings: ***Coal, mine explosion; Explosion, in coal mines.***

Wilde, D. G. "Comparison of Extensibility of Liquid Films," *Cnemistry and Industry* p. 764 (7 May 1966)*

A method is described for comparing the surface elasticities of films of aqueous solutions of surface active agents in terms of the size of the bubbles that can be blown from the film under standard conditions. It is shown that changes in surface elasticity resulting from an increase in the hardness of the water solvent can be detected, that agents can be compared with a view to selecting the best for any particular hard water and that the examination of single films permits an indication of the performance, in hard water, of a large scale foam-making apparatus.

Subject Headings: ***Extensibility of films; Film extensibility; Foam.***

XV. Physiological Aspects of Fire

Pryor, A. J. and Yuill, C. H. (Southwest Research Institute, San Antonio, Texas) "Mass Fire Life Hazard," *Final Report Office of Civil Defense Contract N228-(62479)68665* (September 1966)

A program was undertaken to define the life hazard in a mass fire environment resulting from nuclear attack. The nature of casualties and hazards in peacetime

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* Abstract issued by Safety in Mines Research Establishment, Sheffield, England. Reprinted by permission.

and wartime fires was reviewed, and experimental efforts to simulate mass fire situations were studied.

This state-of-knowledge review revealed a number of areas in need of further definition regarding the true mass fire life hazard. These areas have been specified and limited experimental studies conducted in two of them in order to define their significance with respect to the over-all mass fire life hazard.

Subject Headings: ***Combustion, products of; Fire hazards; Hazards, to life, fire; Life hazards, of fire; Shelters, requirements in fires; Survival in fire; Toxicity, of fire.***

Authors' Abstract

Science News 90, p. 300 (October 1966). "Germs Cause Burn Deaths." Reprinted with permission from SCIENCE NEWS, weekly summary of current science› c 1966 by Science Service, Inc.

Evidence continues to mount for intestinal bacteria as causes of shock and death after severe burns.

Two common intestinal organisms seemed to cause and not merely to accompany death in studies on laboratory mice by Dr. Kehl Markley of the National Institutes of Health, Bethesda, Md.

Dr. Markley reported to a conference on early treatment of burns that an animal contaminated with any bacteria runs a higher risk of burn shock and mortality than an entirely germfree animal. Mice contaminated with a particular organism called *Escherichia coli*—a normal inhabitant of man's intestinal tract—had a significantly higher death rate than those not exposed.

Burned mice, both conventional and germfree, were up to 1,000 times more sensitive to *E. coli* endotoxin—a byproduct of the organism—than unburned mice. Dr. Markley found that building tolerance to the endotoxin with a non-lethal injection significantly decreased the mortality risk.

Mice injected with the endotoxin after a minimal burn, however, became more susceptible to challenge by another organism, *Pseudomonas aeruginosa*, considered the biggest culprit in post-burn infection.

Success with vaccine and plasma therapy to combat this organism was reported by Dr. Irving Feller of the University of Michigan Medical Center, Ann Arbor. The organism is very resistant to available antibiotics, and has been virtually impossible to combat.

The newly developed Pseudomonas vaccine and human hyperimmune plasma have been administered to all severely burned patients entering the Medical Center's Burn Unit during the last three years.

Subject Headings: ***Burn deaths, effect of germs in; Germs, factor in burn deaths.***

BOOKS, MEETINGS, ORGANIZATIONS

Books

Weinberg, F. J. (Imperial College, London, England) *Optics of Flames, Including Methods for the Study of Refractive Index Fields in Combustion and Aerodynamics.* Washington, D.C. and London: Butterworth, Inc., 1963.

The heat released during the combustion process in flames causes steep gas temperature and density changes. Through the close relationship between gas density and refractive index, optical observation methods sensitive to refractive index changes have been powerful combustion research tools for many years. As the first authoritative compilation of such methods, this monograph is especially welcome.

It is written for a wide circle of readers, who may or may not be experts in the field. After an excursion into the elements of optics with an introduction to interference of light beams, their deflection in refractive index fields and the influence of temperature, pressure, composition, and wavelength (Chapters 1 and 2), the reader is made familiar with the combustion phenomena in flames, detonations, etc., their optical properties and the practical application thereof (Chapter 3). This chapter discusses combustion of premixed reactants in terms of kinetics, combustion wave structure, propagation, flow pattern, quenching distance, and ignition limits, as well as combustion of nonpremixed reactants (i.e., diffusion flames) which, in spite of its wide practical application, is treated only briefly by other authors, presumably because it lacks the characteristic combustion parameters such as burning velocities, flammability limits, optical and electrical combustion properties determined by fuel concentration, etc. With regard to the optical techniques, the schlieren and shadow methods, the deflection mapping and the interferometric methods are presented in great detail in Chapters 4, 5, 6, and 8.

