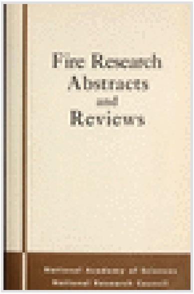

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FIRE RESEARCH ABSTRACTS AND REVIEWS

Robert M. Fristrom, Editor

Geraldine Fristrom, Associate 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.

Editorial Staff: Emma Jane Whipple, Mary L. Swift

Volume 13 Number 1

Fire Research Abstracts and Reviews

Committee on Fire Research
Division of Engineering
National Research Council

NATIONAL ACADEMY OF SCIENCES
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FOREWORD

On November 17, 1970, the President announced the establishment of a National Commission on Fire Prevention and Control, composed of eighteen members. This Commission was authorized in 1968 as part of the Fire Research and Safety Act. It is hoped that this will bring about a thorough survey which will convince the President and the public of the importance of the fire problem and outline a national set of priorities. We in the fire research field feel that the Commission can do the country a great service by underlining this grave problem and thus bring it to public attention. Your editor feels that he speaks for all members of the fire community in offering best wishes and sincere cooperation in this appointed task.

The members of the Commission are:

David K. Wilson, Nashville, Tennessee. President, Cherokee Equity Corporation
W. Howard McClennan, Arlington, Virginia. President, International Association of Fire Fighters
Louis J. Amabili, Hockessin, Delaware. Director, Delaware State Fire School
Tommy Arevalo, El Paso, Texas. Fire Lieutenant
Percy Bugbee, Winchester, Massachusetts. Honorary Member of the Board, National Fire Protection Association
Dorothy Duke, Lorain, Ohio. Housing Specialist in Home Ownership for Low Income Families, National Council of Negro Women, Inc.
Ernst R. G. Eckert, St. Paul, Minnesota. Professor of Mechanical Engineering, University of Minnesota
Roger M. Freeman, Jr., Providence, Rhode Island. President, MFB Mutual Insurance Company
Peter S. Hackes, District of Columbia. Correspondent, NBC
Robert A. Hechtman, McLean, Virginia. President, R. A. Hechtman & Associates
Albert E. Hole, Sacramento, California. California State Fire Marshal
John F. Hurley, Rochester, New York. Fire Commissioner, City of Rochester
John J. Jablonsky, New York, New York. Director, Codes and Standards, American Insurance Association
Keith E. Klinger, San Clemente, California. Fire Chief Emeritus, Los Angeles County Fire Department
Anne Wight Phillips, Boston, Massachusetts. Assistant in Surgery, Massachusetts General Hospital
John A. Proven, Evanston, Illinois. Executive Secretary, Fire Equipment Manufacturers Association, Inc.
Baron Whitaker, Chicago, Illinois. President, Underwriters' Laboratories, Inc.
William J. Young, Newington, New Hampshire. Chief of Newington Volunteer Fire Department. Secretary, Volunteer Committee, International Association of Fire Chiefs

This issue begins with five papers presented at the American Association for the Advancement of Science (AAAS) meeting held last December. The subject of the session, organized by the Committee on Fire Research of the National Academy of Sciences—National Research Council, was "Are We Winning the War on Urban

Fires?" These papers were well received by the public and the press. Your editor thinks that readers of FRAR will be interested in these papers which were prepared for the general scientific public. Such interpretive papers improve the public understanding of fire problems and of the contributions that science and engineering make to their solution.

ROBERT M. FRISTROM, *Editor*

CONTENTS

Volume 13 Number 1

Page

PAPERS PRESENTED AT AAAS MEETING—Are We Winning the War against Urban Fires?

ABSTRACTS AND REVIEWS

A. Prevention of Fires and Fire Safety Measures

B. Ignition of Fires

C. Detection of Fires

D. Propagation of Fires

E. Suppression of Fires

F. Fire Damage and Salvage

G. Combustion Engineering

H. Chemical Aspects of Fires

I. Physical Aspects of Fires

J. Meteorological Aspects of Fires

K. Physiological and Psychological Problems from Fires

L. Operations Research, Mathematical Methods, and Statistics

M. Model Studies and Scaling Laws

N. Instrumentation and Fire Equipment

O. Miscellaneous

BOOKS

MEETINGS

EQUIPMENT AND PRODUCTS

HISTORIC FIRE DISASTERS

JAMES W. KERR

Staff Director, Support Systems Research, Office of Civil Defense

As we meet here we are in an area burned over by the Great Chicago Fire, 99 years, 2 months and 18 days ago. (Fig. 1, Currier & Ives of State St.) Or would you rather not be reminded of that bit of information? A couple of other bits of information that almost always get ignored should also be tossed in here:

> On the very same date in 1871, a Sunday, there was a *really* big fire in Wisconsin, wiping out 17 towns and causing 1,052 deaths. A fire the week before had burned out the telegraph lines, and the next boat to Green Bay was Tuesday. Communications were so poor, in fact, that the Chicago fire preempted the telegraph and the headlines, and only fire buffs or almanac writers ever heard of Peshtigo or the other 16 towns. Large parts of this general business district of Chicago burned out again in 1874 and again in 1924. The areas weren't so big as in 1871, but as fires go, they were far from insignificant.

We are not here today to examine, and I surely hope not to reenact the Great Chicago Fire. But should anyone be interested in a fuller study of that noteworthy event, the Chicago Historical Society at North Avenue and Clark Street, a few blocks from here, has on display many artifacts of the fire, some first-hand holograph descriptions, and a fine collection of prints, etc. (Fig. 2, Currier & Ives of Waterfront; Fig. 3, State St.)

Fires, like any major event, leave a wide variety of impressions. Say "Chicago Fire" and some wag always responds, "Mrs. O'Leary's cow." And why not? This is what sticks in one's mind, and often these primary impressions lead to the more significant technical inferences. Certainly the O'Leary cow has her special niche in some incendiary pantheon. But in the height of irony, it should be noted that while her fate is uncertain, and her barn started things off, just about the only building left standing two days later in a burned-out area of 3⅓ square miles was the O'Leary home! (Fig. 4.) The reasons for the Chicago fire, as reported in the press of 1871, are interesting in their own right:

A group of Irish holding a party in the neighborhood went to Mrs. O'Leary's barn to milk the cow; they upset the lamp they were carrying for illumination.
It was a plot of the lawless who wanted to loot and rob the city.
The communists were responsible.
It was the judgment of God on a wicked city.
The wind enlivened and blew sparks from the fire of the day before into the hay of the O'Leary barn.
The fire was of incendiary origin.
The fire was caused by a fire extinguisher salesman demonstrating the need for his product.
It was divine retribution for the burning of Atlanta by Sherman's forces. This was printed in the Rushville, Indiana paper, *Democrat.*

Other great conflagrations come to mind—the Great Fire of London, in 1666, is claimed by some to have had a beneficial effect in cleaning up after the Great Plague. (Fig. 5.) Or did I read that in *Forever Amber?*

Then there is the Baltimore Fire of 1904. I have an aunt there who was born a few days before the fire, and always has hated people from San Francisco because the quake and fire of 1906 upstaged the Baltimore event so completely that nobody remembers "her" fire. (She never has noticed that she gives away her age when she does this.) Figure 6 shows the pumper of Engine Co. #15. Seriously, the Baltimore fire probably had greater significance for an impact on improving fire department operations than almost any other in that earlier time frame. It was a fiasco from start to finish—the chief was electrocuted by a falling wire early in the game, dynamiting didn't work. It was a monument to ineptitude. Fire wagons rolled all the way from New York to lend a hand, and their hose couplings didn't match. (Fig. 7.)

Fig. 1. Currier & Ives of State Street Bridge.

Tokyo has had its share, too. Aside from the World War II fire bombings (which make Hiroshima and Nagasaki look like Cub Scout cookouts in comparison), there was the horrendous fire associated with the earthquake of 1923. 91,344 lives were

Fig. 2. Currier & Ives of Waterfront.

lost, even among masses of people who had taken refuge in open areas. This fact has led to deep analysis of fire behavior, and a recent research publication of the U.S. Office of Civil Defense joins other authorities in attributing the deaths to fire whirlwinds, approaching tornado intensity, that were generated by the intense and extensive flames and which then swooped across the huddled refugees.

Fig. 3. Currier & Ives of State Street.

Fig. 4. O'Leary home.

Fig. 5. Great Fire of London, 1666.

Fig. 6. San Francisco Fire, 1906. Pumper of Engine Co. #15.

Fig. 7. Baltimore Fire, 1904.

Fig. 8. Test fires by the Office of Civil Defense and U.S. Forest Service.

The same phenomenon was noted at Peshtigo, and in some test fires run by the Office of Civil Defense and the U.S. Forest Service. (Fig. 8.)

Wartime fires have of course won considerable notoriety. London, Dresden, and Hamburg have been widely discussed, and Hamburg has been well documented; London reasonably well; and Dresden not at all, from a scientific viewpoint.

The German fires of World War II left us with one terminological legacy—the word "firestorm." This was apparently created by a reporter who was struck by the swirling flames and smoke, corroborated by some sooty rain falling nearby, and the word has so crept into our vocabulary that considerable effort has been expended on researching it as a scientifically definable phenomenon. Figure 9 shows a building across from the main fire house, just starting to burn. Figure 10 is twenty minutes later. Figure 11 is the central district after the fires were out.

Photos are by Hans Brunswig, then a Battalion Chief, now retired as Full Chief, and are used by permission.

More recently, there are the wide-ranging fires that devastated parts of our own west coast earlier this year. Another speaker will discuss them in a few moments. Let me emphasize here the fact that we urban dwellers can no longer shrug such events off as "just forest fires." Nearly 1,000 homes were lost in the recent California "forest" fires. But then, one should never have shrugged them off: remember Peshtigo—that was "just a forest fire," too.

With that impressionistic gallop through history as a backdrop, let me touch upon some of the technical material that has come to light as a result of urban fires and the research devoted to their prevention and cure. Perhaps the dominant area of uncertainty and of study effort has been and continues to be the development and spread of fire.

Spread mechanisms are three in number: convection, radiation, and firebrands. Everyone who has lived in a home or cabin with a space heater has benefitted from convection, that tangible flow of hot air, rising from the top of the space heater. For the student of fire, this comes to the fore in several cases. First, there is the problem of how a room heats up and progresses from a small fire involving say one piece of furniture to a full-room "flashover," a phenomenon well known to fire fighters the world over. Accounts of the Chicago fire, and the New York City fire of 1835 emphasize the "explosion into flames" of entire buildings, originally considered "fireproof."

FIG. 9. Hamburg, Germany, World War II. Building across from main fire house, just starting to burn.

Convection is the effect that causes smoke to go up chimneys, and in exactly the same way turns some buildings into infernos in such a short period of time. It can be the major cause of fire spread between floors of some types of high-rise buildings, and is an essential ingredient for maintaining a "crown fire" in a forest. Figure 12 shows a sketch of a theoretical surface fire, with its convection maintaining the crown fire; Fig. 13 is a photo of a real fire, doing exactly the same.

Radiation is a familiar word in many contexts. To take the simplest, there is the sun, or even your auto radiator; its job is to radiate off the engine heat picked up by the circulating water, aided of course by the convection supplied by the fan.

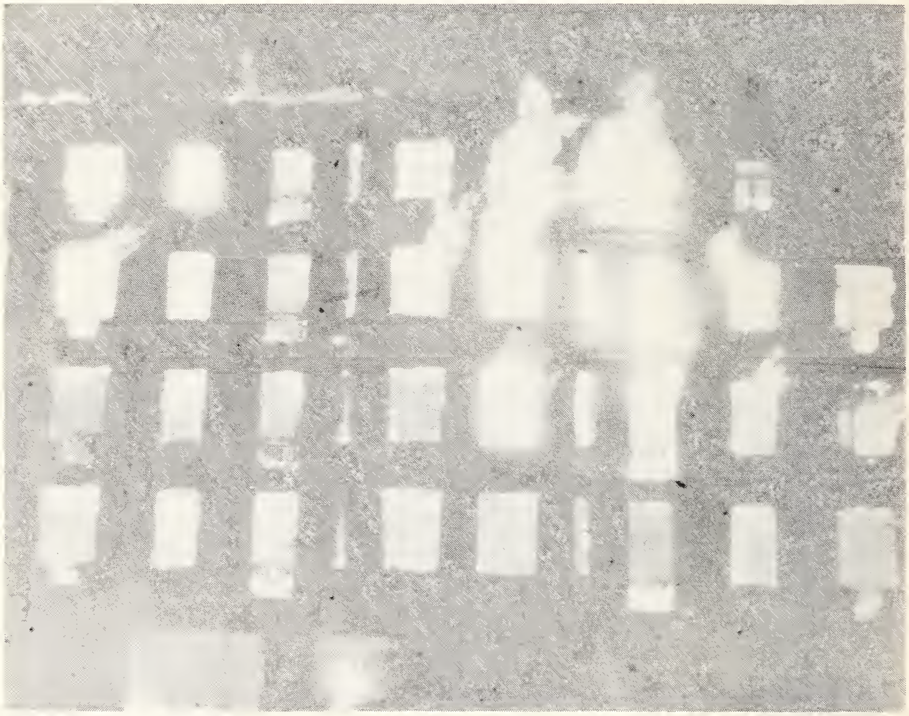

Fig. 10. Figure 9, twenty minutes later.

It is radiation that causes fire to spread from one building to another across an alley or narrow street. When you see your fire department hosing down buildings that aren't on fire rather than or in addition to those that are burning, they are preventing spread by radiation. Figure 14 shows fire spreading from house to house, far beyond the range of licking flames. (Hull, Mass. 1923.)

But the long-distance spread champion is undoubtedly the firebrand. Rather than moving up, as a convective column does, or "shining" across a single street, as radiation does, brands can travel incredible distances. This, too, becomes most obvious in fires involving forests. For example, a few years ago in Tasmania some firebrands were said to be carried 16 miles by the high winds. I must admit this

FIG. 11. Central district of Hamburg after fires were out.

is an extreme case, especially since these were huge strips of oily eucalyptus bark, but an example closer to home is not hard to find. Once more, I will defer to my colleague from the U.S. Forest Service, who will be describing the recent fires in California. When he talks about fires "spotting downwind," he is talking about firebrands.

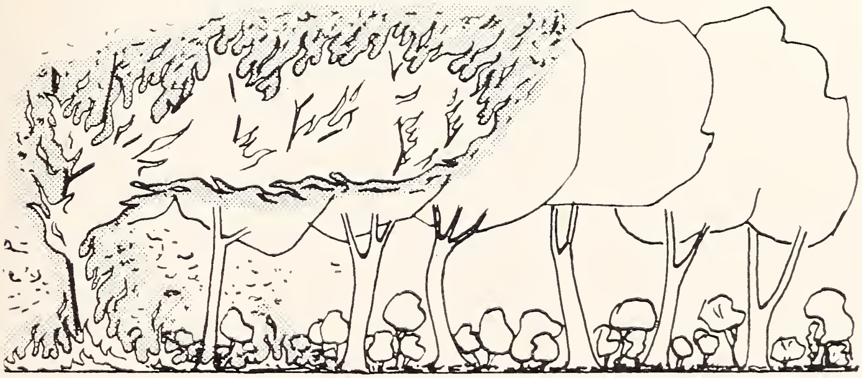

FIG. 12. Sketch of theoretical surface fire with its convection maintaining the crown fire.

And firebrands are perhaps the most difficult spread mechanisms to study. One reason is that in the real world your fire departments work very hard to prevent their development. The Office of Civil Defense has funded considerable work by IIT Research Institute, here in Chicago, watching for firebrand development and their flight during real fires, but they are hard to find in any quantity, thanks to prompt intervention by the fire department. Letting a test building burn unchecked (a risky process) is about our only source of useful data, because laboratory simulations are both difficult and hard to correlate.

FIG. 13. Photo of real fire.

Wind has been brought into this discussion several times. It is the major active factor in all our largest fires, though naturally the ambient weather, particularly recent lack of rainfall, plays a large role. But it is the wind that allows the fires to

FIG. 14. Fire spreading from house to house, far beyond the range of licking flames; Hull, Massachusetts, 1923.

leapfrog the defensive lines, the firebreaks, thus starting a whole new series of ignitions farther along. In the urban context, firebrands carried by the wind have taught us several useful lessons. The first is that cedar shake shingles make frightfully unsafe roofs. The point is that to prevent fire spread we must clean up our buildings so that when a firebrand (or a hot match or a burning cigarette) falls, there will be no ignition. This lends strong support to the need for generally good housekeeping on and near all our buildings everywhere. There is a further need

FIG. 15. San Francisco Fire, 1906. After the fire.

FIG. 13. Salem, Massachusetts Fire, 1914. Mixtures of housing and industry can be risky.

to keep windows closed, or at least screened. In the Tasmania fires just cited, virtually all the house ignitions in the city were from brands blown into open windows, almost none from roof or porch kindling.

What have urban fire disasters taught us about countermeasures? From the individual citizen's standpoint, they have underscored the need for good housekeeping, and for home fire protection. In California, in Tasmania, one could, I hear, go down street after street following the fires and find the homes where the residents had stamped out firebrands or quenched them with their garden hoses: it was easy to find these houses, because all the rest were burned down. Certainly I do not intend to gainsay the ordinary doctrine of your own fire department, which says "Call *us* to fight the fire." But in times of wide-spread conflagrations, in peace or in war, every man becomes a temporary fire fighter.

For regular fire departments, there are lessons related to performance under stress—stress of full commitment of resources to a fire that is still growing and growing beyond any conceivable force that can be mustered to fight it. All good departments are well grounded in the tactics of one- or two-building fires; almost nobody has a grasp of the strategy needed to cope with a huge conflagration.

And there is a new type of stress faced now by fire departments. This is the stress related to civil disturbance. The first study of this problem was conducted by the Office of Civil Defense at the time of the Watts riots; the bewilderment of fire fighters was monumental—after thousands of years of being the "good guys," they were suddenly being shot at! New tactics were called for and were developed on the spot. Studies by various agencies have now been codified, and the changes are being taught our fire fighters.

I mentioned fire-breaks earlier. We tend to forget over a period of time what a really big fire-break it takes to block a really big fire. Hosing down the exposed houses across the alley won't suffice if dozens of buildings are burning at once. When there is no hope for extinguishment of a fire, limitation of its spread is the only remaining countermeasure. Getting qualitative about such matters is a problem in its own right. A recently developed methodology for evaluating areas of high risk of fire spread is a useful tool for fire departments and urban planners, as well as for civil defense purposes. Invented by Gage-Babcock, a nationwide firm of fire consultants, it does not help an experienced fire chief *find* his high risk areas, but it *does* allow a rank ordering of hazards. Quantitative appreciations of fire-breaks, wind speeds, shifts in wind direction, etc., are harder to come by.

Returning now to some historical examples, let us examine fires that have taught us something and view slides of some of them. Some are well-known, some are not. In each case, I will point out the significant features, from the standpoint of the advancement of knowledge.

FIG. 17. Augusta, Georgia Fire, 1916. Fire resistive buildings with ordinary glass windows were gutted, along with 680 other buildings.

First is Indianapolis, where the coliseum explosion claimed several dozen victims. There exists only one photo of the fire, taken by a fleeting spectator, and it shows us very little in the first place. This lesson is the lesson learned by city and county officials, who have greatly strengthened their vehicle dispatch system, their patient/hospital matching system, and their overall coordination capability.

San Francisco, 1906: Fig. 15 is after the fire. *All* the fires were secondary—i.e., caused by the earthquake. Note the radial street system, later widened and reinforced with cisterns under the street intersections. These are still being rediscovered by motorists who suddenly sink through the pavement up to their cartops!

Salem, Mass., 1914: (Fig. 16). Mixtures of housing and industry can be risky. In the background *were* the largest cotton mills in the world. 1,600 buildings burned, thanks to wood shingle roofs.

Fig. 18. Remsen, Iowa Fire, 1936. One firecracker destroyed 34 buildings.

Augusta, Ga., 1916: (Fig. 17). Fire resistive buildings, with ordinary glass windows, were gutted, along with 680 other buildings. Wood shingle roofs and high winds helped the spread, cotton bales piled high in the streets kept the engines away, and those that arrived from elsewhere found the same old problem of hose fittings. Poor codes or poorly enforced codes were due much of the blame.

Remsen, Iowa, 4 July 1936: (Fig. 18) One firecracker destroyed 34 buildings. Bystanders tried to put out the first fire without calling the fire department; then it was found most of the volunteers were gone for the holiday, and the fire burned out the electric wires that fed the water pumps, so there was no water pressure. This comparatively small fire is *loaded* with lessons for city planners, operations planners, citizens, and fire fighters.

FIG. 19. Marshfield, Massachusetts Fire, 1941. Crowded resort construction; small grass fire on edge of town leveled 450 buildings in four hours.

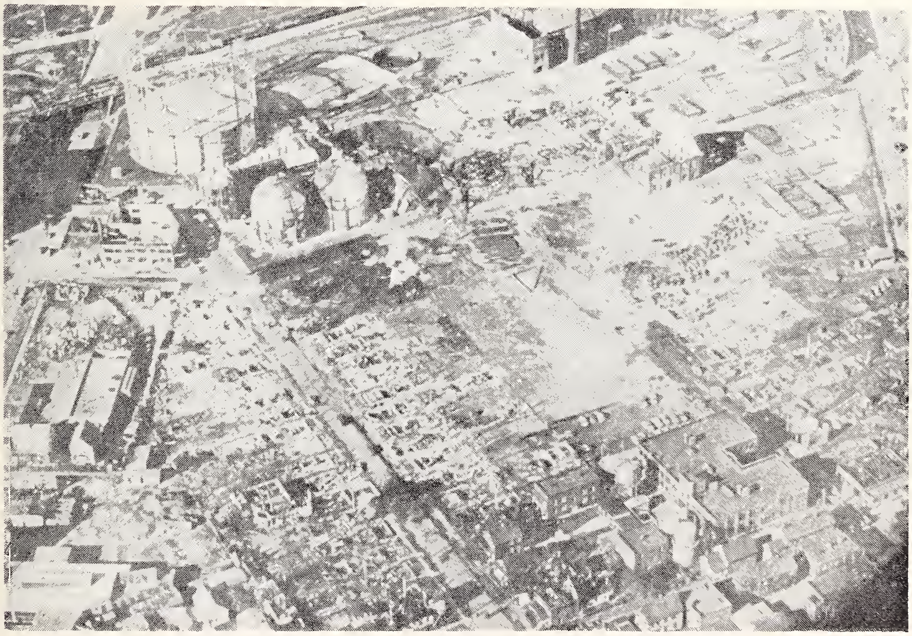

FIG. 20. Cleveland, Ohio Fire, 1944. 128 persons killed, 79 dwellings, and 10 other major buildings destroyed when two containers of liquified natural gas exploded in residential area.

Fig. 21. Medford, Oregon Fire, 1946. Simple fire in unsprinklered wooden plant spread through three city blocks.

Marshfield, Massachusetts, 1941: (Fig. 19) In crowded resort construction a small grass fire on one edge of town needed only four hours to level 450 buildings. A high wind was a factor, along with poor construction and inadequate access for fire engines, and poor water supply.

Cleveland, Ohio, 1944: (Fig. 20) 128 persons killed, 79 dwellings and 10 other major buildings destroyed when two containers of liquified natural gas exploded in a residential area. Zoning, transport restrictions, disaster plans, all were updated and corrected as a result, and not just in Cleveland!

Medford, Oregon, 1946: (Fig. 21) A simple fire in an unsprinklered wooden plant spread through three city blocks. I doubt one could find such a building today in Medford, and most other localities have profited by their example.

NEW TECHNOLOGY IN URBAN FIRE CONTROL

CURTIS W. VOLKAMER

Chief Fire Marshal, Chicago Fire Department

When the question is asked whether or not we are winning the war against Urban Fires, I am sure that proponents will answer "Yes" without a moment's hesitation. I am equally sure that opponents will be just as quick to answer "No." At first glance, it would seem that those who hold with the negative viewpoint might have the more valid position, what with the staggering fire losses which mount year after year, and the appalling death rate by fire which annually surpasses the 12,000 mark. However, I believe that this subject cannot be dismissed quite so briefly and that it merits the most careful and critical analysis.

From time immemorial, fire departments have stood as a bulwark for mankind against the destructive forces of nature, not only against the ravages of uncontrolled fire, man's greatest enemy, but also against the onslaught of tornadoes, floods, earthquakes, and other catastrophic occurrences. In the early days of fire fighting, man's efforts were not always rewarded with success as he threw all the resources at his command into the battle, resources which at times were pitifully weak and totally inadequate. His courage in the face of danger was never questioned, but the end results often left much to be desired. Sometimes he would be forced to retreat and accept an inglorious stalemate, the fire eventually burning itself out. Fire personnel searched diligently for a scientific approach to the resolution of the problem—and found it. Most authorities agree that with the introduction of the hand pumper, science was applied to the fire-fighting field. It is not my intention to present a history of the pumping engine, but with the advent of that piece of equipment, science had now become a definite part of the fire service.

The progress rate in the areas concerned with leadership qualities also began to accelerate at a remarkable pace, and the progressive chief divorced himself from antiquated ideas, if he were not to be swept aside by this wave of progress. Attitudes must be changed. Thinking must be revised, banishing forever the almost legendary fire fighter concept—all brawn and no brains.

The fire fighter of today (and I use the term in its broadest sense to include all ranks) is far removed from his counterpart of former years. He is aware that this is the era of specialization. He realizes that the fire service incorporates all aspects of scientific fire fighting, detection, and protection. The present-day fire fighter studies subjects which were unheard of twenty or thirty years ago, each new item requiring more knowledge and additional training to master it. He is preparing himself against the time when he will have risen, through the ranks, to a position of authority; when the mantle of leadership is placed on his shoulders, and he assumes command of his department to win the war against urban fires.

The growing and urgent need for scientific study courses and training programs was recognized by the Federal Board for Vocational Education in 1930, when a study was made as to what curriculums could best be included to assist municipal fire fighters. A second study was conducted in 1939, by the U.S. Department of the Interior's Office of Education, at the request of the International Association of Fire Chiefs. However, it was not until 1958 that a definite course of action was taken when the New York State Board of Regents granted a charter under the title of The International Fire Administration Institute.

Thus, it can be seen that the years 1930 to 1958 provided the springboard for the implementation of scientific training programs as we know them today. State firemanship training programs offer technical courses at a college level under the broad title of Fire Protection Technology. It is imperative that these skills be acquired by those who have the responsibility of safeguarding the health, safety, and welfare of the citizens of our municipalities. The modern fire fighter requires knowledge in many diversified fields, far too numerous to itemize them one by one, from ladders to leadership, from axes to atomic energy. And it is reasonable to suppose that the complexities of our present-day civilization will bring newer and greater problems into the picture, effecting major changes in our cities, with gigantic manufacturing complexes expecting—yes, demanding—maximum fire protection.

The people of any municipality have every right to expect that their way of life, in accordance with their standards of living, will proceed from day to day with no appreciable change; that they will continue to enjoy the accumulated fruits of their labors; that their children, and their children's children, will inherit a clearly defined sense of tranquility and security that a well-regulated community offers to its citizens. And if disaster strikes, (and here I exclude any police action)they have a right to expect that their fire department will provide them with sufficient protection to insure that danger to themselves and their community will be minimal, and that any interruption of their present mode of living will be of a very short duration. To this end, the fire fighter of today has dedicated himself, committed as he is to a lifetime of training, reading, and study in technical advances. In so doing, he has made a tremendous contribution to the service of his fellow man.

These goals are not a product of mere happenstance; they are achieved only after the fire fighter attends the many seminars, schools, and conferences at local, state, or national levels, and avails himself of the immeasurable help offered technical and scientific groups, such as the one to whom I have the pleasure of presenting this paper today. The American Association for the Advancement of Science is recognized among its peers as the leader in disseminating information which will increase the public understanding of science, by presenting accurate and interesting accounts of new ideas, new findings, and new insights into science. The benefits derived from this medium are invaluable.

Scientific groups, such as yours, throughout the country have long recognized the need for more and better services in the field of fire protection and have assisted greatly in the quantity and quality of new designs in fire-fighting apparatus. They have recognized the challenge made by demands on municipal fire departments now, and which certainly will increase in the future. The complexity of our metropolitan areas continues to grow daily, because as suburban areas increase in size and population, they assume urban overtones. Just recall for a moment the many changes that have taken place in any community you wish to name. I believe this will bear out the startling and thought-provoking announcement made by the National Academy of Sciences in a symposium recently, when it stated that by the year 2000, there will be 312 million Americans, 187 million of whom will cluster in the nation's 14 major urban areas. Try to visualize, in your mind's eye, the problems which the fire department of that day and age will have to face, attempting to maintain its proper role in providing for the safety and welfare of the people in these huge, almost unbelievable cities, averaging 13½ million inhabitants. By comparison, today's modern cities of one, two, or three million could almost be classified as Hamlets, Villages, or Towns, little wonder then, of the urgent need for the fire service to keep abreast of modern times and innovation brought about by our rapidly expanding technological age.

The age of science covers many facets of urban fire defenses, so vast in scope that only a few, per se, can be mentioned here: Municipal Water Supply, Fire Department Organization and Structure, Distribution of Fire Companies, Design of Fire Apparatus, Master Stream Hydraulics, and the Design and Operation of Fire Alarm Systems. There are others, of course, but I mention these merely to show the relationship of science to the total Municipal Fire-Defense Structure.

The progressive fire chief adopts a scientific approach to the basic principles and philosophy of modern fire prevention, evaluating the various fire test methods, the storage and handling of hazardous materials, including radioactive materials which have become so much a part of the national scene.

Fire control operations and related problems, of course, are covered quite extensively, for this is the very life-blood of his existence; in fact, it is the only justification for his being in the demanding profession which he has chosen. His duty is to study and analyze various types of fire situations, from the most basic to the most complex. He must have almost instant finger-tip control over the problems of fire extinguishment, communications, fire-ground tactics and command, logistics, and many others.

One subject which, in my opinion, must be given more and more consideration in the years to come is that of disaster control. Here the fire department must bring into sharp focus all the technological and scientific "know-how" which has been accumulated through experience and study, not only the physical aspects but the psychological side-effects as well. In view of recent developments, it is imperative that we devote some serious thinking to this subject if, indeed, we are to maintain our status quo.

I am sure you appreciate my position, governed as I am by certain policies which preclude my being specific. However, we must analyze human response to man-made disaster situations and know how to deal with it. Knowledge of the control of crowds and crowd behavior will help immeasurably in establishing the role of the fire department in crisis situations, such as civil disorders resulting in arson, harassment, and violence. That word "violence" means many things to the fire fighter trying to do his job—from bricks and stones and bottles to sniper fire from some nearby roof top. Under such conditions, protection must be provided, whether it comes in the form of assistance by local police authorities or guard units on a state or federal level, or possibly a combination of both protective services. Past experience has demonstrated quite clearly that fire departments, as such, are not equipped to cope with these emergencies, nor should they be expected to do so. Their primary function is fire control and extinguishment, and any deviation devoted to extra-curricular activities would tend to reduce the effectiveness of the campaign waged against urban fires. The welcome assistance given by law enforcement agencies enables fire fighters to channel their efforts toward achieving the end result—extinguishment of the fire.

Before I leave this subject of interference by hostile elements, let me say that it is almost impossible to lay down hard and fast rules—situations do vary a bit. However, you must have definite preplanning with enough latitude to come up with a workable solution, regardless of the situation which confronts you.

Unprecedented demands are being imposed on the fire service by rapid social and technological changes, some of which I have mentioned earlier, such as the population explosion, the rapid growth of urban communities, perhaps involving the wholesale annexation of suburban areas with the subsequent transition from suburban to urban norms. These changes require that fire fighters in general, and fire executives and administrators in particular, be better educated than their predecessors. Authorities are agreed that this is the age of science, of professionalization in many areas, one of which, of course, includes the Fire Service.

To support the validity of this premise, one need only to refer to the Gordon-Howell report which suggests criteria for professionalization, granting that professional status begins with education. This report states that a profession should rest on a systematic body of knowledge of substantial intellectual content. The application of this knowledge to specific uses is consistent with the development of personal skill. The report calls for the advancement and dissemination of knowledge and advocates that ways be prescribed of entering the profession by meeting certain minimum standards of training and competence.

It is the thinking of those who support these statements that a systematic and deliberate educational scientific program, leading to a broad knowledge base which is acceptable to the academic community, is the surest approach to professionalization. It is unrealistic to assume that every member of a fire department has a formal education equivalent to a college degree conferred by some institute of technology.

To compensate for this in an attempt to gain an equality rating, levels must be established within the profession. True, this cannot be computed by mathematical formula; yet, we must introduce some empirical coefficient factors whereby one item of major importance will—indeed it must—outweigh a few relatively unimportant items. As you can readily see, this presents a challenge to those in supervisory capacities whose duty it will be to measure the scope, degree, and depth of the scientific educational requirements for efficient functioning of the fire service as a whole. To a large extent, these administrators will rely on the findings of scientific agencies, such as yours, working within framework of solid educational and research programs.

In the final analysis, the implementation of even the finest technical resources must rest on the ability of the individual to whom this task is entrusted. May I say, at this point, that the attitude of the fire fighter himself has contributed immensely toward achieving this goal. By and large, he has a purpose, an aim in life, and this is all-important—he *wants* to be a fire fighter.

The reason I mention this is that Fortune Magazine at one time conducted a survey and published some rather startling facts. Their findings revealed that 4 out of 5, or 80%, of the people were in jobs which they didn't want, didn't like, and for which they were unsuited, physically or emotionally. Because of circumstances, mostly economic, they had been placed in positions or jobs which were available at the time, and they stayed in those positions or jobs. Actually, most of them became quite proficient and did a very good job, never realizing their ambition to do what they really wanted to do. I think we, in the Fire Service, are very fortunate that the overwhelming majority of our men want to be fire fighters—and that makes for a healthy attitude toward the job and toward the people we serve.

The fire department has been quick to adapt itself to technical and scientific changes in the matter of equipment, and please bear in mind that when I mention these it will not necessarily be in the order of their importance and that some will be discussed a little more at length than others—powerful pumping units capable of delivering 1500 to 2000 gallons of water per minute; modern 144 foot metal ladders with telescope action operated hydraulically; the incredible snorkel; jet boats; amazing chemical units for airport protection (twin units, affectionately known as "Big Mo" and "Big John") with multiple intakes, capable of projecting streams to an almost unbelievable distance; and the helicopter.

Pumping engines have progressed both in capacity and design, with an increased tendency to lean toward diesel-powered equipment. Fire departments have placed great reliance on the pumper inasmuch as water is still the most commonly used medium for the extinguishment of fire, to reduce the temperature of the burning material, regardless of what it is, to a point where it no longer will support combustion. Despite the introduction of many sophisticated mediums, such as CO_2, dry powder, wetting agents, light water, foam, Hi-ex, and a multitude of others, water is still used to extinguish 85% to 90% of the fires in urban areas. This is attributed to the structure itself and the contents and their ability to burn, referred to in fire prevention circles as the "fire load."

One hundred forty-four foot metal aerial ladders can be raised quickly to 12 or 14 floors to provide a means of mass escape for trapped occupants. When a sizeable number of persons are to be evacuated from a single area on the upper floors, this method has been unsurpassed.

However, the versatile snorkel is without equal when people are to be evacuated from many different areas on the upper floors. This revolutionary unit is a product of imaginative research in the technological field, and its adaptation toward application in the Fire Service. Never before has one single piece of equipment made such a definite impact, and more and more departments are leaning toward this incredible unit. Snorkels have been used in a variety of rescue situations, from picking off victims piecemeal, lowering them to the ground, and quickly returning for others in different areas, to suicide victims intent on self-destruction.

In addition to these capabilities, the snorkel can with its articulated boom, project tons of water with pinpoint accuracy, in patterns which range from fog or spray to full, wide-open nozzle.

The helicopter, of course, is in a class by itself and is by far the most versatile fire-fighting unit to be introduced into the Fire Service. Actually, to most fire departments, this is placed in the category of the future; but to those departments which have incorporated the helicopter into their operations the possibilities of utilization to the fullest are still in the exploratory stage. If there is any one unit which will ultimately bring about a push-button warfare against our sworn enemy, uncontrolled fire, this, gentlemen, is that unit.

The helicopter is without equal as an observation post from which to direct operations at the scene of any large fire. Closed-circuit television projected from this vantage point will indicate the danger spots, the flaws in any fire attack; and video tape-recorded fires, appropriately edited, will serve admirably as lessons in fire-ground tactics when critiques are held.

I can visualize large versions of this unit as being used more and more in an all-out attack on fires. Hose lines on reels will be lowered above the fires, with water being supplied from auxiliary tanks in helicopters to huge distributing nozzles to serve as a gigantic, air-borne sprinkler system, as is the case of the sprinkler system we now employ. We can even conceive of a master chemical bomb, a heavier-than-air, carbon-dioxide-type, which will be placed on the roof of a burning building by the helicopter crew and activated by remote control. If no lives are involved, the released gases will then blanket the burning area like a giant umbrella, excluding the air and oxygen content, and extinguishing the fire quickly, effectively, and completely.

Helicopters will also be used to bring fire-fighting personnel to the upper floors of the super high-rise buildings of the future that will dwarf our present 80 and

100 story structures. The famous Frank Lloyd Wright had plans on the drawing board for his controversial "Mile-High-Building" which was indeed to have reached 5280 feet into the air. As far as I know, those plans are still in existence.

If I may, I would like to quote from a most authoritative source, above and beyond, the encyclopedia of aviation and space sciences.

> "Perhaps the most revolutionary of all helicopter projects is the expressway air evacuation program, which was first initiated on a full-time basis in Chicago, early in 1967. Close co-operation between the Fire Department using a jet helicopter and the Chicago area hospitals, which provide landing areas, assures expressway accident victims of an airlift within minutes after the helicopter service receives a call for help."

Incidentally, gentlemen, WGN has made a very authentic and interesting Documentary of this phase of helicopter operations.

In the areas of extinguishment, fire departments have availed themselves of all the mediums which scientific agencies have engendered. It is needless and pointless for me to pursue them all. However, a word or two about a new development incorporating plastic $\frac{3}{4}''$ balls with sprayed protein foam. Official tests have shown that these plastic balls, floating on the surface of flammable liquids stored in tanks, greatly reduced the risk of ignition. In the unlikely event of ignition, the fire spreads very slowly and can be quickly extinguished with sprayed foam. Without the "Ball Blanket," most protein foams used for fire fighting are rapidly degraded by liquids, such as methanol, and as a result, the smothering layer may form too slowly or may not even form at all. However, the plastic balls prevent the foam from breaking down and liquefying.

In one of the extensive series of tests, the researchers found that four layers of these plastic balls reduced vaporization of the flammable liquid to such an extent that the flame could not maintain itself above the "Ball Blanket." The flammable liquid could only be ignited by actually pushing a flaming torch through the "Ball Blanket." Even when ignited in this manner, the fire spread so slowly that after 15 minutes, half the surface of the test tank could still be touched by hand. At this point, protein foam spray was introduced, and extinction took only 30 seconds.

To the fire-oriented mind, this is of tremendous import not generally recognized by the average lay-person. It is axiomatic that flammable liquid fires (with the exception of some rare chemical fires) are the most prolific in the propagation of flame and the subsequent rapid rise in temperatures, from 1200 or 1300 degrees to 2200 or 2300 degrees fahrenheit. A pre-burn of 15 minutes of any appreciable quantity of flammable liquid would be of great concern to a chief in any urban community.

In the area of communications, the Fire Service has indeed taken advantage of the many technological, scientific, and electronic devices and mechanisms offered by those in research and development. From the old-time fire fighter stationed in the watch-tower to shout an alarm when the glow of fire appeared on the horizon, to the telephone and telegraph key to two-way radio communication involving many special frequencies. In today's modern fire alarm offices, all messages are recorded on huge 24-hour, 9-channel tapes. A flick of a switch, and 120 engine companies in the metropolitan area are tuned to a "Simulcast" for an emergency announcement.

This is the age of the computer, and the Fire Service has utilized this scientific exponent to the fullest extent. It is also reasonable to suppose that computers will be used in the future to a degree unheard of. I can predict that the day will come when a fire chief will push a button on a device, beamed to the Fire Alarm Office, which will computerize the information needed and on a closed-circuit screen, the answer will be there in a matter of seconds. I have heard that computers are capable of making 6000 calculations per second, and on the basis of this, anything involving computations is theoretically feasible.

There are tremendous possibilities in this electronic marvel. For example, the computer will provide the solution in cases involving the one antidote for a rare poison, or the one way to handle safely an almost unknown hazardous chemical.

Metropolitan areas will be computerized to such a degree that fire chiefs can be apprised of their manpower situation at any given point, and the location of any given vehicle, whether responding to an alarm, operating at the fire scene, or returning to quarters. A chief receives a call to respond to a huge warehouse involved in fire. A push-button request is made for information which has been itemized and tabulated for computer analysis by the Fire Prevention Bureau. Before the men have put on their turn-out gear, the chief has the information on a teletype card, a picture of the building including a schematic view, and a TV picture, beamed from a helicopter of traffic conditions along the route of the fire.

There are many other features which could be considered when the future fire service is discussed. Actually, the scope is so broad that it defies anything but generalization. One very important item to bear in mind is that many new concepts in fire fighting will be presented, some very intriguing. We cannot discount any new idea in the fire-fighting field, because it is through the utilization of all our resources, technical and scientific, that true progress is made. As long as we have men of courage and of vision, we will, indeed, continue to win the war against urban fires.

URBAN FIRE PROTECTION

Studies of the Operations of the New York City Fire Department

EDWARD H. BLUM

The New York City-Rand Institute

This paper describes studies of urban fire protection being conducted jointly by the Fire Department of the City of New York (FDNY) and The New York City-Rand Institute.

Underway now nearly three years, these studies have:

- created the perspectives, methods, approaches, and results of a new analytical field;
- transformed these research products into policies, helped put the policies into practice, and evaluated results;
- helped alter the FDNY's fire-fighting technology, the operation of its dispatching system, and the ways it manages and deploys its men and equipment;
- yielded (and continued to yield) gains in operational effectiveness valued at many million dollars per year—annual returns more than ten times the studies' cost;

- helped the FDNY develop new problem-solving traditions and capabilities and improve its bases for future decisions and policies.

Sponsored by the FDNY, the work has been carried out by an interdisciplinary team: FDNY chiefs and other officials; engineers; an urban planner specializing in organization theory; applied mathematicians—including specialists in statistics, operations research, and computer sciences; economists; and a social psychologist. From the outset, most of the work has been done jointly by members from different disciplines.

This joint character has become reinforced as the work has evolved—from highly technical analyses of operational questions to synthesis and implementation, and to basic research on broader issues. On this last, for example, the FDNY has recently assigned high priority to examining social and physical origins of the demands for its services, and to looking in detail at its probable future milieu and the forces shaping it.

I would like here to convey some of the style and results of our work. To set the stage, and set later descriptions in context, I would like first to describe some of the fire department milieu and to illustrate some of the problems that most urban fire departments—including the FDNY—now face. Then I will describe some of the work and the results it has yielded—albeit necessarily in brief and without the reams of supporting technical details. Afterward, and finally, I would like to comment briefly on what seem to be the work's more general implications.

FIRE DEPARTMENT PROBLEMS

The fire service's mission is traditional and enduring: to prevent fires from occurring and to respond to those that do occur and put them out. Although most urban fire departments stress the preventive role, all are primarily organized to serve in crisis—to react promptly and protect the community when parts of the physical or social order break down.

The fire department on which our work focusses is the Fire Department of the City of New York (FDNY), which provides the sole fire protection, most of the alarm communications, and some non-medical emergency services to the land and port of New York City. With roughly 14,700 uniformed men, 1000 civilian employees, and 400 fire units, the FDNY is the world's largest paid fire department. Its organization and operations—and its problems—are much like those of its counterparts in other cities, but larger and more extensive.

Men and Management

Perhaps more than any other municipal service, the fire service across the nation is linked by a sense of fraternity and tradition, the keystones of which are reliability, dedication, esprit, heroism, and self-sacrifice. In the contemporary city, however, this tradition is gradually eroding and coming to seem anachronistic. Public adulation and even sympathy for the fire fighter has been waning; serious technological problems are mounting; costs are rising; and in the larger cities demands on the fire service are increasingly becoming conspicuous symptoms of deeper social ills.

This erosion of tradition underlies several of the fire service's most serious problems. Fire fighters are increasingly disturbed because their traditions, and the values they represent, appear to be disintegrating. Changing public attitudes, deteriorating relations with minority communities, and a trend toward bureaucratization have dimmed the luster of the job and shaken and transformed many fire fighters' self-image. In larger cities, imbedded in the general national growth of municipal service unions, these trends have helped accelerate a rise in militancy, which has led to growing demands on wages and working conditions and a growing willingness to strike.

This crisis in public and self-identity has also afflicted fire service management. Recruiting of the most highly qualified men has become more difficult, and labor and community relations have become increasingly important, though unwonted concerns. Costs have been rising, but voter resistance to increased budgets and taxes has stiffened. And management itself has become more difficult and more complex, now that tradition no longer suffices to motivate and guide the skilled manpower on which the fire service depends.

Yet, nearly everywhere, some other traditions still dominate: the only road to the top of larger fire departments is from within, and few training programs are available to teach management and organizational skills. Moreover, even among officers, the acculturation toward putting out fires is so decided that many of the best men prefer field command even to top administrative or staff jobs.

Practices and Equipment

Fire management also faces external problems, which are best illustrated through a brief outline of how the fire service operates. Since fire is inherently a physical and chemical phenomenon, much of the fire service's activity is oriented technologically, from prevention through extinguishment. Urban fire departments, for example, inspect or advise on building plans. This activity helps ensure that materials, wiring, heating units, etc., meet the fire codes and will present firemen as few problems as possible should a fire occur.

They also inspect industrial, commercial, and public buildings—and residences to which they are invited—for possible ignition sources, kindling, and fuel, for lack of safe egress, and for other potential hazards. Urban fire departments have special communications networks both into the department from the public—to report hazards and fires—and within the department for contact with mobile units.

When an alarm is reported, the most conspicuous part of the fire service springs into action: fire engines and sirens, pumps, hoses, axes, hooks, and ladders. At a building fire, firemen rescue and evacuate people who are or may be endangered, and put out the fire. Once the fire seems to be out, then the tedious work of overhauling begins—finding and quenching embers and hot spots from which the fire could reignite, and putting the property in order.

To carry out these activities effectively, the fire service depends heavily upon outside persons and agencies: those who formulate and administer the codes, architects and building contractors, fire insurance companies (whose rating practices influence the private fire protection, such as detectors, sprinklers, or brush clearance that property owners provide), telephone companies, private or auxiliary alarm services, and equipment manufacturers and suppliers. These form important additional parts of the fire protection "system." And when they perform poorly, they impair the fire service's ability to carry out its mission.

Further, as this outline indicates, fire departments are essentially line-operating agencies. And, as students of bureaucracy have noted, even without external pressures such agencies are often ill-equipped in outlook, skills, and organization to undertake novel or significant change. They are usually ill-equipped to undertake efforts that involve more than minimal uncertainty and risk. The rewards for success within the organization—and its political setting—are too small, and the price of failure disproportionately high.

This problem is compounded in that the fire service receives little effective support from industry, universities, or the Federal government. It still depends for information and new ideas largely on a few dedicated interest groups and professional associations, which are backed by limited financial resources and next to no research. Most of the research that has been done has either supported existing practices and products or treated subjects that, while important, are peripheral to the main interests and needs of the urban fire service—such as nuclear blast fire problems, forest fires, and the chemistry of combustion. Congress passed a Fire Research and Safety Act (1968) which set Federal responsibility for urban fire research, but only this year have there been supporting appropriations, and these are minute compared with the need.

As a result of all these influences, even with the advent of motorized equipment and mobile radio communications, basic fire department practices seem to have changed little in the past century. Radio has just begun to replace voice and hand signals and messengers for tactical communications at the fire scene. Power tools have just begun to replace axes and crowbars in ventilating roofs and walls. Command-and-control is hampered by turn-of-the-century technology and procedures. New materials, new protective clothing, new fire detectors, new extinguishing agents, or materials to enhance water, have been introduced agonizingly slowly, in part because of the small and atomized fire service market and a fragmented and reluctant supply industry.

New York City

In New York City, fire problems have additionally been driven by demand. Between 1956 and 1969, fire alarm rates more than tripled—from 69,000 alarms per year to more than 240,000. The rate for every type of incident, from false alarm to structural fire, has been increasing exponentially. False alarms, rubbish fires, non-fire emergencies, fires in vacant or abandoned buildings, and deliberate fires now outnumber the accidental structural fires that used to be the fire service's main *raison d'etre*. Indeed, false alarms have been increasing more rapidly than any other type. There are now many more false alarms each year than structural fires; in 1969, about 30 percent of the alarms were false alarms, and 20 percent of the alarms were for structural fires.

A disproportionate share of the increase has occurred in slum areas, where fire incidence seems ineluctably tied to deteriorating housing and facilities, continued overcrowding and under-maintenance, and other accumulating social ills. Between 1963 and 1968, for example, one rapidly deteriorating New York neighborhood experienced an average annual rate of increase in alarms of 44 percent; a stable neighborhood barely two miles away saw an average increase less than 5 percent. In 1968, an area in the Brownsville section of Brooklyn—frequently cited as one of the "worst" in the City—had an annual rate of over 10,000 alarms per square mile, more than thirteen times the city-wide average. Due to these alarm densities, some fire companies in high-incidence areas responded more than 8000 times a year, and more than 20 times a night many nights of the year.

Costs have been rising nearly as fast as demand. Between fiscal year 1957–58 and fiscal year 1970–71, the FDNY's total budgeted expenditures rose from $99 million to $311 million; even in constant dollars (taking out effects of inflation) the FDNY budget doubled in this period. With expenditures of $35 to $40 per capita, fire is the fifth largest basic service in the City—after welfare, education, health services, and police. Manpower costs amount to more than 90 percent of the total fire budget.

Command-and-control still must function primarily with equipment installed shortly after the turn of the century. The system worked well for a long time, but in the last few years the numbers of incidents and the volumes of information to be handled have grown much faster than the system's ability to cope with them. And as alarm rates have continued to rise, strain in command-and-control has increasingly been accompanied by strained field operations.

OUR RESEARCH

As the joint FDNY-Rand research began in January 1968, broader efforts were underway within the New York City government to improve the quality of operations and decision-making. Mayoral staff and program planners in the Bureau of the Budget were working to make analysis part of the budgetary process. And, both in line and staff positions, the Fire Department had begun to develop internal analytical interests and skills.

The initial research program was thus both broad and technical. Rand was asked to help the Fire Department with a wide range of its important problems, focussing on those where the Fire Department felt the greatest need for additional technical expertise. The problems jointly specified for research were, on the whole, those that had troubled the Department for some time, but there was a new urgency with which many of them were beginning to be addressed.