Advantageous fields of application of the described optical techniques are temperature determinations obtained from refractive index (i.e., density) measurements which not only do not disturb the flame but use all components of the flame and not just, e.g., the rotational temperature of one type of molecular species or the electronic temperature of a certain atomic species, visualization of the reference flame front surface for burning velocity determinations and visualization of ignition, quenching and cooling or heating processes, just to mention a few.

In Chapter 7 the effect of the index of refraction gradient on the observed position of the flame front *emission* is discussed. The effect is small only at low pressures and for slow flames; at atmospheric pressures, light beam angular deflection of 6° can be obtained for optical paths only about 10 times larger than the thickness of the flame reaction zone. A list of used symbols and a list of selected references on high-speed photography and short-duration light sources are welcome additions to the author index (latest references are dated about 1959) and subject index.

Flame emission and absorption from the optical spectroscopy point of view (treated in extenso in the monographs by A. G. Gaydon and co-workers) as well as the discussion of electrically augmented flames and plasma torches were omitted here. Besides the statement on page 92 that the use of flat flame burners is confined to burning velocities ranging from 4–12 cm/sec (the reviewer stabilized flat H_2

flames of up to 400 cm/sec on flat porous metal burners), the main criticism concerns the possibility of using this monograph for quick referencing. To locate a detailed description of the excellent reproductions of schlieren and shadow photographs is sometimes difficult; also, the cross-referencing is somewhat casual; often, e.g., in Chapter 3, the reader is referred to the chapters on optical methods as "below" or "further down."

Much of the work (carried out at Imperial College in London), ideas, and explanations of optical as well as combustion phenomena is original and are presented in great detail. The author has not shied away from clarifying difficult or complex passages or from forcing the reader to think. Thus the reader is provided with a selection of useful criteria (a) for a clear understanding of the origin of refractive index gradients in flames, and (b) helpful in applying the optical methods for their measurement.

Subject Headings: *Combustion; Flame, optics of; Optics, of flame; Retractive index fields in flame.*

U. Bonne

Meetings

Fifth Annual OCD Fire Research Contractors Meeting, Asilomar, California, 2–6 April 1967

Summary

The Office of Civil Defense (OCD) has been committed to a program of fire research since 1955, when the predecessor agency requested formation of the still-active Committee on Fire Research under the National Academy of Sciences—National Research Council. The Committee produced a document in 1959, outlining a desirable program of basic research. This report has served as a programming guide within the Federal government ever since. The major involvement of OCD in fire research began in fiscal year 1962, at the time the Department of Defense assumed responsibility for civil defense. Funding in the general area of fire and countermeasures has been on the order of $1 million every year since then, with about 10% in basic research and the remainder in various applied fields. Most of this effort is managed by Support Systems Research Division; the following quote is the "OBJECTIVE" section of the current fiscal year research and development project card (DD 1498):

> "There is a Civil Defense operational need for information regarding: the effect of *thermal radiation* and *fire* from nuclear weapon bursts on people and urban and rural areas in terms of the nature, extent, and probability of *casualties* and *property damage*; and defense systems to eliminate, minimize and counteract this thermal radiation and fire threat, especially in relation to the fallout shelter program. The technical needs are: an understanding of the phenomenology of *nuclear weapon thermal radiation*, transmission and ignition and fire development (inception to *mass fire*) to permit prediction of the fire

problem; and for analyses and development of defense systems in *thermal hardening*, active thermal *countermeasures*, *rescue and damage control* (includes *fire control* and *extinguishment*)."

At the present writing, there are about thirty active work units in the fire area. Papers on twenty-five of these and four other closely related work units were presented at Asilomar.

The papers were monitored by three discussants who summarized the presentations during the final half-day session. These summaries follow.