The joint FDNY-Rand team quickly began pursuing several different lines of work, as the later examples illustrate. Some involved helping the Department with rather well-defined problems and issues, where the Rand staff supplied an independent point of view and an assortment of tools and expertise to support the Department's own activities. Some involved helping the Department grapple with basic, ill-defined problems, where we were able to help clarify just what the underlying problems were and bring analytical expertise to bear on solving them. And some involved more traditionally creative work—discovering things that had not been noted before, and bringing to the Department and the fire profession new insights and capabilities.

The team was urged initially to focus on approaches that would help the Department with forthcoming decisions, but would also prepare sound bases for the range of decisions the Department was likely to face in the next several years and in the next decade. Initially, we thus chose to center on issues that were then important to City officials and on which decisions would have to be made, and on areas where leverage existed—or could be created—for significant change. In our joint research, this immediate, concrete focus, combined with the mandate to develop the capability for a longer range perspective, has led to a number of major results.

I would like here to discuss examples of our work in four broad, closely related areas: communications, deployment, management information and control systems, and new technology. These examples represent a cross section of research styles, impacts, and progress.

- The work on communications has essentially been completed, and most of its results have been put into practice. As a consequence, for example, the peak-period capacity of the Brooklyn Communications Office has effectively been doubled at a very low cost.
- The deployment research has contributed to several innovative changes in Department policies, many of which are already in operation. Working together, these changes have significantly enhanced the Department's fire protection capabilities.
- The communications and deployment research have both helped provide the basis for the work with which the Department has begun to develop a computer-based management information and control system. Now being specified in detail, the new system will enable the Department to make and sustain major improvements in the quality of the service it provides, using novel techniques that lie beyond its current capability.
- The work on new technology has had two major products—the concept for a system that might eventually reduce the incidence of both large and fatal fires, and a breakthrough in fire-fighting technology that now is close to use in routine operations.

COMMUNICATIONS

Early in the work, it became apparent—as some Department officials had already recognized—that the Department's command-and-control system needed comprehensive modernization, rather than continued incremental improvements. Especially critical were the dispatching centers in the communications system, which form the link between alarms from the public and the Department's fire-fighting response. These centers were operating with antiquated equipment and occasionally experiencing noticeable delays and difficulties. In addition, it appeared they would be hard-pressed or even unable to accommodate the new deployment policies then envisioned.

We examined several broad modernization alternatives, including the application of high-speed computers, which appeared attractive. This early work stimulated key officials to decide to invest in possible computerization.

By mid-1968, we began to focus on the dispatching centers. We wanted to know in detail the performance of the then-current system and to be able to evaluate proposed alternative systems. We were especially interested in the dispatching time (the time alarms spend being processed at the centers before fire-fighting units are dispatched) and in understanding when it became significant relative to response times (the times the units take to arrive at the scene once they have been notified).

Dispatching consists of two basic sets of operations: receiving, interpreting, and identifying alarms; and allocating and dispatching fire-fighting units to respond. The first set involves a great deal of noise and activity—counting telegraphic signals, answering telephones, etc.—and is so hectic in busy periods that it readily dominates one's view of the system. Indeed, prior improvement plans—which included new equipment, additional receiving dispatchers, and computer aid for routine tasks—focussed heavily on this first set of operations.

At the start, Arthur Swersey spent many weeks—night after night—in the Brooklyn Communications Office, the busiest in the City, observing both the unusual and the routine and distilling what he saw into a detailed quantitative model of dispatching operations. From these extensive observations, and the discipline imposed by modeling, evolved several important findings. First, Arthur found that the system had a definite bottleneck when busy, not at the point where alarms are received, but at the point where response decisions are made and carried out. Several different men might work at this point at different times, but decisions were essentially made one at a time by one man with the possible aid of another. When the system was busy, its performance was limited by the performance of this single service route.

Moreover, his data showed clearly that the time delay in this bottleneck increased significantly with the number of active incidents, not only because there were more incoming alarms to be processed, but also because service of each additional alarm slowed down as there became more active incidents that had to be considered. These and other results were incorporated into a simulation model, which accurately depicts the system's performance over a wide range of conditions.

That busy periods could strain the system had, of course, been obvious. But the simulation first revealed precisely when and why the system became strained, and how large the delays could become as alarm rates continued to rise. And the model showed that, even though the system then appeared to be performing reasonably well, conditions were rapidly approaching under which the system could come close to breaking down.

The Brooklyn dispatching system performed well at normal alarm rates, routinely dispatching alarms in under a minute. Since the response time for the pumper or ladder closest to an incident typically runs between two and four minutes, these dispatching times seemed tolerable. The model showed, however, that at thirty alarms per hour—at a peak-hour load that rising alarm rates would shortly bring—dispatching time would average nearly four minutes, and at thirty-five alarms per hour the average time would soar to nearly eleven minutes. Delays that long would clearly be intolerable.

Further, the simulation results established that the key problems were not those on which attention had previously been focussed. For example, the model showed that increasing the number of dispatchers by 50 percent in the first part of the process would reduce five-minute delays by barely a few seconds. Even using high-speed computers for the routine tasks would reduce long delays by barely 10 to 15 percent.

Of the several changes we suggested, the most attractive was to divide operations at the decision point. A live test of the idea was conducted. Using the suggested system one busy evening, the dispatchers handled without strain or delays 27 alarms in 30 minutes, and 43 alarms in an hour—more than the system had ever been able to handle before. After some further work, Fire Department top management adopted the idea and ordered it put into practice in July 1969. This Brooklyn installation, which cost less than a thousand dollars, has effectively doubled the system's ability to handle peak loads.

Many of the other changes suggested have also been put into practice. These have served to guide, for example, the communications improvements now underway in the Bronx.

This straightforward dispatching analysis, which followed from a fresh point of view and analytical skills not previously brought to bear, thus has proved operationally quite effective. It also showed that simply automating the then-current system would not significantly reduce peak-period delays. Indeed, it showed that to handle future peak loads one would need computer assistance for the dispatcher making decisions. As the deployment research began to make computer-assisted decisions possible, and to show what the potential gains would be, the Department adopted this point of view as the basis for all future design.

DEPLOYMENT

An important and difficult set of management issues concerns the allocation of fire-fighting units: how many units to have and how to man and deploy them. How these issues are resolved affects both fire protection effectiveness and the cost of providing it. Most urban fire departments have followed tradition. Paid departments, for example, have had the same number of men and units on duty around the clock, even though demand in the afternoon-evening peak period is several times greater than demand during early morning hours. Similarly, most departments have maintained a uniform "standard response" of men and equipment to alarms in most areas at all times, although fire hazards and the likelihood that an initially indeterminate alarm will turn out to be a serious fire vary greatly with area and time of day. Moreover, this "standard response" varies greatly from city to city. Some fire departments initially send as few as one engine (pumper) and one ladder (hook-and-ladder truck), while others send as many as six engines and four ladders.

For an alarm at a given location, dispatchers consult an "alarm assignment" or "running" card to see which units to send. This card contains a list of the units closest to the site, ordered by proximity. In some cities, including New York, it also lists preplanned move-ups or "relocations" to cover the area around the site should there be a large fire that draws many units away. These lists implicitly assume that only the one incident is active in the area at the time. In active periods, therefore, following the cards in areas with high alarm densities can quickly deplete coverage and lead to deployment problems that have to be settled by improvisation.

Thus, as early analysis showed, the traditional system forces dispatchers to make ad hoc deployment decisions when the incoming flow of new alarms most presses them for time. And, as the alarm rate rises, it leads increasingly to responses containing fewer units than planned, to improvised relocations, to longer than normal response times, and to unusually imbalanced workloads.

Problems arising from these traditional procedures had become severe in New York by the late 1960s. Busy periods were depleting coverage rapidly, and dispatchers were increasingly hard-pressed to maintain coverage, especially when several large incidents were active simultaneously. Some units were responding more than eight thousand times per year, and even on shifts when many of the runs were unimportant or unnecessary—minor incidents or false alarms—the units still felt the strain. Adding more units—at a cost per unit of over $500,000 per year—was a possible solution. But new units added earlier had provided less relief than expected, and several had become new high-running units themselves.

Members of the Fire Department had proposed numerous approaches to these problems. Without analysis, however, competing theories seemed more or less equally plausible, so that all but the most conservative ideas tended to lose impetus. The Department needed ways to test ideas that avoided the delays, risks, and costs of trying something new in practice and could distinguish the effects of new policies from the effects of changing circumstances. It also needed ways to help select the best ideas from those that had been put forward, and to help develop new solutions that might be even better.

There existed extremely little prior analysis of fire deployment, and no work on problems as complex as those in New York. Together the FDNY and the Institute thus have had to create, essentially from scratch, the perspectives, methods, approaches, and results of a new analytical field.

We began by creating a wide variety of models that analyze and evaluate Fire Department deployment and suggest new policies. Each model addresses a particular set of policy issues. With the help of the entire team, much of the development work for these models has been done by Jan Chaiken, Edward Ignall, and Grace Carter. Some employ quite complex mathematical analysis; some rely more on the power of the computer to compile, generate, reshape, and analyze large volumes of information; others distill the results of these complex analyses and computer runs into simple rules of thumb.

The choices open to the Fire Department are quite varied. For example, it can embark on a long-range program to reduce the number of fires and other causes of fire alarms. It can add men and equipment, either full- or part-time. It can better allocate men and equipment and match assignments more closely to demand, redistribute work among its men, and reduce the strain and time now called for at incidents of various kinds. The models help the Department examine all these options: some broadly and some in great detail—even down to the level of individual street corners.

The Fire Department has been intimately involved in developing, testing, and refining these models. And the Department has used these models for a wide range of purposes. Both staff and line officials use them to see how various policies can and do perform, and why, and to see how to reshape and modify them to fit new circumstances. They have found that the models reveal key points of leverage, where actions will have their greatest effects, and thus enable the Department to tighten the linkage between decisions and results. Used iteratively, prescriptive and simulation models have helped to create new policies and to distinguish worthwhile ideas from those that would be ineffectual or even potentially harmful. They have helped fire officials develop and gain acceptance for new programs, and have provided new bases with which to prepare for the future.

I would like here to discuss briefly a few examples of results that have led to changes in Fire Department practice.

Early analysis and projections of fire incidence showed that alarm rates from roughly 3:00 p.m. to 1:00 a.m. were and would remain at least twice as high as the rates for other times of the day. It also showed that in high-incidence areas false alarms, rubbish fires, and other minor incidents are most frequent during these hours. These minor events do not require men and equipment needed for structural fires. Yet the FDNY's standard response policy attempted to send three engines (pumpers) and two ladders to all street box alarms. The models, supported by extensive data, showed quantitatively how, during the peak demand hours, the standard response tended to strip high-incidence areas quickly. So many units, in fact, were tied up responding to and diagnosing early alarms that subsequent alarms received much less than the standard response and, if additional units were needed, received them from relatively far away.

Given these conditions, it seemed logical to consider an adaptive response—varying the number of men and equipment dispatched, depending on the likelihood of given types of alarms and hazards at various locations and times of day. To those who wondered how quickly the full standard response could reach a site if a street box alarm proved to be a serious fire, extensive analysis showed, paradoxically, that during peak periods the adaptive response policy on the average got the full response to fires faster than the standard response could; the "standard response" often did not dispatch the full complement of equipment initially, and even when it did, it had so stripped the area that the third engine, say, had to come from much farther away.

For a wide spectrum of response policies and performance criteria, various models showed how many additional units would be needed, and showed clearly that important gains in protection and relief would be realized only with different response policies and even then mainly during the peak hours. Both the Fire Department and the fire-fighting unions drew upon these results and the supporting analytical framework during their 1969 negotiations.

From these negotiations emerged a program of innovation, including an adaptive response policy and new fire-fighting units, called Tactical Control Units (TCU's), that operate only during the hours of peak demand. In helping make this new policy work, we assisted the Department in improving the dispatching centers, choosing and designing the adaptive response areas, and selecting sites and dispatching policies for the TCU's and the new full-time units.

Yet another model provided a quite unexpected bonus. The traditional dispatching rule dictates always sending the units closest to an incident. Analysis showed that when nearby units have widely different workloads other dispatching assignments dominate this traditional rule—by both leveling workload and reducing average response time. Moreover, the gains come essentially free. Accordingly, we have helped the Department put these new rules into practice—in particular, in redesigning response areas for battalion chiefs.

These deployment innovations have now been in practice, in varying degrees, for more than six months. Evaluations indicate that the benefits for men and equipment have surpassed expectations. Tactical Control Units provide the impact of full-time units, but at 40 percent of the cost. Adaptive response has consistently worked well—permitting equipment to arrive sooner, with additional units available for immediate dispatch when needed. Fire officials have estimated that the increased effectiveness these innovations provide would have cost an additional five to fifteen million dollars per year if supplied traditionally.

MANAGEMENT INFORMATION AND CONTROL SYSTEM

In the late 1960's, the Fire Department had begun to explore computer aid for its paper work and dispatching. Initial research suggested that these two problems be treated together—in an integrated management information and control system. Fire Department and other City officials supported this notion and urged the team to proceed in more detail.

The work in communications and deployment helped define such a system. The dispatching simulations showed that simple computer automation of the current system would not pay. The deployment studies revealed attractive new policies that exceeded the capabilities of the present system or of narrowly conceived computer systems. The Fire Department wanted a system that would handle projected future loads with minimum delay, put the new deployment strategies into routine operation, simplify paper work, and strengthen information available for planning and support. After considering previously proposed systems, the Department asked the joint team to prepare a functional definition for a computer-based management information and control system (MICS) that would specifically meet its needs.

Prepared quickly, this functional definition outlined, comprehensively and with detail, what a computer-based MICS should do: the functions it should perform, how it should do them, and why. Following the adoption of these guidelines, we helped the Department and other City agencies involved prepare a detailed invitation for bids on translating the functional definition into detailed system specifications. A large number of companies responded with formal proposals and bids, which we helped the City evaluate.

Rae Archibald, Carol Shanesy, and Warren Walker, among others, are now working closely with the new contractor, supplying the detailed policies, procedures, and computational algorithms that will form the heart of the operating system. These draw upon much of our other work, including extensive deployment analyses that build on the research described above.

Implementation should begin in a year or so. When the system is complete, the FDNY should have the most advanced management information and command-and-control capabilities of any fire department in the world.

NEW TECHNOLOGY

Fire protection has traditionally been viewed as an engineering problem. It should be clear that we view urban fire protection as including much more. Yet, there are some urban fire problems that remain based in technology or for which technology offers potentially attractive solutions. Hence part of our work has been to find new technology that shows promise of enhancing the Fire Department's overall effectiveness; to assess this technology to determine its relevance to Departmental needs and its prospective impact on the City; to devise means of applying it effectively; and to stimulate and, where possible, accelerate development and application of especially promising items.

When this research began, we felt certain of finding "spin-offs" from defense and space programs that would be useful in urban fire protection. Yet, after many months of exploiting contacts in defense and space agencies, we found little new that seemed ready for transfer or even highly promising.

We have thus directed our work toward points where technology appeared to offer particularly important leverage: reducing the gap between the time a fire starts and the time it is reported to the fire department; and enabling firemen to deliver more water through light maneuverable hose.

Under present practice, response to a fire cannot begin until some person reports it to the fire department. Early detection and warning systems (EDWS), usually of the kinds that sense high temperature or smoke, are in fact used in some commercial and industrial buildings. Their wider use is usually dismissed as uneconomical; moreover, existing thermal and smoke detectors are rarely sensitive enough to detect fires before they threaten human life.

More sensitive "ionization" detectors recently have become less expensive and more reliable. We thus became interested in seeing whether they might form the basis for a comprehensive EDWS to save lives and sharply limit the number of serious fires. We examined a potential system which includes the automatic detection of incipient fires and automatic transmission of alarms and alarm information directly to the Fire Department.

The study showed a large-scale EDWS using ionization detectors to be technologically feasible, and to cost—for amortized installation and operation—roughly twelve dollars per detector per year. Although difficult to estimate, the potential gains appear to be significant, especially in valuable or hazardous occupancies.

In fighting a fire, the classic weapon is water from a hose. But the friction the water meets in flowing through the hose creates a classic dilemma: it dictates using a large, bulky hose to get enough water to the fire, while firemen prefer and need a small, light hose for speed and maneuverability. This dilemma has now been resolved by a technological breakthrough initiated and catalyzed by the work of Edward H. Blum at the Institute.

This development derives from the fact that dissolving trace amounts of a special chemical—a long-chain polymer called polyethylene oxide—in the water reduces the water's turbulent viscosity by about 70 percent. The solution has been termed "slippery water." It permits the Fire Department to increase the flow through a hose at a given pressure by 70 percent or more, and to more than double the reach of the stream.

With slippery water, a fireman can deliver as much water with a 1½-inch hose as he previously could only with a 2½-inch hose. With the lighter hose, fire fighters can climb stairs and reach remote locations more rapidly and with less strain, and put out fires more quickly and effectively. Slippery water also permits delivering large volumes of water over greater distances in conventional size hose.

Principally a laboratory curiosity as late as November 1968, slippery water is now in the last stages of a joint development program aimed at bringing it into routine Fire Department use. Involved in this program are the Fire Department, The New York City-Rand Institute, and the Union Carbide Corporation, which makes the special polymer and has contributed highly significant technical and material resources. The first pumper equipped to use slippery water was activated in October 1969 and used effectively in actual operations. Over one hundred new pumpers equipped to accept slippery water have been ordered. Fire Department officials have estimated that in the next few years, when nearly all pumpers should have been so equipped, an increase in operational effectiveness will have been gained that otherwise would have cost many millions of dollars per year.

In developing slippery water and bringing it into fire department use, we have been "technological brokers," playing a unique role in public management. By having experts with extensive professional and industrial contacts working closely with a municipal agency, we were able to identify both an area where major gains could be made and the means of making them. We were then able to bring together the people with the problems and those with possible answers, and help them develop what was needed—for both the local problem and a national market. (Union Carbide plans to market the product nationally under the trademark Rapid Water.) Both the Fire Department and Union Carbide agree that without our active intervention, the chances of slippery water being developed effectively would have been small—the full story demands another paper.

SOME BROADER IMPLICATIONS

Most previous efforts to carry out broad-ranging frontier research on real urban problems have not been noted for success. It may thus be useful to note here a few of the reasons why this work appears to have been successful. These reasons include:

- a receptive agency, which recognized the relative obduracy of its problems and resolved to do something about them;
- a young, energetic staff (most of whom left secure faculty positions at top universities) interested far more in doing first-rate, policy-oriented work to help the Fire Department than in simply publishing papers to earn kudos in their disciplines;
- an effective joint research partnership between the agency and the "outside" research staff, conducted at a scale and over a period of time sufficient to do basic research as well as devise stop-gap measures.

This last has been extremely important, as I hope the preceding discussion has made clear. Indeed, at New York City's request, the partnership has now been made formal. A new organization—The New York City-Rand Institute—has been constituted as a formal, legal partnership between The Rand Corporation and the City of New York. Half the trustees of this not-for-profit organization are appointed by the City; its charter and mission make it much more a quasi-public agency than a traditional consultant.

This organizational form, preserving necessary objectivity and independence with direct, explicit links to the government, may well have wider applicability, as do the results of the studies described above.

COMMINGLING OF URBAN AND FOREST FIRES

(A Case Study of the 1970 California Near-Disaster)

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California suffered a near-disaster in 1970, when a record number of large fires broke out in late summer and fall. These fires were controlled only after a vast expenditure of money and manpower. And only because of this expenditure was the situation kept from getting worse. If we are to prevent a recurrence of conditions that led to these fires, we need to improve our capability to forecast when large fires are likely to occur, how they will behave, and how they can be controlled. And such a capability can be developed only by increasing our knowledge of fire through research.

Introduction

For us to discuss fire in the City of Chicago in 1970 is both timely and seemingly appropriate. Timely because in 1970, more large-scale fires raged out of control than at any other time in California's history. And seemingly appropriate because almost a century ago—on October 8, 1871—probably the most famous fire in American history broke out here: the Great Chicago Fire. Throughout American history, other large fires have occurred. Perhaps most of them are not as well known as the one allegedly started by Mrs. O'Leary's cow. But some were nearly as destructive as the series of fires that swept California in 1970. On the same day of the Great Chicago Fire, for example, a much larger fire wiped out the town of Peshtigo, near Green Bay, Wisconsin. Compare the acreage covered and casualties: in the Peshtigo Fire—1,280,000 acres and 1,150 lives lost; in the Great Chicago Fire—2,124 acres and 300 lives lost.

Between 1825 and 1900, there were 16 major rural fires in the United States: 9 million acres of timber were burned, 19 towns destroyed, and 2,829 lives lost. Of the 43 major "mixed urban and rural fires" recorded from 1900 to 1965, nearly two-thirds of them broke out in California. But the largest acreages burned were in the East—230,000 acres in 1947 in Maine, and 200,000 acres in 1963 in New Jersey. And so urban and rural fires are not a regional problem; they are truly a national problem of long duration.

In this paper, I intend to outline the characteristics of "rural" or "mixed urban/rural fires," describe the magnitude of the "near-disaster" in California in 1970 and point out that the situation could have been much worse, suggest how the potential for disastrous fires could have been reduced had present knowledge about fire control been implemented, and outline the specific problems that urgently need additional research.

Characteristics of Large Fires

First, let me consider the characteristics of mixed urban/rural fires. In general, such fires are characterized by the effects of long droughts, strong winds, high temperatures or low humidities or both, continuous highly flammable natural fuels, and structures in or next to natural fuels.

Drought

The Chicago and Peshtigo fires in 1871 were preceded by a period of long, severe drought in the Midwest. Similarly, the spring and summer of 1970 in southern California were also extremely dry—even for southern California. In the south coastal area of the State, precipitation had been only one-third of normal between April 1 and late September.

Winds

Strong winds, another common denominator of disastrous fires, intensified the severity of fires in 1970. Most months had more Santa Ana winds than normal. These desiccating winds in May probably were effective in nullifying the beneficial effects of the winter rains. During the summer months southern California normally has few Santa Ana days, and 1970 was no exception. July and August had none, but the number in September far exceeded the normal. Santa Ana winds of 70 miles per hour were measured by a Forest Service fire behavior team on the destructive Laguna Fire, near San Diego.

Low Humidity

Another common characteristic of these fires is low humidity (extremely dry air) or high temperatures or both. The Great Chicago and the Peshtigo fires burned during periods of relatively high temperature (79°F) and low humidity. Researchers at the Pacific Southwest Forest and Range Experiment Station recorded 2 to 4 percent relative humidity on the Boulder Fire, just northeast of San Diego this year.

High-Hazard Fuels

For urban/rural fires to spread under critical weather conditions such as strong winds, and high temperatures or low humidities or both, continuous vegetation, which we call "fuels," is needed.

The most common fuel in southern California is what some natives call their "elfin forest." This forest consists (or it did) of some 5 million acres of chaparral—a mixed formation of low, hard-leaved, stunted trees and shrubs. Chaparral grows slowly—shrubs 25 years old may average only 2 or 3 inches in diameter and 5 or 6 feet in height. Forest fire behavior experts say that chaparral is the most flammable brush in the United States. Its litter and dead portions usually are easily ignited, and almost every fire is a crown fire because of the horizontal and vertical continuity of this fuel. Living or playing in chaparral is indeed "hazardous to health."

Structures

Another essential ingredient for large-scale rural/urban fires is the highly vulnerable suburban or rural subdivision. The population explosion has complicated the fire problems for both the urban and the rural fire fighters. Many homes and other structures have been built in suburban or rural areas. These structures vary in size from shack to mansion. They not only increase the chances of disastrous fires, but expose both dwellings and residents to serious fire hazards.

Haphazard development of rural areas sets the stage for disaster. Losses to structures have been great, and they will likely increase. Fire-fighting forces alone cannot always furnish protection. And so measures to compensate for hazardous conditions must be planned and built into developments. Comprehensive and coordinated land-use planning is needed.

If we know the characteristics of rural/urban fires, can we forecast when they are likely to occur? In a sense, we can "predict," although we cannot say flatly that a large fire will break out at a specific time and place. All we can say with any certainty is that a fire is likely any year under present conditions. In some urban/rural areas with surrounding high-hazard fuels, when conditions are "ripe," the question is not *if* a fire disaster will occur but when. The frequency will be higher in some places, such as southern California, but the potential for large fires exists in the Midwest as well as in the East. Human nature being what it is, the longer between fire disasters, the greater the complacency and a lack of awareness of how serious the fire problem actually is. Despite warnings by fire departments, fire administrators, and fire researchers, the public too easily forgets—and so the cycle is repeated—complacency, warning, outbreak.

The 1970 Near-Disaster

The record of disastrous fires in California supports the point I have made—fires are likely to break out when conditions are ripe. And these conditions exist nearly every year at some time in the State. Despite frequent warnings of the likelihood of fire, people too easily forget these warnings.

It is almost impossible to avoid superlatives in describing the fire situation in southern California. This part of the State has the highest temperatures, the heaviest rainfall intensities, and yet the mildest climate in the continental United States. Disastrous fires occur here more often than in other parts of the country. Almost every year, a large fire breaks out in one of the southern counties. The record for 1968, 1969, and 1970 is particularly ominous. In 1968, two major fires in Los Angeles County denuded 87,500 acres of chaparral, destroyed 13 homes, and killed 10 fire fighters. In a single weekend in August 1969, more than 40,000 acres were blackened in Riverside and San Diego Counties.

The pre-season Santa Anas in 1970 wiped out the beneficial effects of winter rains, and it did not take a crystal ball nor great scientific knowledge to predict that 1970 had the potential to be a devastating fire year.