Subject Headings: ***Fire research program, Office of Civil Defense; Office of Civil Defense fire research program.***

J. W. Kerr, O.C.D.
M. G. Gibbons, U.S.N.R.D.L.

Titles of Conference Papers

1—Shelter Habitability

2537A	Mass Fire Life Hazard	A. J. Pryor, SWRI
1132A	Fire Test Rating System for Shelter Components	T. E. Waterman, IITRI
2536G	Operation FLAMBEAU—CD Test Design and Experiment	C. P. Butler and W. H. Yundt NRDL

2—Rescue and Damage Control

2512A	Fire Service Capabilities for Rescue	M. Staackmann, URS
2522E	Fire Service Capabilities for Damage Control	W. Reilly, URS
2511B	Rescue Problem Analysis	J. L. Crain, SRI
2522D	Preliminary Aerial Fire Mapping Systems Analysis	R. Sheeder, HRB-Singer

3—Spread of Mass Fires

2536E	Experimental Study of Firebrand Generation	T. E. Waterman, IITRI
2538B	IITRI Fire Spread Model Development and Calculations	A. Takata, IITRI
2538C	URS Fire Spread Model Development and Calculations	C. Colvin, URS

4—Fundamental Fire Research

2531A	Fundamental Fire Research	A. F. Robertson, NBS W. J. Miller, AeroChem J. R. Welker, U. Oklahoma P. L. Blackshear, U. Minnesota

2531B	Committee on Fire Research	R. M. Fristrom, APL (J.H.U.)
2531C	Fundamental Research in Limitation and Control of Fires	A. E. Lipska and K. A. Lincoln, NRDL

5—Fire Start

2534C	Survey of Fuel Arrays Ignitable by a Nuclear Weapon Thermal Pulse	J. A. Keller, Dikewood
2534B	Fire Start Capabilities of Urban Nuclear Detonations	S. Feldman, NASL

6—Fire Defense

2522F	Fire Department Operations Analysis	W. J. Christian, IITRI
2522G	Public Capabilities to Extinguish Ignitions from Nuclear Attack	K. D. Moll, SRI
2526B	Fire Defense Systems Analysis	
2526A	Mathematical Modeling of Fire Defenses	F. Salzberg, IITRI

7—Thermal Countermeasures

2542A	Exploratory Development of Thermal Hardening Measures	N. J. Alvares, NRDL
2532C	Additives to Improve Smoke Generation	T. Goodale, URS

8—Phenomena in Mass Fires

2534D	Feasibility and Representativeness of Large-Scale Boxcar Burns	W. J. Christian, IITRI
2536D	Fire Storm Exploratory Analysis	F. I. John, SRI
2536F	Mass Fire Characteristics and Development	W. J. Parker, NRDL
2536H	Origin and Properties of Fire Whirls	M. G. Gibbons, NRDL

9—Shelter Research Work Units that Involve Fire Research Problems

1623A	Protective Blast Shelter Systems Analysis	L. Pinzow, Bechtel
1614A and 1125A	Shelter Evaluation Program	W. F. Heugel, IITRI
1614B	Civil Defense Physical Vulnerability System	J. W. Crowley, SSI

Status Summary of Research on Fire Effects on Shelters and Personnel, A. J. Pryor, Southwest Research Institute, San Antonio, Texas

The life hazard in a mass-fire environment yields three main elements which require definition: (1) the mass-fire environment, (2) the shelter or any protective barrier, and (3) the man. Each of these requires understanding before analysis of the fire effects on shelters and personnel can be completed.

For discussion purposes, Fig. 1 is representative of the three areas discussed.

We are concerned with those aspects of an attack model that may be used to assess the scope of any fire that results. The next step is to apply the mass fire environment, where it exists, against any shelter barriers in that zone to determine the resulting exposure to the "protected" personnel within. If no shelter or barricade exists, the application is direct.

Assuming that we had (1) a good definition of the mass-fire environment including its spread, growth or decay pattern, and (2) knew the protective capacity of the shelter barriers within the affected area, and (3) understood the physiological limitations of man—we would then be able to determine vulnerability within the area of definition. This survivability (and accompanying damaged model which is also described) would then determine the requirements for rescue and damage control. Application of the rescue and damage control "units" (i.e., those which survive the attack) as soon as feasible would then provide an indication of total survivability and extent of the post-attack damage model.

The questions remain, how much do we know of these areas to determine the *shelter habitability* or the needs and effectiveness of a rescue and damage control system? And, what is presently being done to provide information where none is available?

The first step, *that of defining the mass-fire environment*, has been under study by the USFS, DASA, NRDL, and OCD on a large experimental scale for approximately 6 years. If we are to get reliable quantitative information, these experimental burns at present are the only means.