Fire Weather

The *California Fire Weather Reports* issued every 10 days from June 1 on by the Pacific Southwest Station's fire meteorology research staff, showed the buildup of "fire season severity" as the months passed by. On June 10, the fire weather severity for the San Gabriel Mountains in southern California was 251 percent of normal. By July 10 it had dropped to only 125 percent, rose to 145 by August 10, and dropped again to 138 percent September 10. But for the last 10 days of September, however, the seasonal severity was from 400 to 500 percent of normal.

Then came September 22! A moderate Santa Ana blew the smog out of the Los Angeles Coastal Basin, and a few fires occurred but were controlled while still small. Meanwhile, on that same day in the San Francisco Bay Area, a fire started at about 10:15 a.m. in dry grass on the east side of the Oakland Hills and, pushed by strong, dry winds, roared downhill toward historic Claremont Hotel. Only 230 acres were blackened, but 36 homes were destroyed and 37 others damaged. Not since September 18, 1923, when a major fire broke out near Berkeley, had a fire of such magnitude struck the Bay Area.

In southern California, the Santa Anas began to strengthen on September 25, and the first of what was to be a series of runaway fires was reported at 10:15 a.m. near the Mexican Border. Before the day was over, five large fires were roaring in San Diego, Los Angeles, and Ventura Counties, spreading rapidly across freeways, through housing developments, moving downhill as fast as uphill. Hundreds of other fires were caught before they became large. In fact, the record shows that 97 percent of the 1,260 forest fires occurring between September 15 and November 15 in California were held to less than 300 acres. That is a remarkable batting average, considering the conditions. The "box score" for this period was:

September 15–November 15

Number of fires	1,260
Acreage	600,000
Homes lost	885
Lives lost	14
Firefighting costs	$12 million
Watershed loss	$100 million
Property loss	$106 million
Rehabilitation cost	$15 million
Total costs (estimated)	$233 million

Major Fires

The 12 largest fires in California in 1970 occurred from San Diego County in the south to Monterey and Kern Counties in the north. Although the Matilija fire of 1932 on Los Padres National Forest, which burned 219,000 acres, still remains California's largest forest fire, 1970 produced the greatest number of large-scale fires burning out of control in California's history. The monstrous Laguna fire blackened about 175,000 acres, took 3 lives, and destroyed 382 homes.

Then, along came Friday, November 13, and with it some even stronger Santa Anas. A brush and timber fire started near Big Bear Lake in San Bernardino County, and before it was controlled more than 53,100 acres (83 square miles), and 54 homes were lost. Although the Pacific Southwest Stations's Forest Fire Laboratory is 18 airline miles from the nearest edge of the fire, ashes fell in the street, and the sky was so clouded with smoke that street lights went on at 4 p.m.

The consequences of these fires may claim lives and property long after the last spark has been extinguished. Water and mud may flow out of the burned watersheds—then people will likely drown in high water and will smother in mudflows; homes will be flooded; and others will be demolished by mud and boulders. Such deterioration in the wildland environment, a direct result of large fires, is drastic and long-lasting.

If all this is true, how can anybody in his right mind call these "near-disasters?" Let me explain.

First, I believe that holding 97 percent of the fires under Santa Ana conditions was a miraculous job. But it took an all-out team effort. More than 1,000 fire trucks and 40 aircraft from *all* California agencies were used. Moreover, 6,000 men fought the blazes—many of them brought in from the other western states. Fires did not stop at administrative or jurisdictional boundaries. Neither did the fire fighters. Once again the situation demonstrated the high degree of coordination and cooperative effort that exits in California. Los Angeles Fire Chief Ray Hill said, "Disaster was averted by the concerted action of many fire departments. These departments were able to work together effectively because of repeated experience."

Second, according to unbiased reports we received, some research and development results paid off. Like fire fighting, fire research in California is a joint venture of the California Division of Forestry, Los Angeles County and City Fire Departments, U.S. Forest Service, and other fire agencies. The State Division of Forestry and Los Angeles County Fire Department have supported the statewide research program by providing manpower, specialized equipment, and funds. From this cooperative effort have come helicopter fire fighting (helitack) methods, the techniques of "bombing" fires with chemical fire retardants dropped from airplanes, and other means of combatting fires.

Payoff from Research and Development

But did new concepts and practices pay off during the September-to-November fires? Didn't the television newsmen say the fires ran wild until the weather changed or they ran out of fuel? A few specific incidents will, I believe, illustrate the variety and value of these new tools that were developed from earlier research.

Helitack

Several fires which did not make headlines hit the Angeles and Cleveland National Forests. They started in heavy chaparral in remote, inaccessible areas. Air tankers and helicopters teamed up with ground crews to control these potentially dangerous fires. Burning conditions were extreme, but fire retardants cascaded along the perimeter slowed fire spread. Then, helitack crews were flown into the area—first, men jumped from the aircraft while it hovered and then cleared helispots for men who came in later. These fires were held to a small size during a period when manpower and equipment were scarce because of other fires.

In Los Angeles County, the County and City Fire Departments used helicopters to scout fires, drop retardants, transport injured personnel, and transport men and equipment to critical sectors when streets and highways were impassable.

Chemical Fire Retardants

On the Boulder Fire (Cleveland National Forest) on October 2, the Cuyamaca Peak Lookout and adjacent structures were threatened. It was too dangerous to bring in fire trucks. And so air tankers dropped retardants on and around the structures. As a result, all the buildings except a small garage were saved.

On the Malibu Fire in Los Angeles County on September 28, a series of retardant drops helped complete a critical section of fireline in Las Flores Canyon. If this section had not been completed, the fire would probably have burned into the densely populated Fernwood area of Topanga Canyon.

The air-slide mixer trailer—a joint effort of the chemical industry, fire agencies, and research team—was used to supply retardants to helicopters. About 25,000 gallons of retardant were mixed on the Malibu Fire. Bulk retardant helped solve the critical logistics problem, and highly viscous materials were essential in the high winds.

Fuel-Breaks

During the afternoon of October 1, the Meyer Fire on the San Bernardino National Forest was sweeping downhill toward the communities of Upland and Cucamonga and approaching the Foothill Fuel-Break. The break was 150- to 200-feet wide with a road (firebreak) within it. The cover on the fuel-break was grass next to heavy brush. Because the fire was heading downhill, the fuel-break had to be fired immediately. Three men from our staff backfired almost three miles of the break before they were relieved. Downslope winds were estimated to be 40 to 50 miles per hour during the operation. Backfiring from the fuel-break may have saved scores of homes and possibly some lives.

On the Boulder Fire on September 28, the Middle Peak Loop Fuel-Break on the Cleveland National Forest provided safe access for fire crews and fire trucks. The work of the crews, combined with retardant drops by air tankers, was effective in stopping the fire burning up a steep slope into the wind. This fuel-break is credited with saving the Cuyamaca State Park, which contains one of the few remaining "islands" of native conifers in southern California.

On the Tecate Fire in San Diego County on September 28, crews used the International Fuel-Break along the Mexican-U.S. Border to backfire and control the flanks of the fire for 4½ to 5 miles. The fuel-break also provided access and safety islands for men and equipment.

What Might Have Been Used

Although some R&D results were used effectively during the September, October, and November siege of fires, much more could have been done to reduce damages. Specific research results, which should have been applied, can be found in fire prevention, fire fighting, and fuel modification reports published during the past 10 years.

Fire Prevention

The Los Angeles County Fire Department developed the "Fire Hazard Alert" system several years ago through which all county employees and the public are alerted as soon as a forecast of critical fire weather is received. Fire prevention becomes the top priority job for all employees. In my opinion this system of "early warning" should be adopted by *all* forestry and fire agencies. The National Fire Weather Service (formerly U.S. Weather Bureau) would also need to participate.

Fire Fighting

We have learned from field tests that viscosity agents added to diammonium phosphate made both a highly effective fire retardant and suppressant. This combination is now cascaded from air tankers and is called "Phoscheck." Pumping equipment is available to mix and apply this retardant from truck tankers on the ground, but for some reason use in ground equipment has lagged. One factor may be lack of funds to buy the needed equipment and manpower. Another may be a failure of R&D teams to work with practitioners on the application after publication.

Fuel Modification

Much greater emphasis needs to be given to application of selective fuel modification. Although the research and action program called "Fuel-Break" has been in existence for about 13 years, only 500 miles of fuel-breaks have been constructed in southern California and only two-thirds of these are wide enough. These prepared breaks can be safely manned, if 200- to 400-feet wide, for offensive action against firefronts, and can help stop the lateral spread of fires. For fuel-hazard reduction to move ahead rapidly, funds must be available before the fires occur. Guidelines are available and have been since 1963. Forestry and fire agencies and public utilities should study, design, and develop fuel-break systems in their high-risk areas. Planning commissions and sanitation districts should consider the use of treated effluent for the irrigation of "green belts" around mountain communities. Public fire agencies should make safety zones and safe entrance and exit routes an integral part of their overall plans. Finally, each resident in a high-hazard area must maintain his own property in a "fire safe" condition; he must assume responsibility for fuel hazard reduction outside his home as well as inside it.

Highest Priority Research Needs

Even if all available R&D results were applied, we would still have large and destructive forest fires. 1970 was not only a bad fire year for California but also for other States in the West. In addition to about 600,000 acres blackened in California, resource losses in Oregon and Washington were extremely high—more than 200,000 acres of prime timber, watersheds, and recreation areas were burned in July and August. This destruction demonstrates the urgent need to strengthen the research programs outlined in long range plans by the Forest Service in cooperation with other agencies of the U.S. Department of Agriculture. For the West, this means strengthening research at Seattle, Washington, and Missoula, Montana, as well as Riverside, California. Research at these other two western facilities complements and strongly supports the research program in California.

At the Pacific Southwest Station, we believe highest priority needs to be given to solving these four problems:

1. *Prevention of Accidental and Incendiary Fires:* A sharp increase in man-caused fires, particularly those caused by children and alienated young adults, during periods of critical fire weather has emphasized the extreme importance of more positive fire prevention techniques. In California, 70 percent of all forest fires are man-caused. For the critical periods between September 15 and November 15, 98 percent were caused by people. Therefore, the key to fire prevention is human behavior.
2. *Mass Fire Behavior:* Fire disasters in southern California during the past decade in which more than a score of fire fighters died have dramatized the need for more precise knowledge on the local interaction between Santa Ana winds and rugged mountain topography. Remote sensors, such as LASERS and vidicon cameras which "see" through smoke, show much promise for increasing our understanding of the characteristics and dimensions of mass fire systems and the interaction between the fire and its environment. Further research and development is, however, needed.
3. *Fire Management Systems:* The application of computer science and systems analysis is critically needed to develop optimum use of existing fire-fighting methods and to develop criteria for improved aerial attack methods and radically new tools to increase the striking power of the fire fighters.
4. *Improved Fuel-Breaks:* Some progress has been made in establishing fuel-breaks to break up the vast expanses of high-hazard chaparral, and a small start has been made in developing low-growing or less flammable species. However, we need to develop protective areas of managed fuel for suburban and foothill areas. Community "green-belts" and patterns of vegetation which are drought- and frost-resistant, but still esthetically pleasing, and have deep root systems for holding the soil in place are needed for this development. Also, much more knowledge is needed of the ecological factors which contribute to the flood-fire sequence of disasters.

Conclusions

From all that has happened, it is clear that the commingling of urban and rural fires is a national problem. And the potential for disaster is growing faster than our ability to cope with it. The 1970 fire season will long be remembered by California residents and fire fighters alike. It was a season marked by three periods in early and late fall, when large-scale fire ravaged about 600,000 acres, killed 14 persons, and destroyed nearly 900 homes. Actual and potential losses and suppression costs are estimated to exceed $200 million. Despite these losses, the record could have been even blacker if efficient mutual aid and close cooperation among fire-fighting agencies had not been the order of the day.

Furthermore, the application of R&D results from cooperative research programs probably kept losses down. We have every reason to believe that helitack techniques, use of air tankers in dropping chemical fire retardants, fuel-breaks, and knowledge of fire behavior helped keep 97 percent of the fires under 300 acres. And the application of these techniques and knowledge may have saved lives and property on the larger fires.

But a lot more needs to be done—not only in applying findings of past research and development but in seeking answers to problems still crying for solutions. The nationwide need for strengthening fire research has been recognized by the Fire Research Committee of the National Academy of Sciences. The Committee, in its first conference in 1956, recommended major increases in fundamental research on fires.

Fire research has not taken a solely "ivory tower" approach—not by any means. Researchers studying fire behavior and fire meteorology have worked closely with fire bosses and forecasters to aid application of new knowledge. We consider assignments such as these mutually beneficial. They not only provide a helping hand to fire fighters, but also help our scientists develop a much better understanding of the behavior of large-scale fires and their interaction with the environment.

Finally, unless research and development efforts on urban/rural fire problems are bolstered soon, a major national disaster may result. The large fires that ravaged California and other parts of the West this year could well portend things to come. But we need not let them happen. We ought not let them happen.

WHERE DO WE GO FROM HERE?

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In considering this question please keep in mind the predictions quoted by Chief Volkamer[1] on the population distribution in U.S. in the year 2000: . . . "312 million Americans, 187 million of whom will live in 14 major areas . . . averaging 13½ million Americans." In addition recall the aspects of New York City's current fire problems related to social unrest, as described by Dr. Blum.[2] Then contrast the recent predictions of Hubbert[3] that the earth's air and natural gas supply will be virtually exhausted by the year 2000 with the hazard to life caused by a superabundance of fuel stored in America's wild lands described by Carl Wilson.[4] We see that:

1) The urban fire problem has intensified and will intensify further, reflecting

deeper social problems; we may well be losing the war against urban fires if the quality of urban life continues to decay.

2) Some of the problems intensified by technological innovations, can be met by technological innovations.

In this paper I will elaborate on the interplay between fire and the greater problems facing society and argue that in applying technology in seeking solutions to fire problems a recognition of the full spectrum of problems is essential, and solutions to fire problems can be found only by first solving the social and ecological ones.

1. *Ecological Problems*

The spectacular magnitudes of fuel burned as described in the Commingling of Urban and Forest Fires by Wilson demonstrate how intimately related fire is to man's most immediate problem—survival on this planet.

For example, if we assume a fuel loading of 30 tons per acre burned in this year's California fires we estimate a fuel consumption equivalent to that of the entire U.S. population for food and 1% of that for all purposes for an entire year.

At present a U.S. resident uses approximately10 kW/person of energy, most of which is from combustion sources[5]; this is approximately 0.1 percent of the solar income. This release of energy, largely derived from fossil fuel, produces CO_2 (which appears to be increasing the atmospheric level dramatically), and heat. It is felt that the release of CO_2 is already dangerously high. Ecologists argue that the upper limit of allowable heat release is no more than 10 times the present value. Roughly 5 times this amount of energy is being stored or cycled in forest stands throughout the country.[5,6]

On the average these stands are sufficiently young for storage processes to exceed the processes of decay, i.e., there is net storage enough to meet our fuel needs if the process of decay is intercepted.[5,6] The processes of decay in forest stands produce heat and CO_2—without recognizable benefit to man. The inventory under some conditions represents a hazard[4]—hence the following example of a dual purpose solution: by harvesting excess stored cellulosic fuels in forests near urban areas an ecologically acceptable source of energy can be gained while reducing the hazard of fire. In other words by transferring forest decay into combustion chambers we can halt the rise in atmospheric CO_2 while halting forest fires.

There is good evidence from extensive experience in European forest management that clearing the ground rubble virtually eliminates forest fires. In France, where this practice was recently halted, disastrous fires ensued.[7] The reason for the fire inhibition brought about by clearing ground rubble can be inferred from the remarks of Kerr.[8] Crown fires cannot be maintained without the support of ground fires. The cost of the 600,000 acre fires in California in 1970 has been estimated at approximately 300 million dollars.[4] Surely a $500/acre subsidy for clearing forest rubble would go far in supporting an otherwise uneconomical fuel source.

In brief: oil and natural gas are rapidly disappearing; meanwhile, we suffer from a surfeit of stored fuel in our wild lands. A long-range solution to both fuel shortage and fire hazard problems may lie in developing means of harvesting forest rubble for the synthesis of gas and liquid fuels while keeping forest-fire-retarded recreational and timber resources.

2. *Sociological Problems*

Blum,[2] Kerr,[8] and Volkamer[1] referred to the increased likelihood of urban fires and the increased hazard in fire fighting caused by social unrest.

Real poverty, begetting poverty of spirit, is thus a fire hazard. A very real consequence in human terms is the tarnishing of the fire fighter's self-image as heroic benefactor.[2] One of the most potentially useful areas of a fire marshal's activity is to render poverty areas safe from fire by working toward the elimination of the causes of poverty.

Fire inspectors who can recognize and sympathize with the deeper causes of fire hazards can work with local citizens toward solutions of the basic problem.

That the fire fighter as a sympathetic and understanding (i.e., modern) hero can emerge was vividly demonstrated in 1969 in altercations between residents of a student ghetto and authorities in Madison, Wisconsin. In the end the sympathetic understanding of the fire department gained the cooperation and support of the one time dissidents.

Once the people are cooperative in fire protection the benefits of education are dramatic. Chief Welch,[9] Minneapolis fire marshal, has impressive figures on the reduction in fire occurrence in factories, hospitals, and neighborhoods which actively participate in fire-safety instruction versus those that do not. Evidence is overwhelming from a number of sources that a society determined to prevent fires and well instructed can greatly reduce their occurrence. Little fires nearly anyone can quench.

How then to gain the sympathetic cooperation of a neighborhood? By listening to the people, understanding their problems, and working to help them solve then where fire is involved, and in so doing educate them in fire safety.

I strongly recommend local citizens advisory groups be organized and encouraged to speak out on the root causes of local fire hazards. If the local fire department representative could in some way help in eliminating the root cause he would discharge his responsibility admirably Antona Richardson, assistant director of F.I.R.E. at the University of Minnesota, insists that women be represented since they are closest to the start of most home fires.[10]

The role of the fire fighter could be of endless benefit to the local community. Some examples: finding meaningful employment for potential incendiaries, finding adequate nutrition and education for nascent incendiaries, working to establish urban fire breaks that would serve as recreational areas for residents, and working actively to improve living conditions where marginal housing persists.

3. *Technology*

It seems clear from the papers given here today that technology will be needed in coping with the expanding problems caused by increased urbanization and the increased technical complexity of society. It is equally clear that this technology can only be really effective if it is used to help solve the core problems of a balanced ecosphere and a healthy society. This means it must be in large measure directed by society, with a strong voice given to ecologists and social scientists.

In what role does technology show the most promise? Several aspects of Ed Blum's paper[2] suggest terribly exciting guide lines.

a) *Modeling.* The spectacular success in discovering operational bottle necks through modeling—and creating effective solutions through modeling is a success story with many implications.

1) It is possible to model societal components and manipulate components to find model solutions.
2) The value of the model solutions are sufficiently obvious to persuade the several groups that make up an enormous fire-fighting apparatus to experiment in seemingly radical changes.
3) The active collaboration of a line operation with a relatively academic research group has been sufficiently successful to warrant expanding the collaboration.

Dr. Blum hinted in his report that the expanded collaboration between Rand and New York City would lead to modeling other problems affecting urban life. The use of high speed computers makes such ambitious undertakings seem reasonable at last.

An idea how such a modeling process can be developed can be gained from work directed by Robert Holt, Professor of Political Science at the University of Minnesota.[11]

Dr. Holt and his team of sociologists, engineers, and mathematicians are searching for models that will predict the dynamic behavior of elements in society (e.g., housing needs, employment, urban growth and decay, etc.), and factors that influence their dynamics. His group soon learned that the necessary information is not presently in hand to produce adequate models; programs are being prepared that will enable the researchers to learn societal component dynamics from the social experiments that each developing (and decaying) urban area represents. Finally it became clear that even if the models were available, the existing apparatus to influence urban dynamics (the various administrations) is incapable at present of appreciating the information available or of acting on it. Thus, a final phase of the program is to model the decision-making apparatus of an urban area so it may learn how to profit from the continuum of urban experimentation about it and act effectively. No long-range goals or value judgments are involved other than asking those elements of society affected by change if the change made life better or worse for them.

Another group at Minnesota is exploring the long-range goals, i.e., the goals and constraints of the Steady State Earth, the earth of stabilized population, of recycled materials, which operates on ecologically acceptable energy sources.[12] Here the aim is to take a broader view of allowable and desirable ecological, sociological, and technological developments in hopes that a model of society may emerge that could survive for a few centuries on this planet.

The acceptance of the model solutions developed by the NYC-Rand team and their success in operations constitute heartening news. It is to be hoped that when a workable model of the society of the future involving radical change is presented to the various elements of society a concerted cooperative effort toward reaching the goals may ensue.

Because the fire fighter's job is so enmeshed in the problems of society, it would seem essential for him to play a substantial role in seeking effective solutions of the major social problems of the future.

b) *Deploying Results of Research and Development.* Much has been written about the need for better communication between line fire fighters and their administrators on the one hand and researchers on the other.

The need for communication is mutual. Again we must thank Ed Blum[2] for an example of how communication can be affected by teaming line operations with a research team. The latter by training and the requirements of continued viability must be familiar with the research literature. To earn their keep with the line organization they must become familiar with the operational problems. I would place the burden of responsibility for communication on the research team. The deployment of turbulence suppressing additives to enhance hose water delivery[2] is an impressive demonstration of effectiveness of this mode of operation.

The problems of New York City are sufficiently staggering to warrant the magnitude of the collaborative effort with Rand. Gradations of this approach may be equally effective elsewhere. Viable research groups in the technologies relevant to line fire fighting, for example, exist in many universities. Trained graduate students with experience in fire research are being produced. A proliferation of the NYC-Rand type collaboration should improve the relevance of university based research as well as the effectiveness in deploying the results of research.

An example of the desire of the modern graduate students to perform relevant research is illustrated in the following.

Our fire research group at Minnesota had been measuring heat and mass transfer coefficient data on fuel soaked wicks.[13,14,15]

One student, Norm Alvarez,[16] showed that ignitable mixtures occurred on radiantly heated cellulosic surfaces first at regions where convective mass and heat transfer coefficients have the lowest values. Students working under Professor Ephraim Sparrow were studying heat transfer coefficients above heated plates in water.

There appeared reason to suspect mass transfer coefficients would assume a minimum value in the region of transition from laminar to turbulent flow. When I described the ignition problem to the graduate student, Jack Lloyd, he proceeded to design his thesis experiments so they would cover the flow regime represented by sloping roofs exposed to fire radiation. He found, indeed, that on roofs of slope less than a critical angle, a local stationary mass transfer coefficient minimum exists and ignition would occur there earlier than would have been predicted by mass transfer coefficients then available in the literature.[17] The students in general are delighted to do relevant research.

Similar arguments could be mustered for teaming line operations with engineering design centers for help in apparatus development. The time is ripe . . . urban problems are a prime concern of university administration, faculty, and students. The fire fighter is welcomed.

SUMMARY

1) The products of photosynthesis stored in forests near urban areas constitute a hazard. With diminishing gaseous and liquid fuel reserves these stores could be harvested to supply the raw material for liquid and gaseous fuel synthesis with simultaneously an ecological gain and a reduction of fire hazard. When the staggering costs of fire fighting, and fire losses are taken into account, the price of fuel thus obtained could well be reasonable.
2) The increased ignition of fires and the obstruction of attempts to fight them caused by social unrest can be most effectively dealt with by attacking the

root causes of social unrest. The role of the fire marshal should be expanded to
   a) seek advice and help from residents of areas of unrest,
   b) champion the causes of the socially deprived when it is clear that improved living conditions will improve fire protection,
   c) seek help from residents in maintaining good fire safety practices.

3) The application of technology by multidisciplinary teams to model the dynamics of components of urban society in search of a healthy, stable, enduring model of society including an enlightened and informed approach to fire prevention appears a most exciting long-range goal. The team linking New York City and the Rand Corporation serves as an encouraging example of what can be done. It also suggests an effective mechanism for communication between the research community and the fire fighter for deploying the results of research as well as guiding research into relevant channels.

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ABSTRACTS AND REVIEWS

A. Prevention of Fires and Fire Safety Measures

Factory Mutual Research Corporation "Rack Storage Tests," *Factory Mutual Record* **47** (3) (1970)

Sections: A, E
Subjects: Rack storage; Warehouse fires

Reviewed by R. L. Tuve

Because modern warehouse storage practices are outstripping effective fire protection information, basic knowledge is needed concerning the factors of the type of product stored, its packaging material, height of storage and type of storage, and their relationship to the arrangement and application rate of fire protection. Economical considerations also require that overprotection or impaired operating efficiencies in storage areas be avoided in the design of protection systems.

Industry-collaborative warehouse storage fire tests have been underway at Factory Mutual for over a year using small-scale and full-scale fire tests. Variables of fuel, vertical spacing of test commodity, depth of space between storage tiers, spacing and location of sprinklers and void area between sprinklers and storage have been imposed. A reproducible, economical test method has been developed for large-scale fire tests with all controllable variables except one held constant. Newer tests are examining variables of sprinkler temperature ratings, types and arrangements of fire detectors, effects of draft curtains, high expansion foam agent, and installation of intermediate-level sprinklers. A multitude of time-temperature readings and time-event records are made.

Firm conclusions relating to actual storage conditions are not available yet but evidence is becoming clear in the direction of reliable standards of protection.