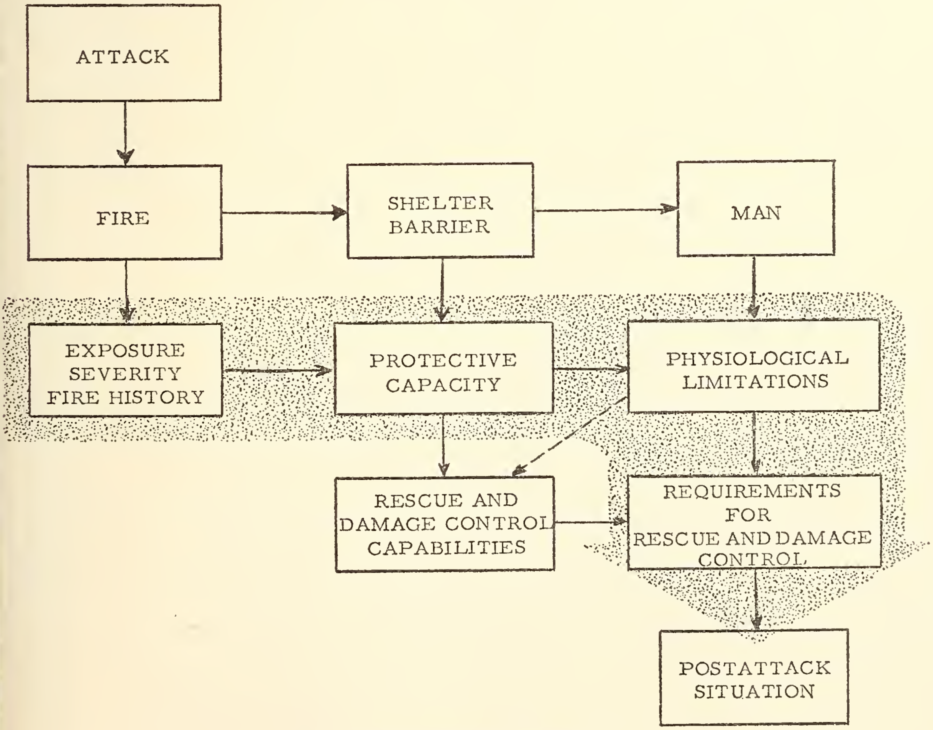

FIG. 1. Mass-fire life hazard elements.

In project Flambeau, all previous fires except the last two were rather limited in scope and provided the base for design and instrumentation of the last two. Nevertheless, these two fires and particularly the last, are expected to yield more basic information about mass fires than any of the previous large burns. At present only one additional large-scale burn in project FLAMBEAU is scheduled for September, 1967, and four or five additional small burns in the Fall of 1967 and Spring of 1968. The single large-scale burn will cover 50 acres, simultaneous ignition of 324 simulated structures. The FLAMBEAU program is planned or funded at this moment only through these burns and the need for continuation of these large-scale burns is essential to further understanding of the mass-fire environment. The need for real data on radiation is an example—what maximum conditions can be expected and for what duration. This applies to complete definition of the mass-fire environment which is the first block in the figure of concern in this status summary.

In addition to these large-scale burns several individual buildings have been burned by IITRI. These structural fires provided information on the levels of heat flux to be expected within various types of structures, the movement of combustion products, their concentrations and the internal pressures developed. While both the large-scale burns and the individual building burns have contributed to the extension of information on fires there is still a pressing need for more definitive data to enable more precise evaluation of this country's defense needs by OCD planners.

The next block in the figure represents the shelter or any protective barrier that may be used in efforts to protect against the attack hazards. Previous work is not adequate for predicting the behavior of various structural elements in the mass-fire environment. Experimental work completed by IITRI does indicate a means for predicting the behavior of homogeneous combustible materials. Logical extension of this work is the development of a relationship for noncombustible materials. This, however, is necessarily a long-range program. To fill the immediate gap a program is being considered presently to provide an answer for common materials found in most shelters. Resolution of this phase allows some determination of the protection factor offered against the fire in a fashion similar to the protection factor offered against fallout. The largest gap in this area is the need for data on gas transmission through shelter barriers.