Butcher, E. G. (Joint Fire Research Organization, Borehamwood, England) "Fire and Car Park Buildings," *Joint Fire Research Organization Fire Research Note 841* (September 1970)

Section: A
Subject: Car park fires

Author's Summary

Brief details are given of the experimental work which lead to the suggestion that an open-sided car park building need have little fire resistance. Supporting information is derived from an analysis of the fire incidents which have occurred in such buildings and from a survey of current practice in their use.

Palmer, K. N. (Joint Fire Research Organization, Borehamwood, England) "Dust Explosion Venting—A Reassessment of the Data," *Joint Fire Research Organization Fire Research Note 830* (August 1970)

Section: A
Subjects: Dust explosion; Explosion venting

Author's Summary

The published data on the pressures developed on vented dust explosions has been reassessed in an attempt to bring it together and form a basis for discussion.

Nine basic assumptions are listed, the most important being that at some instant in a severe explosion the combustion could be taking place throughout the whole volume of the vessel. The assumptions have led to the derivation of equations relating the explosion pressure to the area of vent, the volume of vessel, and explosion parameters of the dusts. Calculated explosion pressures have been compared with the published data. Only unrestricted vents have been considered.

The severe conditions of explosion would be of most interest in practice, to the design engineer, but modified calculations could be made for less severe conditions.

The present ad hoc procedure for stipulating vent area has been compared with calculation, and appeared to be reasonable.

The gaps in the published data were listed, and attention drawn to those aspects where further information is particularly required.

B. Ignition of Fires

Friedman, M. H. (Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland) "A General Thermal Explosion Criterion Application to Initiation by Imbedded Wires," *Combustion and Flame* **13** (6), 567–576 (1969)*

Section: B
Subjects: Explosions; Ignition; Thermal explosion

Author's Abstract

A thermal explosion criterion recently published by the author is used to obtain general solutions for the explosion/ignition delay of an exothermic material surrounding a heated wire which is long and a good thermal conductor.

The case of d.c. heating is treated first and in greatest detail. Equations for explosion delay and explosion temperature are derived, which show how these variables depend on the initial conditions, the properties of the wire and the ex-

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plosive, wire size and the heating rate. Predicted explosion times are shown to agree well with those obtained by numerical integration of the complete set of differential equations which define the d.c.-wire problem. The analysis is used to support a critical review of the "ignition temperature" concept and to analyse earlier experimental parametric studies of ignition energy. The partition of energy between the wire and the explosive, at explosion, is also examined.

A Laplace transform technique is used to derive an explicit approximation to the wire temperature when the heating rate varies with time. The use of this approximation is illustrated for a heating function proportional to $\tau \exp(-\lambda\tau)$, where τ is non-dimensional time. When the explosion time is small, little heat is transferred to the explosive and the interface temperature may sometimes be estimated to good accuracy by assuming the wire to be adiabatic. The use of the "adiabatic wire solution" to predict short explosion delays is illustrated for a simplified exploding bridgewire heating function.

C. Detection of Fires

Nash, P. (Joint Fire Research Organization, Borehamwood, England) "The Detection and Extinction of Fires in Factories. Part 1. Detection," *British Journal of Occupational Safety* Nos. 87 and 88 (1969)

Section: C
Subjects: Detection; Extinction; Factory fires

Reviewed by R. L. Tuve

Information given in this paper is in the nature of general advice for plant and factory management officials concerning fire prevention, protection, and extinguishment matters. Specificity has been avoided in order that a broad treatment of the subjects could be offered to the largest audience in a short time and small space.

In Part 1, the often-neglected need for both flame arresters and explosion relief devices for prevention of damage and transmission of fire is pointed out. Important information contained in Ref. 1, such as the flame arresting capabilities of various types of arresters and specification procedures for devices is mentioned. The problem of dust explosions in factories is touched on briefly so that the reader is motivated to obtain further details from Refs. 2 and 3.

The four principal methods of fire detection (thermal, smoke or ionized combustion products, heat radiation, and sound) are outlined in some detail. Each method is classified as to measurement system and sensitive element used, concluding with a short sentence describing the principle of operation of the type and class. For instance, the ionization chamber detector for combustion products "Minerva", "Cerberus", etc., is described as a "radioactive source which ionizes air in chamber and gives a small electrical current between electrodes—." Its principle of operation is given as "Smoke and/or combustion aerosols entering an open ionization chamber causes a reduction in electrical current—." The condensed information given affords the plant manager an opportunity for narrowing the field of detector-type selection.

In Part 2 a quick survey is made of the uses, merits, and shortcomings of each type of fire extinguishment method available for plant protection. Classed according to agent type, the various systems using water, protein type foams, dry chemicals, vaporizing liquid agents, inerting gases, and high expansion foams, are discussed in variable detail. Systems and methods for the use of water in sprinklers, spray nozzles, and requirements for these, are given major attention and emphasis is directed to various inert gas producers for large volume storage space flame control. The author is disposed to make some generous forecasts concerning the future wide-scale employment of medium (100× to 500×) and high expansion (up to 1,000×) foams in lieu of other currently used agents. It is interesting to note in this paper, as elsewhere in U.K. publications, that the toxicity potential of the recommended vaporizing liquid agents, BTM (bromotrifluoromethane) (Halon 1301) and BCF (bromochloridifluoromethane) (Halon 1211), is not given the degree of emphasis ascribed to them by U.S. authorities.

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O'Sullivan, R. F., Ghosh, B. K., and Turner, J. (Joint Fire Research Organization, Borehamwood, England) "Experiments on the Use of a Laser Beam for Fire Detection. Part 1. Heat Detection," *Joint Fire Research Organization Fire Research Note 823* (October 1970)

Section: C
Subjects: Circuity; Detector; Fire; Heat; Investigation; Laser

Authors' Abstract

This note described an experimental investigation of the response to fire of a novel fire detection system. This system consists essentially of a focused laser beam, projected beneath the ceiling of a compartment, and a photocell receiver whose area is just large enough to contain the incident spot of laser light under

no-fire conditions. When turbulent hot combustion gases from a fire intercept the path of the beam, the laser spot is randomly deflected on and off the photocell.

Frequency analyses have been made of the photocell's output under normal ambient conditions and in response to fires of different powers. It was found that fire can best be discriminated from ambient heat sources by selecting that part of the photocells' output which is in the range 40–80 Hz.

It is shown that a fire of less than 140 kW, at any position in a building 12m high, 15m×41m, can be detected in less than 45s. This performance compares very favourably with the estimated performance of a point heat-sensitive detector of maximum permitted sensitivity.

D. Propagation of Fires

Baldwin, R. and Thomas, P. H. (Joint Fire Research Organization, Borehamwood, England) "Spread of Fire in Buildings—Effect of the Source of Ignition," *Institution of Fire Engineers Quarterly* **29** (74), 183–186 (June 1969)

Section: D
Subjects: Building fires spread; Fire spread; Ignition source for building fires

Reviewed by J. Malcolm

In this paper, the authors analyzed data of the "United Kingdom Fire Statistics"[1] which reported incidents of spread of fire in buildings beyond the room of origin. These data also included the mode of the initial ignition, e.g., by gas appliance, smoking, et al.

Based on data taken over the years of 1964, 1965, and 1966, probabilities of fire spread were calculated for 21 categories of ignition modes, including miscellaneous and unknown categories. Certain fire configurations were excluded from the analysis, for example, fires in single compartment buildings, and fires confined to a single item, since these could not be meaningfully interpreted in terms of probability of fire spread from the room of origin.

In analyzing the data, the authors noted little variation in the overall period considered between the values determined by year for the chance of fire spread as a function of ignition mode.

The authors concluded that the variation in the chance of fire spread as a function of the mode of ignition was very unlikely a result of random statistical variation.

The lowest chance of fire spread (0.09) was found for the category "gas appliances and installations." The higher chances of fire spread were found for the categories shown in the following table.

The ultimate objective of the authors' investigations is to develop means for predicting fire loss or damage as a function of the mode, or source of ignition.

TABLE 1

Proportion of fires attended by the fire brigadessp reading beyond the room of origin for different sources of ignition

Source (mode) of ignition	Chance of fire spread
Unknown	0.44
Malicious or intentional ignition	0.40
Rubbish burning	0.37
Mechanical heat and sparks	0.27
Naked light (no further information)	0.24
Liquefied petroleum gas appliances and installations	0.22
Natural occurrences	0.19
Children with fire (e.g., matches)	0.18
Acetylene appliances and installations	0.18
Oil appliances and installations	0.18
Spontaneous combustion	0.17
Other and unspecified fuel applications and installations	0.15
Smoking materials	0.14
Matches (except children with)	0.13
Explosives, fireworks	0.13
Solid fuel appliances and installations	0.13
Chimney, stove pipe, flue (not confined to)	0.12
Electrical appliances and installations	0.12
Miscellaneous	0.11
Gas appliances and installations	0.09

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E. Suppression of Fires

Jamison, W. B. (Walter Kidde and Company, Inc.) "Stability—The Key to Effective High Expansion Foam. Part II.," *Fire Technology* 6 (2) 140 (1970)

Section: E
Subjects: Foam stability; High expansion foam

Reviewed by R. L. Tuve

This paper is the concluding part to Part I of the same title which appeared in Fire Technology 6 (1), 39–51 (1970). In Part I, the author reviewed the fundamental requirements of high expansion foam, its action on fires and the results of tests which demonstrated conclusively that water retention over periods of time (stability) is important to its effectiveness.

In Part II, the author cites test data on two types of high expansion foam, "stable" and "unstable", which were used to fill a test compartment in which overhead sprinklers were operated at discharge densities varying from 0.15 gpm/sq ft to 0.40 gpm/sq ft. The "stable" foam suffered a shrinkage of 1.5 cfm/sq ft to 1.9 cfm/sq ft with a maximum of 2.0 cfm/sq ft at 0.20 gpm/sq ft sprinkler discharge density. The "unstable" type high expansion foam suffered an unequal shrinkage whereby that foam directly exposed to sprinkler discharge averaged only about 60 percent the foam height of that foam not exposed to water discharge. The comment was expressed that, "foam of low stability under operating sprinklers could move away—and expose a hazard designed to be foam submerged—."

A number of tests are cited showing that the top surfaces of stored boxes or cartons in a volume which has been completely inundated with high expansion foam receive water damage by downward vertical water drainage from foam. There is no horizontal migration of water drainage from foams. Water damage may be minimized by using stable foams of the lowest density consistent with requirements for fire control.

The results of efforts to remove high expansion foam from compartments by a number of methods are given: water spray, ultrasonic generators, foam killing chemicals, and severe mechanical action. The employment of large centrifugal fan devices such as a leaf blower seem to be the best solution to foam removal probems.

Rogowski, Z. W. (Joint Fire Research Organization, Borehamwood, England) "Flame Arresters as Barriers against Hot Metal Particles. Part II," *Joint Fire Research Organization Fire Research Note 757* (August 1970)

Section: E
Subjects: Flame arresters; Ignition; Particle incendive

Author's Summary

Particles produced by fusing of copper wires with a current up to 1200 A 250 v. D.C. penetrated the apertures of crimped ribbon arresters and remained incendive in atmospheres of ethylene and diethyl ether in air. Penetration could be prevented by containing such particles within strong insulating sleeves around the wires.

Troup, E. W. J. (Factory Mutual Research Corporation, Norwood, Massachusetts) "The High-Challenge Fireball—A Trademark of the Seventies," *Fire Technology* 6 (3), 211 (1970)

Section: E
Subjects: Fireball; Warehouse fires

Reviewed by R. L. Tuve

The title of this paper deserves some translation. "High-Challenge" connotes the tendency of modern warehousing and materials storage methods toward high-ceiling, high-volume enclosures where combustibles are stored in dense and close proximity, offering fire hazards of greater intensity than ever before. Construction materials such as plastic roofs and sidings increase the potential toward fire of such storages. When large combustible volume stored materials are ignited, the resultant convection of hot and burning gases and vapors approaches upward velocities similar to the "fireball" from burning flammable hydrocarbon gases and vapors arising from ignited surfaces such as fuel storage tanks, etc.

An analysis is given of the temperature-gas density relationships which cause driving force upward within a fireball and data are presented suggesting that falling water drops from overhead sprinklers never reach burning stored Class A material to accomplish cooling and flame diminution. Factors affecting these mechanisms are discussed, such as: fuel-to-ceiling clearance and fuel-pile array, the latter causing chimney effects.

A number of experimental fire tests were conducted simulating fireball production within a 40 ft by 60 ft building having a 33 ft floor-to-ceiling height. Ground-mounted gasoline burners reproduced a rapidly rising fireball while deluge sprinkler system ceiling grids plus a supplementary special sprinkler grid capable of flexible elevation were used for water discharge "survivability" measurement. Suitable floor catch pans for water were installed. Plain water and gelled water supplied to the sprinkler grids were tested separately. Increased average sprinkler pressures were also evaluated.

When only four sprinklers were operated directly over the fireball, very little water survived the trip down through the rapidly rising fireball. When twenty sprinklers were operated, survivability of water increased markedly, suggesting that some water entered the fireball from the side, some distance below the ceiling. Gelled water discharged from similar sprinkler heads more readily survived the rigorous flight through the fireball than did plain water, especially at lower pressures at the nozzle.

Young, R. A. and Lange, A. (Joint Fire Research Organization, Borehamwood England) "Water Distribution from an Array of Four Sprinklers," *Joint Fire Research Organization Fire Research Note 685* (May 1970)

Section: E
Subjects: Distribution; Measurement; Sprinkler; Water

Authors' Summary

The distribution of water at depths of 0.61, 1.22 and 3.66 m (2, 4 and 12 feet) beneath a square array of four similar sprinklers operating at a pressure of 0.70 kgf/cm^2 (10 lb/sq in.) and spaced to give a coverage of 12.08 m^2 (130 ft^2) per head, has been measured. Five makes of conventional and spray sprinklers, both upright and pendent, have been examined in this way, a total of 23 different sprinkler types and positions.

The uniformity of distribution over the central part of the square collecting area beneath the array has been assessed from 25 percent and 100 percent samples, in order to provide the basis for developing a method of approval of sprinkler distribution.

F. Fire Damage and Salvage

Lotspeich, F. B., Mueller, E. W., and Frey, P. J. (Alaska Water Laboratory, College, Alaska) "Effects of Large-Scale Forest Fires on Water Quality in Interior Alaska," *Report of Federal Water Pollution Control Administration, Department of the Interior* (February 1970)

Section: F
Subjects: Alaska; Forest fires; Water quality

Reviewed by R. L. Tuve

This report concerns an analysis of the effects on the Alaskan taiga (swampy coniferous northern forest area) ecosystem caused by large forest fires and efforts to control them. Multiple sampling stations were established to accomplish this by analyses of soils, water, and aquatic organisms on burned and unburned areas. Samples were collected nine months after the forest fire had subsided; when ice breakup was occurring; one month later in June 1967; in September 1967 prior to freezing; in May 1968, 22 months after the fire.

The Alaskan forest fire involved in this study was caused by lightning on July 23, 1966. In spite of valiant efforts by smoke jumpers, adverse winds and dry forest conditions caused the fire to increase in size so that it had burned an area of 40,000 acres by August 1, with an advancing fire front of about 15 miles. The fire continued in size with only temporary diminishment during periods of rainy weather until August 23, 1966, when cloudy moist conditions allowed direct attack by the 600 men who were fighting the fire. Total extinguishment was achieved September 13 after 250,000 acres had been burned. Heavy rains and snow were potent assistants to its control. Over 400 miles of fire trails were built during the 44-day burning period.

The general results of the soil and water analysis after this fire were:

1. Burning did not destroy the entire organic soil overburden layer.
2. The burning of the organic layer caused a decrease in cation exchange capacity of the soil.
3. Potassium content increased in the burned organic layer and this salt was high in streams draining from burned areas.
4. The depth of thawing of permafrost was not affected by the fire.
5. The only evidence of increased soil erosion was in the fire trails and it was concluded that fire control methods may cause more serious, long-lasting damage to the aquatic ecosystem within the burned area than the fire itself.
6. There was no change of statistical significance to the benthic fauna of the streams attributable to the fire.
7. Artificial revegetation should not be attempted where burning did not remove entire organic horizons. Natural processes will revegetate a burn more rapidly.

G. Combustion Engineering

Cook, G. A., Meierer, R. E., Shields, B. M., and Nevins, H. E. (Union Carbide Corporation, Linde Division Research Laboratory, Tonawanda, New York) "Effects of Gas Composition on Burning Rates inside Decompression Chambers at Pressures up to 300 Feet of Sea Water," Papers presented at *54th Annual Meeting, "Under-Ocean Technology," Compressed Gas Association, Inc.* (January 17, 1967)

Section: G
Subjects: Burning rates in decompression chamber; Decompression chamber burning

Reviewed by R. L. Tuve

At an ocean depth of 200 feet, divers must be supplied with breathing gas at a pressure of 7.06 atm (absolute). If the gas is compressed air, the partial pressure of oxygen is about 1.5 atm and that of nitrogen about 5.5 atm. Because of the narcotic effect of nitrogen, higher pressures and deeper diving depths require the use of helium as a diluent, a gas which facilitates breathing because of its lesser density. The decompression period for a diver is often hastened by enriching breathing gases with oxygen. Such actions increase dangers from fire.

The work reported in this paper concerns an experimental study of the comparative burning rates of standardized paper strips when subjected to different mixtures of nitrogen-oxygen and helium-oxygen at pressures ranging from 0.21 atm to 10.1 atm absolute (300 feet of sea water). The effect of angular inclination of the paper strip sample on burning rates was studied as was the ignition temperature variation in gaseous mixtures at various pressures and the ignition delay changes using helium and nitrogen as diluents.

It was found that the burning rate depends primarily on the partial pressure of oxygen and the percent of oxygen in the gas surrounding the paper strip sample. The rate of increase in burning rate becomes less, at a constant percentage of oxygen, with increasing pressures (up to measured pressures of 300 feet of sea water), with the greatest increases in burning rate occurring at pressures up to about 125 feet of sea water (4.75 atm absolute). The diminishing rate of burning rate with increase in pressure is particularly seen in oxygen-helium gas mixtures. At total pressures (constant oxygen percentages) ranging from 0 to 200 feet of sea water, the burning rate of paper strips is slightly higher when helium is the diluent gas than when nitrogen is used as a diluent.

The angular inclination of the paper strip sample was found to definitely affect the burning rates at greater or lesser angles than 45°. In the horizontal position, little or no increase in burning rate with increase in pressure could be found.

Ignition temperatures of the paper strip sample show a definite decrease as gas pressure is increased. Temperatures are nearly identical for helium or nitrogen gas diluents at similar pressures.

Ignition delay was measurably longer in helium gas atmospheres than in nitrogen because of the difference in thermal conductivity of the two gases.

Cook, G. A., *Dorr, V. A., and Shields, B. M. (Linde Division Research Laboratory, Union Carbide Corporation, Tonawanda, N.Y.) "Region of Noncombustion in Nitrogen-Oxygen and Helium-Oxygen Diving Atmospheres," *I & EC Process Design and Development* 7, 308–311 (1968)

Section: G
Subjects: Diving atmospheres; Helium–Oxygen; Nitrogen–Oxygen; Noncombustion region

Reviewed by P. Breisacher

Deep ocean exploration has increased the need of supplying life-sustaining apparatus to persons participating in such work. The safety aspects of using breathing gas at high pressures is explored. The danger from fire is accentuated

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by the inability to escape the confines of the decompression process if an emergency arises. The danger of fire is further enhanced by the possibility of inhaling toxic vapors of combustion.

Experimental determination of the maximum oxygen concentration at a given pressure that will suppress combustion completely was accomplished. A Whatman No. 1 filter paper was suspended vertically in a stainless steel pressure vessel. The volume of O_2 was always in vast excess of the amount needed to completely burn the sample. The strips were ignited by the grid of a Chromel-A wire in contact with the paper. A uniform initial temperature of 1400±50°F was used. The wider the strip the higher the burning rate. Moisture content was not significant. Results showed that in the region of highest O_2 concentration at every pressure the paper burned completely. In an intermediate region of somewhat lower O_2 concentration the strip burned for a distance of at least 1 cm above the igniter before extinguishing itself. A third region was defined as that of cessation of burning within 1 cm above the igniter. A final low O_2 containing atmosphere did not permit combustion of the sample at all.

Only a small region exists where combustion is not possible when using O_2–N_2 mixtures. Human breathing atmospheres are considered safe physiologically when the O_2 partial pressure is between 0.21 and 1.5 atm. The small safe area is rarely usable, therefore extra precautions need to be taken when operating with O_2–N_2 mixtures. When helium is used the noncombustion range is greatly extended (to 12 atm). The greater thermal conductivity of He serves to reduce the rate of heating of the surface until at 12 atm He pressure the diffusion rate of O_2 in He (as opposed to O_2 in N_2) becomes more significant than the net heat conduction of the He. The O_2 concentration noncombustion limit is 5.8—8.0% at total pressures from 3.6 to 16 atmospheres. In helium, the O_2 is safe from 3.6—10.8% at pressures from 0.5—42 atmospheres.

Corbeels, R. J. (Texaco Research Center, Beacon, New York) "Flame Propagation in Slowly Combusting Fuel–Air Mixtures," *Combustion and Flame* **14,** 49–60 (1970)*

Section: G
Subjects: Burning velocity; Flame propagation

Author's Abstract

Flame propagation in fuel-air mixtures that are undergoing slow combustion is directly relevant to combustion in internal combustion engines. In connection with knock there is the question of whether end-gas slow-combustion reactions can lead to flame speed promotion. In the present work various fuel-air mixtures were

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reacted in a burner tube of variable length under stationary flow conditions. The reacting gases, upon emerging from the nozzle at the top of the burner, were either analyzed by gas chromatography or ignited and their flame speed measured. Fuels investigated were n-heptane at 250–270°C, diisopropyl ether at 190–270°C, and various diisopropyl ether-diethyl ether mixtures at 195°C. The n-heptane and the ether mixtures produced cool flames. The results show that, in the absence of or before the cool-flame stage, the hot-flame speed is only slightly affected by the extent of prereaction. In the post-cool-flame gases no hot flame could be stabilized because of blowoff. Upon coalescence of cool and hot flames, flame speed increases of up to 80 percent were observed. The mechanism of this flame speed promotion is discussed as well as the implication with respect to the mechanism of engine knock.

Dorr, V. A. (Ocean Systems, Incorporated, Tarrytown, New York) "Fire Studies in Oxygen-Enriched Atmospheres," *The Journal of Fire & Flammability* **1,** 91–106 (1970)*

Section: G
Subjects: Fire in oxygen-enriched atmospheres; Hyperbaric chambers; Ignition in oxygen-enriched atmospheres; Oxygen-enriched fumes

Reviewed by P. Breisacher

The use of oxygen-enriched atmospheres in hospital hyperbaric chambers, oxygen tents, and decompression chambers has presented an increased risk from sudden fires. To reduce the hazard three potential ignition sources must be carefully scrutinized—electrical sources, flammable materials, and the degree of oxygen enrichment. The study divided the experimental work into three phases. First, determine the effect of pressure, oxygen concentration, and diluent gas-type upon the burning rate of standard materials such as filter paper. Second, determine the the minimum oxygen concentration required to burn solid flammables in the presence of nitrogen and helium. Third, tabulate the suitability of cloth fabrics, elastomers, and insulating materials according to a newly defined fire resistance scale.

Tests were conducted in 15×51 cm instrumented cylinder. Filter paper burning rates were determined over a pressure range of 1 to 10 atm in mixtures of 15–100% O_2 in He or N_2. Raising the pressure or increasing oxygen concentration always raised the burning rate. Accelerated burning rates are evident when helium is substituted for N_2 as diluent gas at the same partial pressure.

At high pressure the oxygen partial pressure is limited physiologically. There is a region where no combustion can occur. When N_2 is used as diluent gas then this region is very limited (4–6 atm and 4–5 mole % O_2). Helium expands this

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region to 4–35 atm and 2–8 mole % O_2. When it is impractical to operate within the confines of these regions it is of prime importance to make certain that minimum risks are incurred from materials of construction or clothing. Tests were conducted of many fabric, elastomer, and insulating materials for determination of their qualities as fire-safe materials. Classification of these substances was made on the following scale.

Class 0	Burns readily in air at atmosphere pressure
Class 1	Has a greater ignition T° and/or burns at a lower burning rate in air at 1 atm than cotton cloth or paper
Class 2	Nonflammable or self-extinguishing in air at one atmosphere pressure
Class 3	Self-extinguishing at 4.03 atm pressure
Class 4	Self-extinguishing at 7.06 atm pressure
Class 5	Self-extinguishing in 25% O_2—75% N_2 at 1 atm pressure
Class 6	Self-extinguishing in 30% O_2—70% N_2 at 1 atm
Class 7	Self-extinguishing in 4% O_2—60% N_2 at 1 atm
Class 8	Self-extinguishing in 50% O_2—50% N_2 at 1 atm
Class 9	Nonflammable in 100% O_2 at 1 atm

Preliminary evaluations of test results show the following materials falling into Classes 7–9 with usable properties in their respective applications.