The remaining unknown in this three-part question is man. After some 23 years, what killed so many people in Hamburg is still open to question. A reasonably accurate assessment of man's vulnerability within a mass-fire environment requires some understanding of his physiological limitations. For OCD purposes this would indicate some knowledge with regard to combustion products (heat, smoke, noxious gases). In September, 1966, SWRI completed a study of the mass-fire life hazard under an OCD contract. This study indicated areas needing further investigation and it has been extended for one additional year at SWRI. This extended work in the form of animal tests is designed to indicate the magnitude of the significance of exposure to a combination of combustion products. This will then allow better interpretation of the data generated by the USFS, NRDL, DASA, OCD, and others in controlled burns with regard to life safety. This may reinforce the present lack of knowledge regarding shelter protection with regard to gas transmission through shelter barriers. IITRI, while studying shelter components, recognized the need for such analysis; however, such evaluations were not included in the scope of their work.

The three areas noted in this summary are receiving attention with experimental study programs. Each is expected to provide better tools with which to estimate the nuclear post-attack situation, to allow the studies of rescue and damage control needs or shelter requirements to evaluate needs more accurately.

These studies will provide needed input to the work underway at URS, SRI, HRB-Singer, IITRI, Bechtel, and System Sciences on damage control, shelter siting, and rescue requirements.

Subject Headings: *Fire, effect on shelters and personnel.*

Status Summary of Research on Fire Phenomena and Fire Spread, S. Martin, URS Corporation, Burlingame, California

The summary will be presented in three parts: (1) fire-spread modeling, (2) mass-fire behavior, and (3) fundamental fire research.

Fire-Spread Modeling

There are basically three different kinds corresponding to three different levels of detail depending upon the nature of the application:

1. Deterministic (point-by-point analyses, e.g., Five-City Study—fire vulnerability of specified resources—structures used as shelter)
2. (Semi)-detailed stochastic (class average properties such as building spacings, dimensions, street widths, etc. These models generally discriminate between spread within block and spread across streets, e.g., *Gage-Babcock Confl. Potential*)
3. Nondetailed stochastic (empiric probability-of-spread functions such as those of Wolverton from World War II). Good for "homogeneous" areas such as narrow streets, blast damaged areas.

Model types 1 and 2 are based on a *radiation-like* spread mechanism as a model concept. This is, they treat pairs of buildings at the spread interface as though spread was governed by heat flux from the source building to the receiver building, and the calculation is based on some geometrical consideration such as configuration factor. Whether spread occurs or not (or alternatively in stochastic models, the probability of spread) is a function of building dimensions, construction features and building separations.

I want to stress the term *radiation-like*; because convection *can* be handled in the models in a credible fashion by suitable addition of convective flux to radiative flux and by judicious choice of fire initiation thresholds.

It should be pointed out, however, that these models suffer some lack of correspondence with reality in that they are based on *ambient* and *undisturbed* characteristics of the target. In other words, they do not account for blast damage or for fire-induced winds and other interactions.

The empiric probability-of-spread functions are neither very reliable nor do they reflect variations in use-class, structural, and other characteristics of urban areas.

Theoretically guided, semi-empirical functions might be derived for a variety of different urban characteristics based on combined mechanisms of radiative and convective heat transfer coupled with short- and long-range brands, but insufficient information is presently available.

Two kinds of information are required:

1. Frequency distributions of structural dimensions, characteristics, and spacings for different urban categories.
2. Basic inputs for convective-heating and firebrand spread.

The first can be obtained readily by survey and from maps. The second should eventually be supplied by experimental studies such as Welker's work on flame-blown fires and Waterman's work on firebrands.

If reliable probability-of-spread functions were available for urban areas of various descriptions, formal fire-spread models, such as the *Phung and Willoughby model*, provide a straightforward means for estimating both rate and extent of fire spread.

Information Needs

1. Free-burning behavior of various classes of structures
    a. Fire history and duration
    b. Spatial and temporal distribution of heat release
    c. Mechanisms of brand generation
    d. Initial trajectories and frequencies of occurrence as functions of size and stage of building fire
2. Fire-initiating potential of brands impacting on various roofs and structural surfaces—with and without accompanying heating by remote sources
3. Behavior and fire potential of fire whirls
4. Fire-spread behavior in blast-damaged structures and debris
5. Influence of multiple fire interaction on fire-spread behavior (e.g., strong, gusty fire-induced winds)

Mass-Fire Behavior

We seem to be a long way from really understanding the nature of mass fires. There seems to be general agreement that they are characterized by a large area of high fire density serving as an intense and extensive heat source to drive a coalesced convection column to heights which are large compared to the height of the lower atmosphere and drawing large quantities of air from the boundary layer at the base of the column. Nonradial components of velocity, possessed by the air drawn in, are thought to be concentrated and to appear as vorticity in the column. This may show up as large-scale rotation in the coalesced column or as relatively localized fire whirls. The source of vorticity could be either ambient rotation or wind shear. Significantly, whenever fire whirls appear in pairs, as they so often do in large fires such as the Flambeau burn of last June, their direction of rotation is opposed, suggesting that they originate from wind shear in the boundary layer, but this is not the only plausible cause. Large-scale circulation, which has been postulated to be important in limiting the inflow of air *above* the boundary layer remains to be demonstrated as an inherent characteristic of mass-fire convection columns.