Fabrics	*Class*
a) Beta-Fiberglas (Owens-Corning)	9
b) Teflon, labeled Super-beta (Dupont)	9
Elastomers	
a) Refset (Raybestos)	9
b) Fluorel(3M)	8
c) CNR (Thiokol)	9
Electrical Insulation	
a) Kapton (Dupont)—over Cu wire	9
Kapton (Dupont)—plain	7

Beta Fiberglas does not burn in pure O_2 even when ignition is attempted with intense flames of burning cellulose. It does melt at high temperature and has poor abrasion resistance and wear durability. Super-beta is made by coating the Fiberglas with Teflon prior to weaving. This fabric is strong and more pliable. Refset forms only a brittle ash upon exposure to pure oxygen at high pressure. CNR rubber vaporizes when in direct contact with the igniter. A 7 mil thick coating of Kapton over a 1 mm diameter wire proved to be a Class 9 substance. The heat absorbing nature of the wire made a distinct difference to the behavior of Kapton when subjected to pure O_2 conditions. Kapton itself (of the same thickness) was only rated as a Class 7 material. Teflon itself is good insulation except the poor abrasion resistance. Teflon should be used as a double sheath to give added protection against mechanical damage. The enclosed wiring should be further protected by enclosure in a flexible metal armor conduit.

A comprehensive list of other materials in all classes are given in an appendix.

George, C. W. and Blakely, A. D. (Intermountain Forest and Range Experiment Station, U.S. Forest Service, Missoula, Montana) "Energy Release Rates in Fire Retardant Evaluation," *Fire Technology* 6 (3), 203–223 (1970)

Section: G
Subjects: Energy release; Evaluation of retardants; Retardants

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Rate of spread and other indirect measurements of fire intensity are often used as measures of flammability when fire-retardant chemicals are evaluated under laboratory conditions. The authors describe a system for obtaining the energy release rate directly and show its importance and relation to retardant effectiveness.

Hughes, R.* and Simmons, R. F. (University of Manchester Institute of Science and Technology, Manchester, England) "Cool Flame Phenomena in the Oxidation of *n*-Pentane," *Combustion and Flame* **14,** 103–112 (1970)†

Section: G
Subjects: Cool flames; *n*-Pentane

Authors' Abstract

The temperature and pressure changes associated with the passage of a cool flame through mixtures of *n*-pentane and oxygen (mainly 1:1 and 1:2 mixtures) have been examined simultaneously in the temperature range 277–364°C. The maximum temperature rise can be up to $\sim 250°C$; it reached a "ceiling" value at high initial pressures of reactants. As the initial pressure was reduced, however, the magnitude of the temperature pulse suddenly decreased sharply and at the lower pressures the maximum temperature rise was $<50°C$. The passage of a cool flame gave a permanent increase in the pressure that was approximately half the magnitude of the pressure pulse, and this is consistent with analytical data, which show that a significant proportion of the *n*-pentane is consumed during the passage of the cool flame. The use of a fast-response recording system has shown that the pressure pulse associated with the cool flame possesses an abrupt, almost isothermal step that precedes the thermal component of the pressure pulse. Thus the present results do not indicate that a critical temperature rise is required for the appearance of a cool flame. It is suggested, therefore, that the chain-branching reactions are important in the mechanism leading to cool flame formation when *n*-pentane is the fuel and that the corresponding very fast reaction produces the thermal effects accompanying the passage of a cool flame.

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Masliyah, J. H. and Steward, F. R. (University of New Brunswick, Fredericton, Canada) "Radiative Heat Transfer from a Turbulent Diffusion Buoyant Flame with Mixing Controlled Combustion," *Combustion and Flame* **13** (6), 613–625 (1969)

Sections: G, I
Subjects: Mixing controlled combustion; Radiant transfer; Turbulent flames

Reviewed by J. Singer

A simplified mathematical model of a turbulent buoyant diffusion flame above an open liquid fuel source is described which makes possible computations for the radiative flux density distribution on a horizontal plane around the base of the flame, and the liquid fuel burning rate. Two zones are assumed for convenience: the first extending from the liquid fuel source up to the point of stoichiometric composition (the bottom combustion region), and the second from this boundary to infinity (the upper hot plume region). A number of other assumptions are made to further simplify the treatment, with recognition and discussion of their inadequacies, especially the assumptions of negligible radiation from the flame (gray flame emission), and of instantaneous mixing and reaction of entrained air in the bottom zone, keeping the temperature uniform throughout this region.

Profiles of the jet radius as a function of axial distance and the concentration of the source jet fluid throughout the jet were obtained for the combustion and hot gas plume regions as prerequisite to the computation of radiative emission throughout the flame. The radius and concentration profiles were derived from force balance equations that equated the change in jet momentum across a differential element with the buoyancy force acting on the jet fluid. The treatment was simplified by introducing dimensionless variables of momentum and mass flux into the dimensionless continuity equation and the force balance and mixing equations. An important parameter, the axial height (H) of the combustion zone at stoichiometric mixing is shown to be:

$$H = CA^{1/5}F_m^{2/5}$$

where $A = [12k\rho_0'/5(1-\rho_0')\pi^2(\rho_0')^2 g]$

$C = 5[5(\rho_0')^{2/5}/4k][(r_s+1)^{2/5}-1]$,

F_m = fuel mass flow rate throughout the source

$2k = 0.1125$, the mixing coefficient for circular turbulent jets

ρ_0' = (density of source fluid/density of ambient fluid)

g = gravitational constant

r_s = mass of air required for stoichiometric mixing (lb air/lb total)

The jet radius profile in the lower combustion zone is given by, $y' = y/y_0 = (4kx'/5\rho_0'^{1/2}) + C_b^{1/5}/(\rho_0')^{1/10}$ where $C_b = [12k\rho_0'(\mathrm{Fr})/5(1-\rho_0')]$; $(\mathrm{Fr}) = u_0^2/gy_0$, the Froude number; x' = the axial distance along the flame/y_0; y_0 and y = radius of source fuel and flame respectively; and u_0 = velocity of fluid in the flame at source.

The concentration of source jet fluid throughout the lower jet is given by

$$f=\rho_0'/[4kx'/5C_b^{1/5}+\rho_0'^{2/5}]^{5/2}$$

where f = concentration of original source fluid in flame, (lb/lb).

The radiative analysis is also based on several simplifying assumptions such as gray flame emission (emission independent of wave length), negligible scattering of emission, emission proportional to concentration of original source fluid at that point, and black body receiving surface. Radiant emission from the carbon particles in the bottom and top zones to the surface surrounding the base of the flame were derived from equations that are based essentially on the parameters: KH, ρ_0', or T_0/T_a, r_s, and z/H where KH is the "darkness factor" of the flame, K is the proportionality constant defining the absorption coefficient; T_0 = absolute temperature of the liquid source; T_a = absolute temperature of the hot gas; and z = distance from jet axis on surface surrounding the base of the flame.

Calculated numerical results are given of the radiant flux density distribution along the base for various values of the "darkness factor" KH for a combustion zone temperature of 2300°R, and for various values of the combustion zone temperature with an intermediate KH value of 6.5. With these results, it was possible to predict the burning rate of a liquid fuel source of a given diameter and fuel type, using a graphical solution. Assuming that one to five percent of the fuel will form carbon particles, and using a "degree of darkness" computed by the empirical method of Hottel and Sarofim,[1] the computations of fuel mass flow rate versus source diameter agreed reasonably with the data of Blinov and Khudiakov.[2] The agreement seems to indicate that radiation is the major mechanism of heat transfer for liquid fuels in pan diameters of one foot or more. It is noted that for small pans (diameters of an inch or less), the major mechanism appears to be conduction down the side of the pan.

References

1. Hottel, H. C. and Sarofim, A. F.: *Radiative Transfer.* McGraw-Hill, New York (1967), pp. 244–246.
2. Blinov, V. I. and Khudiakiv, G. N.: *Dokl. Akad. Nauk S.S.S.R. 113,* 1094 (1957).

McAlevy, R. F., III and Magee, R. (Stevens Institute of Technology, Hoboken, New Jersey) "The Mechanism of Flame Spreading over the Surface of Igniting Condensed-Phase Materials," *Twelfth Symposium (International) on Combustion,* Pittsburgh, The Combustion Institute p. 215 (1969)

Section: G
Subjects: Flame spread; Plastics; Surface flame spread

Reviewed by R. H. Essenhigh

This paper reports measurements of the speed of flame propagation (V) over the surface of two nitrate ester propellants, and two thermoplastic polymers [Polymethylmethacrylate (PMM), and polystyrene (PS)]. All samples were tested in mixtures of oxygen and nitrogen; for the thermoplastics, additional tests included measurements in O_2/He and O_2/Ar mixtures. The oxygen mole fractions used (Y_{Ox}) ranged roughly from 0.2 to 1.0. Total pressure (P) was also varied, over two orders of magnitude, from 4 psia to 400 psia. The incentive for these experiments seems to have been primarily interest in ignition in solid propellant and hybrid rocket motors (the work being supported by NASA), but it is also relevant, as the authors point out, to fires in buildings, forests (and spacecraft).

The authors report that all data for the four materials specified could be correlated by the following simple expression

$$\text{Velocity of flame spread, } V \propto (PY_{ox}{}^{m})^{\Phi} \qquad (1)$$

where m and Φ are semi-empirical indices whose values, at present, have to be determined experimentally, though some agreement with calculation is also indicated for PMM. The expression obtained is even more general than these results suggest since the authors of this present paper had demonstrated in a previous paper[1] its applicability to (solid) ammonium perchlorate in a fuel gas environment and to solid composite propellants in chemically active environments. The total number of experiments substantiating the expression now exceeds 1500.

Measurements were made with the samples inside a cylindrical pressure chamber, 10 in. i.d. and 18 in. long, and connected to a large surge tank (10 cuft) to maintain constant pressure during an experiment. During an experiment, the samples were observed through an observation window cut in one of the faces of the pressure chamber. This permitted direct measurement of flame speed, either by stopwatch for the lower speeds, or by cine (framing) camera for the higher speeds. In 200 of the experiments, surface temperature profiles with time were also obtained using very fine thermocouples (15 micron bead) fixed to the specimen surface. Other experimental details provided in the paper are of value to readers interested in using the same technique. The samples themselves were strips 3 in. long, by 0.375 in. wide, and 0.125 in. thick, mounted by means unspecified on backing plates of material unspecified and a little larger than the strips (3.25 in.×0.5 in.). To prevent flame spread along the sharp edges to dominate the observations, reaction along the sides was inhibited by application of an adhesive cement. The strips were ignited by a hot wire along the 0.375 in. edge, and propagation then ensured, spreading along the principal (3 in.) length of the strip, across the line of sight of the camera.

Analysis of the results and developments of the Eq. (1) above is based on a theory published by the authors elsewhere,[1] on which general comment would be out of place here. It must suffice here to say that the theory is based on a mechanistic model in which it is assumed that heat from the flame front (drawn as a vertical plane) pyrolyzes fresh material ahead of the flame front, the heat being transferred either by conduction through the solid, and/or by some unstated mechanism through the gas phase. The pyrolyzed material then diffused upwards, forming a combustible mixture with down-diffusing oxidant, with an optimum ratio between the two being generated at a finite height above the solid surface. Flame then spreads through this self-heating, gas-phase mixture (and a plane flame front is then a surprising result), with the flame front reaching any given location just as the reaction in the local region develops a "run-away to ignition." [Ignition evidently refers here to the gas-phase mixture, but definition seems a little variable. The opening sentence of the relevant paragraph states "Ignition starts at a certain surface location in advance of the flame . . . ;" and there is reference to a "measured ignition temperature" which is constant independent of P, Y_{ox}, or inert diluent, and which seems, in fact, to be the pyrolysis temperature.] The model takes into account reaction ahead of the flame.

Mathematical development of the model, largely given in the earlier paper,[1] enabled prediction of an "ignition time," t_{ig}. This, together with experimental measurement of an "influence distance," δ (and associated with heuristic assumptions about pyrolysis rates with time) led to derivation of Eq. (1), together with indications that the indices m and Φ should have certain dependencies on P, Y_{ox}, inert diluent, etc.; thus:

m should be a function of inert diluent and type of specimen;

Φ should depend on the specimen type, but be insensitive to the environmental gas.

The experimental results broadly supported these qualitative predictions; quantitative agreement was generally less satisfactory.

The authors therefore conclude that they believe their results generally substantiate the proposed mechanism, at least qualitatively if not quantitatively, though they also recognize that they have only so far satisfied a necessary but not a sufficient condition for proving the validity of the theory. The reviewer would agree with the proviso. Experimentally, there would seem to be little doubt that the authors have now established that Eq. (1), even if regarded as semi-empirical, still represents an important and significant generalization. Any theories of flame spread must predict either this or something close to it, and without agreement on this point a theory must fail. Theoretically, however, the reviewer agrees with the authors that agreement by itself is insufficient. The reviewer does nevertheless feel that this paper is likely to prove a landmark in development of understanding of flame spread over surfaces, even if only for the establishment of the Eq. (1) as a semi-empirical but general equation (that might be thought of as "Ohms Law" for Flame Spread). The reviewer would also advise readers that the paper also contains many details and minor points on which there is no room to comment in this review but which deserve careful reading and discussion.

Reference

1. McAlevy, R. F., III, Magee, R. S., Wrubel, J. A., and Horowitz, F. A.: *AIAA J. 5*, 2 (1967).

Mackinven, R., Hansel, J. G., and Glassman, I. (Princeton University, Princeton, New Jersey) "Influence of Laboratory Parameters on Flame Spread across Liquid Fuels," *Combustion Science and Technology* 1, 293–306 (1970)*

Section: G
Subjects: Flame spread; Pool fires

Authors' Abstract

The rate of flame spread across the surface of liquid fuels (mainly n-decane, but also n-nonane, n-undecane, dipentene, kerosene, and n-butanol) has been examined

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in detail for a wide range of laboratory variables. Many hundreds of carefully controlled tests have been performed aimed at elucidating the dependence of the flame spreading velocity on (1) the purity of the fuel, (2) the mode of ignition, (3) the temperature of the fuel, (4) the dimensions and material of the fuel container, and (5) the depth of the fuel layer. The effects of environmental parameters (atmospheric pressure, air temperature, and relative humidity) have also been investigated, but non-systematically. The results show that the flame spreading velocity is susceptible to changes in most of these parameters. This work constitutes the first systematic variation of all the laboratory variables with the view to obtaining flame spreading data which are meaningfully applicable to any apparatus and also to 'real' liquid fuel fires.

The results and their relationship with the previous work of Burgoyne et al. and Tarifa and Torralbo are discussed qualitatively in terms of the hydrodynamic and heat transfer processes which occur in the burning liquid fuel and the criteria necessary to produce meaningful flame spreading data are rationalized.

Mulcahy, M. F. R. and Smith, I. W. (Division of Mineral Chemistry, C.S.I.R.O., Chatswood, New South Wales) "Kinetics of Combustion of Pulverized Fuel: A Review of Theory and Experiment," *Review Pure and Applied Chemistry* **19,** 81–108 (1969)

Section: G
Subjects: Coal combustion; Kinetics of pulverized fuel; Pulverized fuel kinetics

Reviewed by R. H. Essenhigh

This 25-page Review (with 89 references and 14 figures) is a useful addition to the literature of pulverized coal combustion, since it assembles substantial quantities of experimental material from a variety of sources with some useful re-analysis in terms of a coherent model. The approach is simplified to the extent that pyrolysis is ignored, with attention confined to the kinetics of the burnout of the carbon char formed by pyrolysis. This is a common, and acceptable, assumption since burnout determines 90% or more of the burning time although it frequently involves only 60 to 70% of the mass to be burned. The authors interest in the kinetics is derived from the practicalities of requiring to know the dependence of combustion times (and hence also combustion volumes) on the fundamental mechanisms of carbon reaction since this information may help to answer such practical questions as: should grinding be finer? or what plant size reduction can be expected from an increase in total pressure? However, since the principal topic is the reaction mechanism of carbon this Review has significance outside the limited area of pulverized coal combustion.

The Review opens with a (necessary) summary of mostly familiar, simple theory of reaction of a nonporous carbon particle with oxygen. This is Section 3: *Simple*

Theory of Particle Combustion. The equations are set up for reaction when controlled separately (1) by mass transfer (boundary layer diffusion), (2) by oxygen chemisorption, and (3) by CO/CO_2 desorption. The rates separately predicted are then compared graphically for different selected values of activation energy, temperature, particle size, total pressure, etc. The dependence of combustion intensity on these various parameters is also developed and discussed briefly. [Readers should remember, however, that the reaction "resistance" equation quoted as Eq. (1) is only true for oversimplified reaction conditions. More completely, as shown in ref. 82 of the subject paper, the "simple" reactivity equation is a quadratic, with significant consequences following therefrom.]

The subsequent sections of the Review then contain extensive and detailed discussion of experimental behavior reported in the literature, and re-examined in terms of the theory already indicated, together with extension to include the effects of particle porosity. This latter is given extensive discussion (6–7 pages) and is an important contribution to this aspect of reactive behavior. A further addition of considerable significance is discussion of the nature of the oxidant where there is evidence that OH radicals could be important-to-dominant at the higher temperatures (say 1500° to 2000°K and above). The sections referred to are titled: 4. *Comparison of Theoretical and Observed Burning Times and Combustion Rates*; 5. *Porosity of P.F. Particles*; 6. *Kinetics of Combustion of Porous Particles*; 7. *True Kinetic Parameters of Carbon Combustion* (*Zone I*); and 8. *The Nature of the Oxidant.*

The material covered in these five discussion sections, however, is much too detailed for summary in the space available here, more particularly as the conclusions reached on the less well established aspects are still tentative—and arguable—rather than firmly quantitative. The interested reader is therefore referred either to the original paper, or to the points of difference between the authors and this Reviewer set out below as the best means of determining some of the details discussed.

The essential conclusions of the authors (sec. 9) are: that combustion is mass transfer controlled above 100 microns, from 1200° to 2300°K; below 100 microns, the chemistry of the process becomes increasingly dominant, with reaction being mainly internal where the particles are derived from bituminous coal. Very dense particles (e.g., from anthracite) or very highly reactive particles (e.g., from brown coal) could possibly react mainly at the superficial surface—regarded as rough—and therefore obey the "shrinking sphere" model. This might also be true for very small particles formed in smoke (of 400 to 500 Angstroms). The oxidative process is primarily by oxygen, forming mainly CO by primary reaction, but contributions from OH radicals generated during CO burnup could contribute substantially to the oxidation rate. CO_2 back reaction, on the other hand, is not considered important. The best estimates for reaction order and activation energy in the range, roughly, from 1000°K to 2000°K are considered to be 0.5 to 1.0 (for order) and about 40 kcal/mole.

This Reviewer does feel, however, that some of the conclusions listed above are still arguable. There is evidence that the larger particles are not mass transfer controlled throughout the whole of the temperature range indicated. The view taken by this Reviewer is that mass transfer dominance is imposed at about 1000°K in accordance with most published data, but the high temperature coefficients observed, for example, by Smith and Gudmundsen[1] around 1500°K could quite likely be due to CO_2 becoming the dominant oxidation reaction in a chemically dominant regime. This is consistent with the rate data for CO_2 with carbon reported by

Walker, Rusinko, and Austin.[2] Physical dominance is then re-established at 1800° to 2000°C by imposition of a double film, consistent with the results of Golovina and Khaustovich.[3]

There is also good reason to believe that the real reaction order for the high activation energies quoted (of the order of 40 kcal) must be zero. Trapnell's[4] summarized arguments are convincing to this Reviewer that the adsorption activation energy must be very low since chemisorption takes place as low as −70°C (Barrers quoted measurement was 4.3 kcal at low surface coverage). The high activation energy values of 20–60 kcal cannot therefore be for adsorption. More recently, Froberg[5] and Kurylko[6] have confirmed that for one high purity, very dense carbon studied, the Zone I reaction was zero order with an activation energy of 45 kcal, and half order at 22 kcal in Zone II. Froberg also showed that spurious fractional orders could be obtained unless careful measurements were made of the carbon sample temperature: furnace temperatures and even ambient gas temperatures are not good enough. This zero order is contrary to both the Beer and Thring[7] and the Lee, Thring, and Beer[8] results but, as discussed recently,[9] there are discrepancies between the raw data and the reported reaction orders. In particular, Lee empirically found a *second* order to be a best fit to the reaction data, in agreement with a very recent result obtained by Magnussen.[10] Beers data, on the other hand, are equally consistent with a zero order reaction.[9]

In summary, this is a very detailed review that requires careful reading. Exception can possibly be taken to some of the conclusions, but even alternative interpretations are still largely in the realm of personal judgment rather than established scientific fact. This room for disagreement supports the conclusion of the authors that more definitive work is urgently needed in this area. Otherwise, as matters currently stand, this is a valuable and important Review for those already familiar with the topic; and it can serve as an excellent introduction for newcomers to this subject.

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Patel, N. K. and Chu, Chieh (School of Engineering and Applied Science, University of California, Los Angeles, California) "Studies of Opposed Jet Diffusion Flames. I. Temperature Distribution," *Combustion and Flame* **14,** 137–144 (1970)

Section: G
Subjects: Diffusion flames; Opposed jet flames

Reviewed by G. S. Pearson

Opposed jet diffusion flames close to blowout conditions are largely independent of the transport properties of the reactive streams and predominantly reflect the effect of chemical kinetics. Such flames overcome the difficulties of precise measurements in the very thin combustion zone of premixed flames and of the obscuring of chemical kinetics by the low rates of heat and mass transfer in ordinary diffusion flames.

This paper is the first of a series aimed at using opposed jet diffusion flames to study various fuel–oxidant mixtures of interest to air pollution control. In this paper temperature distributions in opposed jet flames of ethylene, methane, and carbon monoxide with oxygen are reported. Nitrogen is also present in the fuel stream for the carbon monoxide flames.

The apparatus consisted of two brass tubes each 2.5 inch in inside diameter and 9 inch long. Spirally wound alternate strips of corrugated and plain brass sheets were inserted in the two ends of the brass tubes that were held horizontal 6.6 mm apart. Flames were stabilized in this gap and their temperatures measured by a 0.001 inch diameter Pt/Pt–10% Rh thermocouple coated with silica. Thermocouple position was determined to within 0.1 mm by a micromanipulator. Flame temperature profiles are reported without correction for radiation losses.

Results for ethylene flames show that the flame is flat, has maximum temperatures near the periphery and that the combustion zone is slightly on the fuel side of the geometrical center plane. The effects of variation in (1) the average mass flux of both streams, (2) the fuel concentration, and (3) the oxidizer concentration on the temperature and the location of the combustion zone are shown graphically for the ethylene flames. Peak temperatures increased with the ethylene and oxygen concentrations at about 53°F per % increase in ethylene concentration and 15°F per % increase in oxygen concentration.

Results for methane are not shown graphically but the profiles are said to be very similar to those for ethylene. Effects of fuel and oxygen concentrations on peak temperatures are 46°F per % methane and 20°F per % oxygen. One experiment with the methane stream at the top and oxidizer stream at the bottom (opposite to usual arrangement) showed very different temperature distributions indicating a significant gravitational effect.

The carbon monoxide flames were very difficult to stabilize. Profiles are shown for experiments in which the mass flux of nitrogen in the fuel and the mass flux of oxygen were varied.

The authors draw no conclusions from the results.

Reed, S. B. (Watson House, The Gas Council, London, England) "An Approach to the Prediction of Aerated-Burner Performance," *Combustion and Flame* **13** (6), 583–595 (1969)*

Section: G
Subjects: Aerated burners; Burner performance

Author's Abstract

Over the past twenty-five years or so relationships have been given in the literature which express various aspects of the behaviour of aerated burners in terms of fundamental quantities and in a generalized way. These relationships, along with newly derived relationships, are collected together in this paper in an attempt to form a fundamental basis for the prediction of the performance of practical aerated burners. The relationships presented allow the effect of changes of gas characteristics on light-back, quenching dimensions, blow-off, yellow tip formation, inner cone size and shape, heat input and primary aeration to be assessed for a given burner geometry from a knowledge of the composition of the fuel gas and its burning velocity only. They also provide a ready means of making semi-quantitative feasibility studies of several aspects of burner design and performance. A newly derived light-back relationship is given

$$g_f x/S_u = [0.062\ p c_p S_u x/k]_{(Pe)>80}$$

which is valid for a wide range of conditions. Lean hydrogen-air mixtures show deviations from this equation but these deviations are only about one-tenth of those that occur for similar mixtures at blow-off, which shows clearly how the degree of flame stretch determines the extent to which preferential diffusion affects flame stability.

It is suggested that the existence of a minimum flame diameter must be allowed for when predicting the quenching dimensions of a burner port and it is shown, by means of a calculation involving the light-back equation, that allowance for the minimum flame diameter gives quenching dimensions in reasonable agreement with those determined experimentally. Additional details are given for the prediction of the yellow tip limit of gas mixtures. Finally, suggestions are made for further work which should be carried out in order to realize a comprehensive method for the prediction of aerated-burner performance—a goal of considerable practical importance.

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Shibaoka, M. (Coal Research Laboratory, C.S.I.R.O. Division of Mineral Chemistry, Chatswood, New South Wales) "An Investigation of the Combustion Processes of Single Coal Particles," *Journal of the Institute of Fuel*, p. 59 (February 1969)

Section: G
Subjects: Coal; Combustion of single particles; Particle combustion

Reviewed by R. H. Essenhigh

This investigation was on the combustion behavior of submillimeter coal particles photographed on a hot stage microscope to investigate the influences, primarily, of: petrographic type, coal rank, heating rate, particle size, and swelling. In the past, many quantitative investigations have been made of burning of single coal particles.[1–6] (A review of Ref. 6, p. 68 of this issue of FRAR supplements this review very well.) However, two factors of concern that were largely ignored in many instances were: the influence of internal burning, and swelling. Internal burning has recently been given much more attention,[6] but swelling effects are still more or less neglected.

In this investigation particles of 50 to 100 microns, and 400 to 700 microns were attached to chopper heated thermocouples so the couples acted both as heater and pyrometer and burning was watched under a microscope with cine attachment. Four coals were used: a high volatile bituminous, a medium volatile bituminous, a sub-bituminous, and a brown coal. Petrographic components—fusite, vitrite, and resinite—were identified by microscope at the surface of polished lumps of coal, and cut out with a needle for use in the combustion experiments. Heating rates ranged from 5°C/sec to 1800°C/sec (compared with 10^{4}°C/sec found in flames). At the higher heating rates the finer particles burned out before the temperature reached a very high value (this Reviewer therefore feels that one might question whether the thermocouple really measured the particle temperature), so to prevent this, the oxygen concentration was reduced by mixing one part of air with nine parts nitrogen.

The results are reported mainly as qualitative description of details of the observed behavior, but including three plots of the variation of relative volume with time. Substantial fine detail is described that does not lend itself to simple summary, but some broad-based conclusions emerted. The degree of swelling influenced the burning characteristics substantially, with burning rate increasing with the swelling factor (measured as a relative volume change). The author reported that he was unable to account for this trend. The degree of swelling in turn was influenced by rate of heating, coal rank, and petrographic constituent. At low rates of heating (5°C/sec) there was generally only marginal swelling, and in some instances the particles shrank instead. Swelling (up to a volume increase of a factor of 8 or a doubling of diameter) was observed for vitrites at 1800°C/sec, with the swelling factor correlating with the crucible swelling index, so the nominally similar vitrite particles were strongly influenced by the rank of the coal sample they were extracted from. For the same coal rank, there was also marked difference between petrographic constituents. Under heating conditions when the vitrites would swell, the swelling was substantial; but fusite under the same conditions neither swelled nor became plastic. In contrast, resinite (indurite) expanded almost explosively. Particle size also seemed to have some influence, with swelling apparently greater as particle size decreased. Some behavior of ash was also observed, with the presence of calcite and pyrite allowing otherwise infusible ashes to melt.

The Reviewer feels that the following comments are pertinent. The swelling behavior reported in the subject paper is a little at variance with a previously published study by R. H. Essenhigh and G. C. Yorke,[7] where nine bituminous coals with crucible swelling numbers ranging from noncaking to 6.5 were found to have average swelling factors (diameter ratios) of about 1.5 (independent of rank). The Essenhigh and Yorke results, however, were on particles of whole coal, with mixed petrographic constituents, which probably accounts for the difference. Adopting a common swelling factor, however, enabled Essenhigh[8] to show excellent agreement between theory and experiment for the combustion times of single coal particles. The theory tested also explained why the swollen particles burned faster, even under diffusion dominance, in spite of the increase in diameter. The burning time was proportional to the particle density and to the square of the initial diameter. Density, however, is inversely proportional to the cube of the diameter so that, with swelling, the burning constant was found to be inversely proportional to the swelling factor.

The significance of the work in the subject paper lies in the detailed information on the influence of interacting factors, particularly swelling and petrographic constituents, on the combustion behavior of coal particles. What this paper makes equally clear is the paucity of such information, thus indicating major gaps to be filled in future work.

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Sirignana, W. A. and Glassman, I. (Princeton University, Princeton, New Jersey) "Flame Spreading above Liquid Fuels—Surface-Tension-Driven Flows," *Combustion Science and Technology* **1,** 307–312 (1970)*

Section: G
Subjects: Flame spread; Liquid fuel flame spread; Surface tension; Pool fires

Authors' Abstract

Convective heat transfer through the liquid fuel below a spreading flame is considered as a rate controlling mechanism. Thus, a surface-tension-driven liquid flow, induced by the temperature profile ahead of a spreading flame, is analyzed. Velocities, pressures, and surface heights are determined for a two-dimensional flame spreading at a steady rate. It is demonstrated that convection can occur near the surface ahead of the flame and in the direction of propagation and, thus, that liquid-phase convective heat transfer can be a plausible rate-controlling mechanism for flame propagation.

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Dorr, V. A. and Schreiner, H. R. (Ocean Systems, Incorporated, Tarrytown, New York) "Combustion Phenomena in Space Vehicle Environments," *Proceedings of the Eighth International Symposium on Space Technology and Science, Tokyo, Japan* (1969)

Section: G
Subjects: Combustion in space vehicles; Space vehicle environment

Reviewed by R. L. Tuve

The artificial atmospheres utilized in most manned space vehicles are considered oxygen-enriched atmospheres (OEA) in that they contain greater than 21% oxygen and/or the oxygen partial pressure exceeds 160 mm Hg. This paper reports the results of measuring the combustion rate of filter paper strips held at an angle of 45° and ignited in air and pure oxygen and in oxygen-nitrogen mixtures at atmospheric and less than atmospheric pressures.

Data obtained show that the combustion rate of the paper samples increased from 1.2 cm/sec in air at atmospheric pressure to 4.2 cm/sec in pure oxygen at atmospheric pressure. In pure oxygen, as the pressure is decreased to 0.5 atm abs and 0.2 atm abs the burning rate decreases to 3.1 cm/sec and 2.3 cm/sec, respectively. In a mixture of 50% oxygen and 50% nitrogen the burning rate of paper ranges from 2.4 cm/sec, 1.4 cm/sec, and 1.1 cm/sec at successive pressures of 1.0 atm abs, 0.5 atm abs, and 0.2 atm abs.

Tests of cotton garments ignited in a hyperbaric chamber at various oxygen and oxygen-nitrogen atmospheres at normal and subatmospheric pressures are described in some qualitative detail.

I. Physical Aspects of Fires

Bellet, J. and Deshayes, G. (Laboratoire d'Energetique, Poitiers, France) "The Propagation of Detonations in Hydrogen–Oxygen Mixtures in Supersonic Flow," *Comptes Rendu* **268** (4), 289–292 (1969). In French.

Sections: I, B, D
Subjects: Combustion instrumentation; Detonations; Electrical ignition; Hydrogen; Oxygen; Oxygen–Hydrogen combustion; Supersonic flow

Translated and Reviewed by K. M. Foreman

Almost all recent detonation research has been concerned with its propagation into stationary mixtures. The influence of the fresh reactant gas flow has been studied only by Bollinger *et al.*[1] for the case of speeds less than or equal to 100 m/s, and by MacKenna[2] for $0.14<M<4$ in the presence of a significant longitudinal gradient of speed. In order to study the structure and propagation of detonations into supersonic flow of H_2–O_2 mixtures, where Mach number, M, remains as constant as possible all along the test section, the authors made a special flow facility. It consisted of a square cross-sectioned duct, of 20 mm sides, and of 180 mm length, and with transparent side walls for photographic instrumentation. The reactants were introduced and mixed just upstream of the nozzle throat. Interchangeable nozzle contours permitted experiments at M 1.7, 2.8, and 3.5. At the downstream end of the test duct a high energy spark igniter was used to initiate the detonation.

Photographic data showed that the detonation front had a multidimensional structure which remained stable beyond the short distance needed to form it. This structure consisted, more or less, of a normal wave in the central portion of the duct, some shock waves, and oblique combustion waves which originated in the boundary layer along each wall. At M 1.7, the oblique waves were slightly developed but they became more significant as M increased.

The investigators conclude that the absolute detonation speed, D_0, tends to become constant (to within 5%) after the front travels a certain distance, which becomes shorter as the igniter energy, W, increases. Also, D_0 increases with mixture richness, r. Significantly, the velocity relative to the reactant gas, D, (where $D=D_0+Ma_0$, a_0 being the sonic speed) was found to be close to the Chapman–Jouguet velocity, D_{CJ},[3] for weak Mach numbers. However, when the oblique waves that originate at the walls penetrate further into the organized central flow, the difference $(D-D_{CJ})$ approaches 15% of D_{CJ} for M of 3.5.

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Williams-Leir, G. (National Research Council of Canada, Ottawa, Canada) "Another Approximation for Spatial Separation," *Fire Technology* 6 (3) 189–202, (1970)

Section: I
Subjects: Building separation; Spatial separation of buildings

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The author discusses a new method for determining how far apart buildings should be to prevent the ignition of one by the other. It is simple to use, and it applies to some practical problems not adequately treated by earlier methods.

J. Meteorological Aspects of Fires

Canadian Forestry Service, Department of Fisheries and Forestry. "Canadian Forest Fire Weather Index," *Published under the authority of the Minister of Fisheries and Forestry, Ottawa, Canada* (1970)

Section: J
Subjects: Canadian fire weather; Index of fire weather

Reviewed by R. L. Tuve

This "how-to-do-it" manual for use by Canadian forest fire control observers and authorities charged with daily forest fire preparedness and suppression activities gives detailed instructions for calculating the "Fire Weather Index." (FWI)

Weather observations of wet and dry-bulb temperatures for percent relative humidity, wind speed and direction, and rainfall for last 24-hour period are employed in conjunction with appropriate tables in the manual and the following code blocks are entered with numerical ratings:

Fine Fuel Moisture Code
Duff Moisture Code
Drought Code
Initial Spread Index
Adjusted Duff Moisture Code

Instructions are included so that the final "Fire Weather Index" may be arrived at using the above numerical code values.

Since this numerical rating system applies to all Canadian provinces, the degree of fire hazard for numerical fire weather index values is established on a regional basis with flexible values assigned over six classes of fire danger from very low to extreme. Each of these classes are qualified, for example, a *moderate* danger is described as: "Flaming matches, etc. may start fires; spread is moderate in forests, fast in open areas; fires burn on the surface with moderate flames; some of the duff may be consumed on dry sites; control is not difficult and light to moderate mop-up will be necessary."

L. Operations Research, Mathematical Methods, and Statistics

Chandler, S. E. (Joint Fire Research Organization, Borehamwood, England) "Fires in Hospitals," *Joint Fire Research Organization Fire Research Note 831* (August 1970)

Section: I
Subjects: Fatalities; Fire-cause; Fire statistics; Hospitals

Author's Summary

The number of fires in hospitals has been increasing at about the same rate as all fires in buildings, having risen from 590 in 1963 to an estimated 684 in 1968. This report is based on information obtained from a 1-in-4 sample of reports of fires which occurred in 1968.

Two hundred and ninety-two of the fires were in mental hospitals.

Nearly two-thirds of all the hospitals involved were built before 1910.

It is estimated that 144 fires occurred in wards, 48 being attributed to smoking materials and 40 to malicious ignition. The peak time of the day for hospital fires was between 1800 and 2059. Next to wards, the worst areas were stores (80 fires) and kitchens (76 fires). Eight fires occurred in operating theatres.

The most important causes of fires in hospitals were smoking materials (184), malicious ignition (104) and cooking appliances (all fuels) (68). The first two of these causes accounted for 65 percent of the fires in mental hospitals.

Only 6½ percent of the fires spread beyond the room of origin. Five hundred and fifty-six of the fires were tackled before the arrival of the fire brigade; of these 396 were successfully extinguished. The most common methods of extinction used before the arrival of the fire brigade were extinguishers (160 fires), water from buckets or immersion (112 incidents) and inside hose reels/hydrants (104 fires).

During the period 1963–1968 there were 62 fatal casualties in 38 fires, 24 of these occurring in the Shelton Mental Hospital fire.

Mental hospitals did not appear to have a higher fire risk than other hospitals, although the fires were different, particularly with respect to source of ignition and place of origin.

Chandler, S. E. (Joint Fire Research Organization, Borehamwood, England) "Fires in Road Vehicles 1968," *Joint Fire Research Organization Fire Research Note 836* (September 1970)

Section: L
Subjects: Casualties; Causes, fire in vehicles; Extinguishing; Fire statistics; Incendiarism; Spread of fire in vehicles; Vehicle crashes

Author's Summary

Fires in road vehicles increased from 10,716 in 1963 to 15,188 in 1968, the year on which this report is based. About half of the fires (6892 in 1968) were in cars. This is a rate of 0.64 fires per thousand licenses. Lorry fires numbered 3900 in 1968, and like cars, had been increasing steadily over the previous five years. Fires in motor cycles decreased to a level of 1348 in 1968 (1.02 per thousand licenses). Fires in tankers and buses, although small in number approximately doubled in the five years 1964–1968. This coincides with the greater use of rear-engined vehicles, but there is no evidence to suggest that these vehicles are a greater fire risk. It appears that the number of tanker and bus fires in which liquids other than petrol and diesel fuel oil were ignited initially would be sufficient to explain this increase. The fire incidence rate for goods vehicles is estimated to be about 3.16 per thousand licenses and that for buses is as high as 5.27.

Car fires are most frequent during the later part of the day and lorries between 0900 and 1500. This may be related to the mileages covered. Sixty-seven percent of motor cycle fires occur after 1500.

The most important sources of ignition in road vehicles fires are wire and cable (4752 fires), engine (4264 fires) and mechanical heat and sparks (1044 fires). This last cause and "ashes and soot" were major causes of lorry fires. An increasingly frequent source of ignition is malicious ignition, having risen from 68 fires in 1963 to 436 in 1968.

In 4112 fires petrol was ignited and insulation accounted for 4020 fires.

Road vehicle fires do not usually spread and about 27 percent are extinguished before the arrival of the fire brigade. The figure for cars is 33 percent and for buses 28 percent. For lorries the percentage successfully quelled is only 17. First aid fire-fighting by removal or disconnection, smothering or buckets of water generally appears to be more successful than using extinguishers.

Three coaches needed to be evacuated during the year. There were 31 fatal fire casualties in vehicles and an estimated 212 non-fatal casualties. The overall casualty rate for vehicles was 16.0 fire casualties per thousand fires—this rate was substantially higher for tankers (34.1) and motor cycles (27.4).

Gordon, B. B., Drozda, W., and Stacey, G. S. (Battelle Memorial Institute, Columbus, Ohio) "Cost-Effectiveness in Fire Protection," *Battelle Memorial Institute Report* (December 31, 1969)

Section: L
Subjects: Cost effectiveness; Cost effectiveness in fire protection; Fire protection

Authors' Abstract

The purpose of this study was to analyze fire department operations and identify applications of cost-effectiveness methods to fire protection problems. This objective could be best achieved by examining real problems in a real setting so that the results obtained would be practical. The emphasis of the study was directed toward the development of some tools for future analysis and the development of methods for computerization of fire department data. This emphasis resulted from the finding that little work had been done in the application of systems analysis techniques to fire protection.

Many problems appear to be amenable to cost-effectiveness analysis. Among these are decisions regarding:

1. What should be the criteria for deciding when to hire more fire department employees.
2. How many additional employees should be hired. (Or how many should be released.)
3. What factors determine when the fire department should construct a new fire station with all ancillary equipment.
4. Where the fire department should build a new fire station.
5. How the fire department should relocate its stations for an optimal fire loss prevention strategy.

6. How the maintenance of fire department equipment should proceed.
7. Under what circumstances the fire department should offer services to other communities.
8. Under what circumstances the fire department should purchase services from other communities.
9. The proper price to charge (or pay) for services exchanged with other communities.

Each of these decisions could be important enough to warrant the expense of conducting an analysis if the required tools were available. However, the search of the literature indicated that the proper techniques were not fully developed and the examination of the data from a specific fire department indicated the information was not available in the required format.

With this background, it was decided that the next step should be the development of the proper tools and data base. The effort at this point was divided into three tasks:

1. Development of methods for evaluating costs and benefits within the entire fire protection system.
2. Computerization and analysis of fire department operational data.
3. Development of a simulation model which could be used for evaluating effectiveness.

The work accomplished on each of these tasks is described in detail in separate sections of the report. The development of the simulation model was, perhaps, the most interesting part of the project.

The Simulation Model

The analysis of a system, such as a fire department, involves the estimation of expected performance for the alternatives being studied. Since a fire department is a complex system with major interaction between its components, the estimation of performance would be difficult. It was decided that a simulation model could be developed which would permit alternatives to be studied by observing simulated system operation. This appeared to be the most practical approach to the problem of estimation of system performance.

The simulation model, developed during this program, is a computerized description of a fire department and its method of operation. Changes in the structure or operating rules of the system can be introduced into the simulation model and evaluated in terms of changes in the simulated system performance. If the model simulates the real system with sufficient accuracy, the real system can be optimized by experimentation with the simulation model.

The approach used was to start with a greatly simplified model and add refinements, one at a time. In this way there was always a working model, programming bugs were identified more easily, and improvements were made with small increments of time and funds.

The model simulates the operation of a fire department for a specified period of time. Fires are generated from probability distributions of the experience of the fire department being studied. The city is divided into zones and the fires are generated with proper consideration of location within the city as well as type of fire call and time of day. The fires are detected and alarmed after a random delay. The fire alarms are handled, in turn, by the communications/dispatching center.

Equipment is dispatched to the fire on the basis of proximity, and the type and location of the fire. The equipment travels to the site of the call. In the case of a building fire, the condition of the fire is estimated on the basis of the time between the start of the fire and the first arrival of equipment, along with a random variable. The first arrival equipment can cancel other dispatched equipment or call for an extra alarm, depending on the condition of the fire. The equipment then fights the fire, with the time determined by the condition and a random variable. Finally the equipment returns to the station house and returns to available status as soon as possible. Throughout the simulated operation statistical records are kept so that performance can be measured.

In its present state, the simulation does not include all of the complexities and capabilities that would be desired. However, there is sufficient detail now to demonstrate the potential utility of the model. Some of the improvements that should be made in the model include a more realistic method for estimating time to fight a fire and a more realistic method for calculating travel times.

The output report for the example run contains the following data:

1. Input data
2. Unavailable equipment
3. Travel times, and
4. Equipment utilization

The input data states the number of calls of each type made during the simulated time period. This permits the analyst to assure himself that the randomly selected fire calls do match the expected number and type of call reasonably well. It appears that the model should be run for a simulated period of two years in order to obtain usable results.

The reports on unavailable equipment and travel times are measures of how adequately a city is being served. If the equipment housed nearest to a fire were frequently out on another fire call, it would be an indication that either there was insufficient equipment or that its distribution throughout the city could be improved. The average travel time to fires provide another measure of the same factors as unavailable equipment.

The equipment utilization reports can be used as an indicator of the dispersion of fire equipment. It is not necessarily true that equal utilization of equipment should be the decision rule for equipment dispersion because it may be achieved by increasing travel times in the more sparsely settled areas of the city.

The output report is meant only to be typical of the performance measures that can be printed out. For any given application, additional reports can be generated with slight additional programming. After the model has been used for several applications, a library of reports will be available and can be selected as needed.

Applications

The simulation model is useful for those analyses where measures such as time to reach a fire or equipment utilization are important. This would include activities such as:

1. Selecting location of a new fire station.
2. Deciding on the number and types of pieces of equipment required.
3. Assigning equipment to fire stations.

4. Establishing the logic for dispatching equipment to fires.
5. Incorporating a new type of equipment in the system, or
6. Altering the basic method of operation of the fire department.

Specific decisions to use this tool will depend on the particular problem at hand. However, the large number of potential applications should make a more detailed development of the model worthwhile.

Ramachandran, G. (Joint Fire Research Organization, Borehamwood, England) "Some Possible Applications of the Theory of Extreme Values for the Analysis of Fire Loss Data," *Joint Fire Research Organization Fire Research Note 837*

Section: L
Subjects: Fire statistics; Large fire losses

Author's Summary

This paper discusses the possibility of applying the statistical theory of extreme values to data on monetary losses due to large fires in buildings. The theory is surveyed in order to impart the necessary background picture. With the logarithm of loss as the variate, an initial distribution of the exponential type is assumed. Hence use of the first asymptotic distribution of largest values is illustrated. Extreme order statistics other than the largest are also discussed. Uses of these statistics are briefly outlined. Suggestions for further research are also made.

Ramachandran, G. (Joint Fire Research Organization, Borehamwood, England) "Fire Loss Indexes," *Joint Fire Research Organization Fire Research Note 839* (September 1970)

Section: L
Subjects: Large fires; Loss index

Author's Summary

Economic justification for expenditure on fire protection measures depends upon the expected annual monetary damage due to fire. As a crude index we could express the risk as loss per square foot of floor area or as loss per hundred pounds of value at risk. With the data available these loss indexes for manufacturing industries have been calculated and presented in this note.

The values obtained in this paper indicate, in a broad sense, the relative risks in the different industrial groups considered. If they are to be of practical value the indexes require refinement in the light of further information which may become available. It is recognized that indexes are needed for each sub-sector or field of activity within an industry.

The object of this paper is to stimulate discussion on the economic level for fire protection of various industries taken as a whole rather than to deal with specific risks.

N. Instrumentation and Fire Equipment

Belason, B., Castle, G., Crowley, D., and D'Avanzo, L. (AVCO Systems Division) "A Fire Simulation Facility for Materials Response Testing," *Fire Technology* 6 (3), 179–188 (1970)

Section: N
Subjects: Fire simulation; Material response; Simulation of fire; Test methods

Reviewed by B. M. Halpin

A means of testing materials designed for fire protection has been constructed at Avco to "permit evaluation of the one-dimensional response of a material in a real fire environment." The design of the facility is basically built around the concept of having simultaneous convective and radiative heating with the appropriate emittance to control the temperature and effective emission of the gas.

The radiant energy source for the test chamber is an electrically resistance-heated hood which has an inner surface of ceramic. The temperature can be programmed for steady-state conditions of room temperature to 2300°F. The hood is 7.2 in. wide at the base, and it is 21.6 in. long. The ceramic material of the inner surface has an emissivity of 0.9 at 1800°F.

The convective flux is supplied by an oil burner which generates the hot gases. The temperature of the gas is adjusted to equal the hood temperature during a test run. A convective flux can also be supplied by burning methane in a multi-pored tube mounted at the inlet of the hood.

A viewing port is also provided in the hood to enable visual observation of the test specimen during the test. This port provides a minimum view factor of .96 for the specimen.

A specimen that is 5 in. square is mounted in the center of the floor of the test chamber, and the flow of the convective gases is parallel to the surface of the specimen. A water-cooled shield is utilized to keep the specimen isolated from the heat flux until the desired thermodynamic conditions are reached. The shield is manipulated through the viewing port in the hood.

An automatic guard heater is used at the rear face of the test material to maintain a nearly adiabatic boundary condition.

The surface temperature of the radiating hood is measured with pyrometers and thermocouples. The radiative and total heat fluxes can be measured by mounting two Hy-Cal asymptotic calorimeters next to the test specimen. The pressure and temperature of the convective gases, and the air and fuel flow rates are also measured. All the readings are recorded on a multichannel recorder.

Palmer, T. Y. (Pacific Southwest Forest and Range Experiment Station, U.S. Forest Service, Berkeley, California) "Comparison of Aspirated and Radiation-Compensating Thermocouples," *Fire Technology* 6 (3), 224–228 (1970)

Section: N
Subjects: Aspirated thermocouples; Radiation-compensating thermocouples; Thermocouples

Editorial material from Fire Technology and Conclusions of Author.
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As a part of an effort to develop techniques for making more accurate flame temperature measurements, the author compared the performance of a self-compensating thermocouple with that of the more complex and expensive aspirated thermocouple.

Author's Conclusions

This comparison of thermocouples is part of an on-going research program in exploring the opportunities and limitations of prescribed fire in brush fuels. One of the aims of the program is to develop techniques of making more precise measurements of flame temperatures.

The self-compensating thermocouple clearly performs just as well as the much more complex and expensive aspirated type. The data obtained with both instruments indicate that the test fires propagated from the top downward at a rate of about 0.25 fps. In addition, there was evidence of spectral peaks in the temperature variations. Limitations on further analysis of the temperature spectrum were imposed by the data sampling recorders.

O. Miscellaneous

Butcher, E. G. and Bedford, G. K. (Joint Fire Research Organization, Borehamwood, England) "Fire Tests in Two Caravans," *Joint Fire Research Organization Fire Research Note 835* (September 1970)

Section: O
Subjects: Caravans; Escape means; Fire tests; Mobile homes; Sprinklers; Trailers

Authors' Summary

This report describes fire tests carried out in two caravans, the purpose of which was to determine the time available for escape in the event of fire. This is of considerable importance because a sleeping risk is involved.

Both caravans had identical linings and furniture. They had smoke and heat detectors fitted, and in addition one caravan had a simple sprinkler installed.

The fire in both caravans developed quickly, and the results of the tests show that the time available for the occupants to make their escape is very limited.

BOOKS

Electrical Aspects of Combustion by J. Lawton and F. J. Weinberg Published by Clarendon Press (1969)

Interest in the electrical characteristics of flames can be found in the earliest literature on natural phenomena; indeed, it is as old as man's interest in electricity itself. The list of implements of the early inquirers included flames as well as amber rods and the skins of cats. However, as knowledge became compartmentalized and disciplines were formed, general interest faded in the electrical aspects of combustion. Nonetheless, research and writing continued sporadically.

Since World War II a great deal of interest has developed in both the chemical aspects of flame ionization and practical applications using electric fields and flames. During this time there developed the notion that most of the observable phenomena could be explained by the "electric wind", and that there was little evidence that changes in combustion chemistry were responsible for the origin of the effect of fields on flames. Recently, it has been recognized that there is no need to explain the flame-field interaction in either aerodynamic or chemical terms, but that it is possible for chemical effects and aerodynamic effects to occur simultaneously with varying degrees of importance.

Thus, it is appropriate that "Electrical Aspects of Combustion" has arrived at the present time. Felix J. Weinberg and his colleagues at the Imperial College have made significant contributions to the understanding of the flame-field interaction, and Lawton and Weinberg do an excellent job of providing a systematic, comprehensive, and unified survey of the subject for the uninitiated and the devotee alike. The digestion of their work, the work of others, and the juxtaposition of the literature of the related disciplines of kinetics, fluid mechanics, and plasmas reestablishes a unity that has been overdue.