The Flambeau fires show a great deal of promise as a full-scale means of investigating mass-fire characteristics. However, they are very costly and not many can be burned in a year's time. Reduced-scale models, however, cannot be modeled exactly, because some of the coupled transport processes scale differently. A high pressure test chamber mounted on a centrifuge would allow scaling down by an order of magnitude or so, but this approach seems entirely infeasible.

The dimensionless Grashof number appears to be particularly troublesome, but terms in the heat and mass transport equations that contain the Grashof number become small enough to be neglected if the model fire is not made too small. Even so, the coupling of heat transfer to the fuel and its burning rate cannot be duplicated on a reduced scale. It appears that the best dodge is to artificially simulate the heat-release rate, with electrical heating for example; and to program the heating to approximate the characteristics of a burning city area. The use of a fluid other than air may be indicated for a model of this sort. Nevertheless, some very difficult problems could arise in trying to simulate the fluid mechanical structure of the atmosphere; particularly the turbulent motions in the boundary layer.

Fundamental Fire Research

Studies at AeroChem of ions in inhibited, low-pressure diffusion flames have failed to demonstrate that the electron-attachment affinity of the inhibitors used was a factor in the mechanism of inhibition. Particularly effective agents, such as $Fe(CO)_5$, appear to be acting mainly through the formation of *in-situ* particles which diffuse into the flame zone and act as chain-terminating sites.

In Blackshear's work at the University of Minnesota, a relatively simple dependence of burning rate of solid fuels on fuel size for fully ventilated conditions has been found experimentally for cellulose dowels burning in air. The rate of weight loss is independent of time over most of the period of burning and is related in a simple way to the dimensions of the fuel element.

The burning behavior of pools of liquid fuels is controlled by a combination of radiant heat transfer and convective heat transfer and largely independent of pool diameter for diameters of a few hundred centimeters and up. That is, flames are optically thick and fully turbulent. This suggests that fires several feet in diameter and larger behave like very large fires, and that radiant interactions of multiple-pool fires should be small.

At NRDL, the kinetics of the thermal decomposition of cellulose have been measured up to 350°C. These data are outstanding in that they represent the first kinetic measurements which are clearly *not* heating-rate or mass-transport limited. They give evidence of a change in pyrolysis mechanism from low to high temperatures.

Results also show that when trace catalysts are present, rate of pyrolysis is substantially increased and that char residue is markedly increased approaching the theoretical limit.

Mass-spectrometer results though incomplete indicate a kinetic shift in cellulose pyrolysis at low temperatures (about 230°), and that secondary decomposition occurs to a significant degree. Other results cannot as yet be interpreted mechanistically.

Subject Headings: ***Fire phenomena; Fire spread.***

Summary of Sessions on Fire Start, Thermal Countermeasures, and Fire Defenses, W. J. Christian, IIT Research Institute, Chicago, Illinois

Fire Start

Two major efforts in progress are concerned with fuel-array surveys in Providence, R.I., Albuquerque, N. Mex., and Detroit, Mich. (Keller, Dikewood and Bracciaventi, Naval Applied Science Laboratory). Information gathered includes location, type, and number of fuel arrays, both interior and exterior. Density or frequency of occurrence of fuel arrays would be determined in both programs for various use classes, such as: residences, subdivided according to family units and economic class; industrial, light or heavy; institutional; and commercial.

In both surveys estimates of burning time and heat release are used to judge the ability of fuel arrays to cause sustained fires; however, requirements for production of sustained fires are not yet well defined. Previous Office of Civil Defense research by IIT Research Institute has shown that certain situations invariably lead to sustained fires, but minimum requirements were not determined. However, the results of current investigations for the Defense Atomic Support Agency at the Naval Radiological Defense Laboratory and the IIT Research Institute will provide quantitative data on fire spread between items within a room, as well as on the buildup of fire in an ignited fuel array to full room involvement. When available, these data will permit reassessment of the survey results.

The importance of window coverings in shielding other combustibles from radiation is well recognized. Additionally, a common conclusion of both surveys is that most of the ignitions which occur will be in window coverings. As mentioned, however, the ability of these coverings to cause sustained fires is in doubt.

In Keller's opinion, presently available data on the critical ignition energies of materials are inadequate to cover the wide range of material types encountered. The writer concurs that there will indeed be uncertainty in assignment of critical ignition energies to identifiable materials. Nevertheless, this uncertainty would appear to be much less than uncertainties involved with identification of materials and definitions of requirements for sustained fires.

Immediate use of the data from both surveys will be application to prediction of fire damage in the Five-City Study. Nevertheless, it is inevitable that analysis and generalization of the data will take place so that application may be made to other cities and other attack conditions. Certainly the amount and quality of information available from these surveys is orders-of-magnitude greater than the limited data obtained by Bruce and Downs, upon which a good deal of reliance has been placed in the past.

Related studies, described elsewhere, involve calculation of fire histories and ultimate damage in four of the five cities (IITRI, URS). Included in the URS study are limited fuel array surveys of San Jose, Calif. and New Orleans, La., for the specific purpose of determining ignition densities for the attack conditions of the Five-City Study. The data collected is not intended to be of a general nature, however, and probably will not be useful outside of the intended application. The IITRI program will produce no new data on fuel arrays, but will use data available from the Dikewood and NASL programs. However, limited amounts of data will be collected on window sizes and frequency of occurrence of window coverings in Detroit, San Jose, and Albuquerque.

Thermal Countermeasures

Two experimental programs were described, dealing with methods for reduction of primary ignitions. One concerns reduction of ignitability of materials (Alvares, NRDL) and the other concerns attenuation of radiation by smoke (Goodale, URS).

The former is a fundamental study of the ability of fire-retardant materials to prevent ignition of cellulosic materials by thermal radiation. Present studies involve the use of salts of weak acids and bases, commonly regarded as fire retardants for fabrics. Later work will be directed toward the use of materials which, upon heating, produce flame-retardant gases, diluents, or reduced oxygen content, thereby preventing ignition.

The general conclusion has been reached that good combustion retardants are also good inhibitors of flaming and glowing ignition. However, the applicability of the laboratory results to real situations remains an unanswered question. For example, small pilot sources (such as lint) may negate the fire-retardant effect by igniting combustible gases being driven off by incident thermal radiation. Following the identification of technically feasible fire retardants, the problem will remain of determining methods for durably applying these materials without introducing unacceptable alterations of other material properties.

The URS work is concerned with the improvement of the effectiveness of simple smoke generators previously developed for OCD. Available information indicates that the effectiveness (smokiness) must be increased if costs are to be acceptable. The study is directed at methods for increasing the free-carbon content of generated smoke. Three mechanisms of carbon enrichment are being studied: (1) catalytic dehydrogenation in the gas phase, (2) inhibition of oxidation of carbon, and (3) nucleation of carbon particles.

Preliminary results have shown that smokiness of pool-burning liquids is increased by additives, and the use of some derivatives of the hydrocarbons in liquid fuels.

Fire Defense

One study already in progress (Labes, IITRI), and one just beginning (Moll, Southwest Research Institute), will provide information on the capabilities of the fire services and of the general public to extinguish fires following nuclear attack. IITRI's study of fire department operations involves collection of data on fires in the Chicago area, and analysis and correlation of results. By observations during each fire and interviews shortly afterward information is obtained on time, water, manpower, and equipment required for normal peacetime fire extinguishment. Results obtained by analysis of data from about 70 fires have been correlated to show relationships between time, water, and man hours used, and the maximum floor area involved in fire. Distinction is made between residential and commercial or industrial occupancies.

The information gathered tends to show that the professional fire services will be inadequate to handle large numbers of fires, and that methods for their optimum use must be identified.

The SRI program, which is just beginning, is concerned with the capability of the general public to extinguish ignitions following nuclear attack. The study is intended to tie together previous work on the subject, such as: derivations of procedures, pools of public attitudes, operations analysis, and experimental evalu ations of fire extinguishment capabilities. The final result of the work will be a summary of the ability of the public to extinguish ignitions and prevent fire spread.

The final program discussed (Salzberg, IITRI) will begin shortly, and will be directed toward development of a mathematical model of fire defenses. The study will draw on previous IITRI work, in which the concepts of self-help teams and brigades for fire fighting by the public were developed. As defined, the self-help team consists of two persons with minimal training and equipment, and capable of suppressing fires prior to room flashover. The brigade, on the other hand, consists of four trained persons equipped with ladders, axes, water supply, and booster pump, and capable of extinguishment of single room fires if significant structural involvement has not occurred.

Based on existing data on times required for various extinguishment procedures, relations will be developed between the numbers of brigades, self-help teams, and organized fire department units required for extinguishment of various fractions of the total fires. This information will subsequently be integrated with a fire spread model being developed and determinations will be made of the effects on the over-all fire situations of various levels of suppression effort.

The information obtained from the three programs described above will have direct application to Fire Defense Systems Analysis, which is currently the subject of competitive bidding. That study should ultimately identify the optimum method for integrating the efforts of the general public and the fire services in the suppression of fires following nuclear attack.

Subject Headings: *Fire defense; Fire start; Thermal countermeasures.*

Organizations

The *Interagency Fire Research Committee* has been organized by the Secretary of Commerce at the request of the President's Office of Science and Technology. The function of the Committee is to act as a policy level focal point for fire research activities in the Federal Government. The Committee is chaired by Mr. John P. Eberhard, Director of the Institute for Applied Technology of the National Bureau of Standards. As his Special Assistant, Mr. John F. Christian serves as the Executive Secretary.

LETTERS TO THE EDITOR

Woodland Fire Research and Urban Fire Situations

The argument about the value of "woodland fire research" to "urban fire situations" and vice versa has been raging for many years, all too often along disruptive rather than profitable lines.

It is obvious, as pointed out by Chief Walsh,[1] that urban fire fighters face many problems which the woodland fire fighters rarely, if ever, see. It does not follow, as has unfortunately too frequently been the case, that the two groups should ignore each others' efforts and each act as if the other were working in a remote, unrelated portion of the universe.

Many of the more fundamental fire research studies are equally applicable to woodland and urban fire problems. For example, my own studies on the pyrolysis and combustion reactions of cellulose,[2] while potentially applicable in different ways in the two types of problems, are pertinent to both. However, even more distressing to me is the unwillingness on the part of any fire-fighting agency to learn from the most practical field experiences of another "unrelated" group.

As a case in point, Chief Walsh says "establishing firebreaks and applying special extinguishing agents from planes are inappropriate for fires in buildings." This statement is no doubt true if one considers the usual urban fire situation—involving one or, at most, a very few buildings. However, I have yet to see a meaningful description of how an urban fire department plans to handle a mass-fire situation—like the Chicago fire of 1871, the San Francisco fire of 1906, the Hobart, Tasmania fire of February 1967, or the potentially more disastrous fires of a future nuclear holocaust. Such fires are not going to be fought as single-building fires with thousands of conventional urban fire-fighting units doing simultaneously what each does individually in the usual urban fire situation. If such techniques as establishing firebreaks, either before or during the disaster, are not attempted, such mass fires will burn pretty much at will. Yet for years a number of us with some knowledge of wildland fire-fighting techniques have been trying, with almost universal lack of success, to have "firebreak potential" included in city planning decisions concerning location of freeways, parks, etc. Nor have we seen any alternative plans developed by urban fire departments to better handle the urban equivalents of large-scale forest fires.

Lest the above be taken as a universal condemnation of urban fire departments, let me hasten to add that as our urban areas expand and the distinction between urban and wildland areas tend to disappear, more and more urban and rural fire-fighting agencies see the need to forget past differences and merge their efforts in a common cause. Thus, in the recent Tasmania disaster, major roles were taken by Forestry Commission personnel and Rural Fire Brigades as well as by the Hobart (City) Fire Brigade and its auxiliaries. Nor did the Hobart Brigade feel called upon to protest when the Forestry Commission's Fire Prevention Officer prepared a special radio release urging the populace to keep houses closed and making the rather ingenious suggestion that spouts be plugged with tennis balls and gutters on roofs filled with water to minimize the possibility of burning brands igniting the litter which inevitably collects in such places. Thank God no one will ever know how much worse this disaster, which took more than 60 lives and destroyed more than 1400 major structures, would have been without the active participation of all the fire-fighting agencies in the Hobart area.

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Subject Headings: ***Fire, woodland, simulating urban fire; Fire, urban, simulated by woodland.***

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