The list of chapters shows the breadth of coverage of the book. Chapter 2 provides an introduction to the behavior of charged particles in gases and at gas-solid interfaces. The emphasis is on the collision dynamics of molecules, ions, and particulates, and on the chemical processes resulting from such collisions. Topics include a survey of the kinetic theory of gases and the processes of ionization (thermal and collision induced), electron attachment, charge exchange, recombination, electron emission from surfaces, and particle charging in regions of space charge. The review of the specific reactions involved in the formation and recombination of ions in flames, and ionization resulting from additives is delayed until Chapter 6.

Chapters 3 and 5 contain a thorough survey of laboratory burner systems and Langmuir probes, and a brief survey of resonant circuits and mass spectrometry. The chapter contains sufficient underlying theory, plus practical tips to please the experimentalist. While the coverage is consistent with what can be found elsewhere, it is cast in ways particularly useful to measurements of electrical phenomena in flames.

Chapters 4, 8 and portions of 7 consider the forces and motion arising from charged particles in and near flames subjected to fields. Attention is given to the motion of ions, electrons, charged clusters as well as the motion induced in the neutral bulk gas for a number of flame-field configurations. The latter, the "ionic wind" has been one of the author's strong suits for years and is central to the book. The case is presented with compelling clarity. Differences between predicted performance and experimental findings are reconciled with candor and insight. The significance of saturation current density has been a cornerstone of the research of Weinberg's group at the Imperial College and a great deal of valuable information has been obtained. This subject too is presented with clarity and cogency.

The emphasis in Chapter 7 is on engineering devices and processes which have either been tested or which appear practical. Applications are grouped as follows:

1. Electrolysis—fluid droplets, particulates, flame carbon and soot
2. MHD and EGD power generation
3. Heat transfer from flames

Applications dealing with aerosols, soot and particulate matter enjoy widespread current interest and are discussed cogently and in detail. The twenty or so pages devoted to MHD and EGD power generation are interesting but somewhat beside the point, since combustion issues remain peripheral to the larger problems facing these devices and since more exhaustive reviews exist in numerous specialized books. The case for the enhancement of heat transfer from flames is made with persuasion.

The reviewers have only two criticisms for the coverage of the book. First, despite the inclusion of some historical literature in the separate chapters, we wish the authors had devoted a dozen or so pages to the history of the subject. Men such as Gilbert, Bacon, Boyle, Priestley, Desagulier, Watson, Franklin, Volta, Faraday, Thomson, and Wilson to name just a few whose works appear in the English speaking literature, have established a heritage that is more than mere heuristic academicism.

Secondly, the organization of topics could have been better. The division of the subject matter of chapters 4, 8, and part of 7 into three chapters seems unnecessary and is unfortunate in the respect that the novice may infer more independence than indeed exists. More importantly, a casual reader looking only to chapter 7 for "practical" things will miss the numerous issues distributed throughout the book. For example, the discussion of electrically boosted or augmented flames is good, but is presented in chapter 5.

On the whole, equations, theories, etc. are sufficiently explained and referenced such that readers can pursue issues independently. The references appearing at the end of each chapter are numerous, complete to 1968, and the authors do not seem to have made any omissions. The book is not parochial. Differing schools of thought on the nature of the flame-field interaction are given in an even handed fashion and the authors do not overemphasize their own considerable research. The subject and author indexes are detailed.

In the introduction the authors state that they wish to introduce the subject from three independent disciplines, review well-established concepts, summarize the literature of less well-established concepts, and lastly to survey experimental methods. On all counts, they have succeeded admirably. Long-time workers will find the book valuable as a reference, the unitiated and the student will find it a valuable sourcebook, and the inquisitive reader will find the book an understandable assessment of the current understanding of the electrical aspects of combustion.

Reviewed by R. J. Heinsohn, Associate Professor, and P. M. Becker,
Assistant Professor, Mechanical Engineering
(Fuel Science Section, Material Science Department, P.S.U.)

Introduction to Fire Science by Loren S. Bush and James McLaughlin. Glencoe Press Fire Science Series, Glencoe Press (Division of the Macmillan Co., Beverly Hills, California, Collier-Macmillan, Ltd. London.) Harvey N. Gruber, General Editor and David B. Gratz, Consultant. (1970) 377 pages.

Reviewed by R. L. Tuve

For the past three or four years a new trend in education has arisen. It is gathering speed and momentum every year, especially on the west coast of the United States, whence come the authors and publishers of this new textbook designed especially for "the entering college student."

The authors of this book combine the pragmatic problem approach of a very well-known engineer, Loren S. Bush, with the skills developed on the fire field and in the fire department, possessed by Assistant Chief James McLaughlin. In the preface the aim of the book is pointed out "to provide a brief look into the various fields of study encompassed by the fire science curriculum"—"each (subject) should be studied in greater depth." The book does just that.

Fire department organization and administration is heavily emphasized in this text with six of its ten chapters titled on subjects such as: "Careers in Fire Service", "Fire Protection Services", "Private Fire Protection", and "Municipal Fire Defense."

A well balanced technical and engineering emphasis on important fire protection technology is not apparent in the book. Of a total of 328 pages of text, only 113 pages deal with the enormously intricate technical phases of a specialist in fire protection. The coverage of subjects such as sprinkler systems, extinguishing agents, and pumping equipment is wondrously broad in scope but so wanting in detail that much corollary reading of other reference material would be needed by the serious student who desires more than a general orientation survey.

To many young aspirants toward a career in the professional fire sciences, the book creates an alarming feeling that a fire officer's life is crowded with inspection forms and record-keeping duties without end. Grant we must that this is very close to the case, but something should have been said about the alluring opportunities in this newly named profession which will require the utmost of future officers in alloying all the best knowledges of *all* the sciences to forge an effective future.

There are well-stated summaries at the end of each chapter. Bibliographies of appropriate reference material are unfortunately missing with the exception of frequent notes interspersed in the test concerning NFPA publications or technical pamphlets. Many of the latter are arid and unrewarding reading for *new students*. The index coverage for the generous number of different topics that appear in this text is much too small, being in a ratio of 1 page to 83 pages of text. Modern textbooks are in the range of 1 page to 30 or 40 pages of text. The appendices contain a full hunting bag of blanks and forms of all kinds.

As a text book for ambitious young high school graduates who have recently become fire-fighting personnel—"probies", they're called in New York City—this very general treatment of what's ahead of them in their career will be a real eye-opener to most of them. The very serious and real-life world of the fire expert comes early in this book. It is not light reading! It falls short of some of its aims to interest those who might not yet be interested in a career as a fire professional, but those who heed all its contents well will be the much better for it.

Fire Weather (A Guide for Application of Meteorological Information to Forest Fire Control Operations) by M. J. Schroeder, Weather Bureau, Environmental Science Services Administration, Department of Commerce and Charles C. Buck, Forest Service, Department of Agriculture. *U.S. Department of Agriculture, Forest Service Handbook 360.* $3.75 from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 229 pages.

This excellent, well illustrated, elementary text has as its objective the presentation of elementary meteorological information for those interested in forest fire control, as indicated in its preface below.

> "Weather is never static. It is always dynamic. Its interpretation is an art. The art of applying complex information about weather to the equally complex task of wildland fire control cannot be acquired easily—especially not by the mere reading of a book.
>
> "The environment is in control in wildland fire-fighting. Free-burning fires are literally nourished by weather elements, atmospheric components, and atmospheric motion. Outguessing mother nature in order to win control is an extremely difficult task. We need to soothe her with understanding.
>
> "We have attempted to present information in such a way that your daily and seasonal awareness of fire weather can begin with reliable basic knowledge. We have kept the use of technical terms to a minimum, but where it was necessary for clear and accurate presentation, we have introduced and defined the proper terms. Growing awareness of fire weather, when combined with related experience on fires, can develop into increasingly intuitive, rapid, and accurate applications. Toward this end, we have preceded each chapter with a paragraph or two on important points to look for in relating weather factors to fire-control planning and action."

The authors have succeeded in their objective. This text can be recommended to anyone seeking an introduction to the interaction between meteorology and fire. The presentation in the text is clear and the three-color illustrations are very graphic and informative.

The coverage by the text is indicated by the contents.

R. M. Fristrom,

MEETINGS

13th Symposium (International) on Combustion—University of Utah, Salt Lake City, Utah (August 23–29, 1970)

The 13th Symposium on Combustion was held the week of August 23–29, this past summer. Some twenty sessions were held on a wide variety of topics of interest in combustion. As usual a number of papers of interest in the fire field were presented. The titles of a number of these are listed below. Abstracts of the papers are available through The Combustion Institute and the Proceedings are scheduled for publication this year. At that time a number of these papers will be reviewed.

Fluid Mechanics and Combustion—H. W. Emmons

The Three-Body Recombination and Dissociation of Diatomic Molecules: A Comparison between Theory and Experiment—V. H. Shui, J. P. Appleton, and J. C. Keck

The Temperature Coefficients of Diatomic Dissociation and Recombination Reactions—D. L. S. McElwain and H. O. Pritchard

Rates of Gas-Phase Hydrogen-Atom Recombination at Room Temperature in the Presence of Added Gases—J. E. Bennett and D. R. Blackmore

Catalytic Effect of Metal Additives on Free Radical Recombination Rates in $H_2+O_2+N_2$ Flames—E. M. Bulewicz and P. J. Padley

Absolute Measurements of Rate Coefficients for the Reactions of H and O Atoms with H_2O_2, and H_2O—E. A. Albers, H. Hoyermann, H. Gg. Wagner and J. Wolfrum

Studies of the Combustion of Branched-Chain Hydrocarbons—P. Barat, C. F. Cullis, and R. T. Pollard

Inhibition by Nitrogen Dioxide of the Slow Oxidation of Butane at Low Temperatures—J. C. Dechaux and M. Luchquin

Multistage Ignition in Hydorcarbon Combustion: Temperature Effects and Theories of Non-Isothermal Combustion—J. F. Griffiths, B. F. Gray, and P. Gray

The Use of the H_2+O_2 Reaction in Determining the Velocity Constants of Elementary Reactions in Hydrocarbon Oxidation—R. R. Baker, R. R. Baldwin, and R. W. Walker

Low Temperature Oxidation of Hydrocarbons-Round-Table Discussion

CO Reactions in the Afterflame Region of Ethylene/Oxygen and Ethane/Oxygen Flames—T. Singh and R. F. Sawyer

A Spectroscopic Study of the Hydroxyl Radical in an Internal Combustion Engine—D. S. Smith and E. S. Starkman

Burning Velocities of Methane-Air Mixtures Using Hot Wire Anemometers in Closed Vessel Explosions—D. Bradley and G. Hundy

The Effect of Hydrogen Bromide on the Structure of Propane-Oxygen Flames Diluted with Argon—C. Pownall and R. F. Simmons

Some Observations on Near-Limit Flames—A. L. Furno, E. B. Cook, J. M. Kuchta, and D. S. Burgess

Chlorine-Fluorine Flame Structure—L. L. Ambs and E. A. Fletcher

Inhibition of Hydrogen-Air and Hydrogen-Nitrous Oxide Flames by Halogen Compounds—M. J. Day, D. V. Stamp, K. Thompson, and G. Dixon-Lewis

Experimental and Mathematical Study of a Hydrogen-Oxygen Flame—K. H. Eberius, K. Hoyermann, and H. Gg. Wagner

The Rate of Combustion of Soot in Turbulent Flames—B. F. Magnussen

Pyrolysis of a Slab of Porous Material—R. L. Panton and J. G. Rittman
Problems Associated with the Theoretical Analysis of the Burning of Wood—A. F. Roberts
Mechanisms of Ignitions of Thermally Irradiated Cellulose—N. J. Alvares and S. B. Martin
Fire Spread in Paper Arrays—H. W. Emmons and T. Shen
The Structure of Some Quasi-Steady Fire Spread Waves—A. L. Berlad, R. C. Rothermel, and W. Frandsen
Flame Spread Over Fuel Beds: Solid Phase Energy Considerations—F. A. Lastrina, R. S. Magee, and R. F. McAlevy, III
Laminar Free-Convective Burning of Fuel Surfaces—J. S. Kim, J. deRis, and F. W. Kroesser
Fuel Preheating in Free-Burning Fires—H. C. Hottel, G. C. Williams, and G. K. Kwentus
A Theoretical and Experimental Study of Non-propagating Free-Burning Fires—J. A. Block
Modeling of Ceiling Fires—L. Orloff and J. deRis
Polymer Degradation Theory of Pressure Sensitive Hybrid Combustion—R. N. Kumar and D. B. Stickler
Ignition of a Solid Polymeric Fuel in a Hot Oxidizing Gas Stream—T. Kashiwagi, B. W. MacDonald, H. Isoda, and M. Summerfield
Radiative Ignition of Polymeric Materials in Oxygen/Nitrogen Mixtures—T. J. Ohlemiller and M. Summerfield
Partial Oxidation of Propane in Metal and Pyrex Glass Reactors—Che-I Kao and L. F. Albright
Quantitative Studies of the Role of Alkenes During the Combustion of Alkanes—T. Berry, C. F. Cullis, and D. L. Trimm
An Experimental and Analytical Investigation of the High-Temperature Oxidation Mechanisms of Hydrocarbon Fuels—C. T. Bowman
A Calculation Procedure for One-Dimensional Laminar Flames—D. B. Spalding, P. L. Stephenson, and R. G. Taylor
Laminarization of Turbulent Flames in Rotating Environments—J. M. Beér, N. A. Chigier, T. W. Davies and K. Bassindale
Burning of Well-Ventilated Wood Cribs—A. M. Kanury
Pyrolysis and Burning of Single Sticks of Wood under Isothermal Ambient Conditions—A. M. Phillips and H. A. Becker

Conference of National Fire Service Organizations, Williamsburg '70 (National Goals of the Fire Service) Williamsburg, Virginia (August 31–September 1, 1970)

On August 31, 1970, representatives from a number of fire service organizations met in Williamsburg, Virginia, with the objective of formulating national goals for the fire service. The representatives constituted themselves as the "Joint Council of National Fire Service Organizations." Members of the following organizations were present and the sessions were moderated by Professor John L. Bryan of the University of Maryland.

Fire Marshals Association of North America
Fire Protection Research International
International Association of Arson Investigators
International Association of Fire Chiefs
International Association of Fire Fighters
International Fire Administration Institute
International Fire Service Training Association
International Society of Fire Service Instructors
Metropolitan Chiefs Committee of the International Association of Fire Chiefs
National Fire Protection Association

The group proposed the following national goals for the fire service as reported in a National Fire Protection Association Bulletin.

1. To develop nationally recognized standards for competency and achievement of skills development, technical proficiency and academic knowledge appropriate to every level of the Fire Service career ladder.
2. To make the public aware of the significant contributions made by the Fire Service of this nation in protecting life and property from fire, and the contribution made to the standard of living to which all citizens are entitled.
3. To make public officials at every level of government more aware of their responsibilities in providing increased financial and moral support to aid the Fire Service in carrying out their mission.
4. To reassess public fire protection in light of contemporary demands, assuring appropriate fire protection for all communities at a reasonable cost.
5. To establish realistic standards of educational achievement, and provide to every member of the Fire Service equal educational opportunities commensurate with professional requirements.
6. To identify and establish nationwide information systems that will enable improved analysis of the fire problem with particular emphasis on the life and safety factors for the public and the fire fighter.
7. To encourage and undertake the research and development necessary for the prompt and successful implementation of the goals stated above.

Interschutz—Der Rote Hahn. Exhibition Grounds of the City of Frankfurt am Main, West Germany (June 24–July 2, 1972)

The Association for the Support of Fire Fighting in Germany (VFDB) in cooperation with the Fair and Exhibition Company of the City of Frankfurt is organising an International Exhibition for Fire Protection and Civil Defense.

A comprehensive industrial exposition will deal with all technical developments in the fields of defensive and preventive fire protection, of technical aid, rescue services, civil defense, development of equipment and vehicles.

At the same time, the nontechnical section of the exhibition comprises special exhibits and demonstrations by the fire brigades and their professional organizations and other associations of rescue services.

Concurrently, the following events will take place in Frankfurt.

Conventions

Association for Support of Fire Fighting (VFBD)—Annual Conference
German Fire Chiefs Association (AGBF)—General Meeting
Comite Technique International de Prevention et d'Extinction du Feu (CTIF)—Symposium
German Firemen's Association (DFV)—Conference of Delegates
Heissian Firemen's Association (HFV)—Hessian Fire Fighters Convention
Union Conference of Public Services Trade Union (CTV)

Organisationburo
INTERSCHUTZ—Der Rote Hahn-Branddirektion
D-6000 *Frankfurt am Main*
Hanauer Landstr. 77
West Germany

EQUIPMENT AND PRODUCTS

The processes of efficient, useful, and complete communication in the interdisciplinary field of research and development on fire protection and fire phenomena are served in many ways, not the least of which concern dissemination of that information developed by the test and research programs conducted by industrial firms engaged in the manufacture of fire protection equipment and materials. Recent issues of this publication have increased the space devoted to abstracts of industrial research appearing in the open literature.

Because of the nature of competitive free enterprise, many industrial firms find it necessary to restrict the open flow of technical information to that which is important in the selling program of a newly developed product, be it an equipment, system, material, or a testing project of universal interest. Much knowledge may be imparted in such a manner.

The goal of this new section in the pages of FRAR will be to abstract and condense for its readers that openly published factual engineering and technical data which become available from industry concerning new methods of fire prevention and protection. Every effort will be made to confine this space only to those items which promise progress and learning. Other publications adequately inform the reader who is interested in novel devices or improvements. It is hoped that a wide range of topics will become available which will promote the interfruitfulness of fire research with the practicing worker.

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Volume 13 1971 Number 2

Fire Research Abstracts and Reviews

National Academy of Sciences

FIRE RESEARCH ABSTRACTS AND REVIEWS

Robert M. Fristrom, Editor

Girard L. Ordway, Associate 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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Committee on Fire Research
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National Research Council

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FOREWORD

The main body of this issue's Foreword takes the form of a Guest Editorial. Our distinguished contributor is an old friend to workers in the field of fire research. He is Professor Richard E. Bland of The Pennsylvania State University, University Park, Pennsylvania, who has recently been appointed by President Nixon to head the National Commission on Fire Prevention and Control, which was mentioned in the Foreword of the preceding issue of FRAR, Volume 13, No. 1. During this busy initial stage of committee work, Professor Bland has kindly taken the time to summarize his thoughts on his Commission's problems and mission. Your editor feels that he speaks for the fire community as a whole in thanking Professor Bland for providing this preview and wishes him and his Commission well in their endeavors.

A second pleasant task of your editor is to introduce a new member of the FRAR staff. Dr. Girard Ordway has accepted the position of Associate Editor. He brings many skills to our Journal: physical scientist, linguist, mathematician, analyst, and now editor. His efforts will strengthen our efforts in gathering and disseminating fire research information.

This issue begins with a well-written review of the characteristics of fire detectors by Dr. John Wagner of the Applied Physics Laboratory, The Johns Hopkins University.

Robert M. Fristrom, *Editor*

GUEST EDITORIAL

The National Commission on Fire Prevention and Control has as its singular objective the reduction of loss from destructive fire. Public Law 90–259, which under Title I, authorizes fire mission related research under the Bureau of Standards and concurrently establishes, in Title II, an independent Commission. As Chairman of that Commission, I believe the intent of Title II is a genuine expression of eagerness by the President and the Congress to develop direction to the citizen as he attempts to control an ever present threat. The Act implies such questions as: a) what is the fire experience in our country? b) how can the effects of the entire fire fraternity (engines, devices, building practices, regulations, insurance, etc.) be made more effective within the framework of real economic constraints? c) what are some realistic goals? d) what are the guidelines applicable to these goals? e) what should the Federal Government's role be in life safety protection of the individual citizen, for the protection of the products of his current and past labors and for the preservation of his heritage and his potential for the future?

The Commission, as an appointed deliberative body charged with advising at the highest levels of Government, stands currently subservient to what might be described by many as an ill defined system. Ill defined as it may be, it is an operative process that has historically done and continues to do a creditable job in the face of a threat rapidly increasing in both magnitude and technological content. Hence, there should be no general condemnation of either America's fire suppression forces or the ancillary agencies that stand in support. It's the soft spots in the process that the Commission will look for, not for purposes of fault finding, but to aid and encourage improvement.

Is the Membership of the Commission capable of accomplishing this task? Yes . . . By observation, the disciplines of the eighteen Members completely cover the fire fraternity, the experience and the intellectual depth brought to the table is profound. This is a credit to the Appointees and the Appointer. As the Chairman, I am awed by its potential . . . Yet the sometimes cruel process of building a productive deliberative body requires that each Member put forward a massive effort to pull himself from his mundane environment, no matter what the intellectual depth or tenure in his expertise. In a time compressed frame he must become a generalist in contrast to the specialist . . . a visionary is the goal!

To attain the attributes of a practical visionary will require the aid and encouragement of the entire community. I include here by definition all those specialists and generalists who contribute to and read this document. The National Commission on Fire Prevention and Control, as a duly constituted agent of the President and the Congress, asks that each one of you evaluate your efforts against the criterion of predicable reduction in fire loss and apply your ample talents to this singular end. We then ask that you communicate your work and your views to us in the most useful form.

Your communications to our offices at 1730 K Street, N.W., Washington, D.C. 20006, or to my attention at P.O. Box 30, State College, Pennsylvania 16801, are sincerely solicited. *Something can be done to reduce the effects of destructive fire!*

Richard E. Bland, *Chairman*
National Commission on Fire
Prevention and Control

CONTENTS

Volume 13 Number 2

ABSTRACTS AND REVIEWS

A. Prevention of Fires and Fire Safety Measures

B. Ignition of Fires

C. Detection of Fires

D. Propagation of Fires

E. Suppression of Fires

F. Fire Damage and Salvage

G. Combustion Engineering

H. Chemical Aspects of Fires

I. Physical Aspects of Fires

J. Meteorological Aspects of Fires

K. Physiological and Psychological Problems from Fires

L. Operations Research, Mathematical Methods. and Statistics

M. Model Studies and Scaling Laws

BOOK

PERIODICALS

TRANSLATION

MEETINGS

A Survey of the Principal Operational Characteristics of Fire Detector Mechanisms*

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Applied Physics Laboratory, The Johns Hopkins University

Introduction

In this survey a review of the current state of the art of the leading fire detector designs is presented. Because of the wide scope this field encompasses, the complete automatic detection system, consisting of detector(s), plus extinguishing systems, warning devices, etc., is not considered herein, i.e., detectors, per se, are examined. These are classified into two categories:

a) Conventional—readily available from a commercial supplier and in current use.
b) Non-conventional—in the research or development stage and/or not used in the fire detection field.

Fire type, its rate of progression, and convective ascent and lateral spreading of a fire plume are also examined because they are important to the detection problem.

The objective of this survey was first to examine the operational characteristics of fire detectors under different test conditions and second to comment on promising detector developments.

Background

The importance of accurate early warning fire detection needs little justification. In the U. S. alone, estimated values for the year 1970 were that 12,200 lives and 2.7 billion dollars worth of property damage resulted from fires. Many if not most of these losses could have been minimized or prevented if the fires had been detected at an early stage. This requires some type of an automatic detection system. Although there has been an ever increasing dependence on fire detectors in recent years, man is still the prime detector. The major deterrent to installation of a suitable detection system is cost. From a relative viewpoint, the cost of the detection system (including installation and regular maintenance fees if required), vs. the cost of fire insurance and the price attached to the protected area is a key factor. For commercial- and other institutional-type concerns detectors are justified on an economic basis, whereas for residential dwellings they generally are not. In the absence of a low-cost, accurate detector, it appears that insurance costs and perhaps building or housing codes will determine the use of detectors. Nevertheless, their importance cannot be overemphasized. The Canadian Research Council[2] estimates that 41% and 8% saving of life is realizable with an ionization (see p. 100)

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* Supported by National Science Foundation, RANN Division (Research Applied to National Needs) under Grant NSF GI-12.

and thermal detector (p. 103), respectively, based on the information in Ontario dwellings.

Information on the different types of fire detectors is available in the NFPA reference books[3,4], in a very limited number of survey articles[5,6,7], and from many corporations in the form of engineering notes (e.g., Refs. 8, 9), or sales brochures.

The choice of a proper detector and selection of its location with respect to an anticipated fire is a difficult process and usually requires professional help. Some of the problem areas which one encounters in the decision making process are outlined in this article.

Fire Ecology, Fire Types, and Fire Products

A number of important concepts which one needs to know before a fire detection system can be designed were outlined by Wilson under the heading, "Ecology of Fire Protection":[10]

a) Fire Itself—need to know the relationship between the fuel and surroundings. The type, the amount, the arrangement, and the heat release rate of the fuel, as well as the size of the enclosure, enter into the picture.
b) Damageability of the area—e.g., computer room vs. storage room.
c) Response time of the agent that puts the fire out—e.g., water vs. Halon 1301.

Fires are classified according to NFPA[3] into four general types:

Class A: Fires involving ordinary combustible materials (wood, cloth, paper, rubber, and many plastics).
Class B: Fires involving flammable or combustible liquids, flammable gases, and greases.
Class C: Fires involving electrical equipment. These are treated as Class A and B fires after the electricity is turned off.
Class D: Fires involving combustible metals (e.g., Mg, Na, etc.).

Different temperature vs. time histories are evidenced in these four classes. Class B would be fairly fast as in a gasoline fire (flash fire type), while Class C would be expected to be slow as in the burning of an insulated wire or cable (smoldering type). Class A would generally fall in between these two types. Actually, both smoldering and flash types can be obtained for Class A depending on the oxygen content and the heat load. Type D would generally be very fast—e.g., Na fires under certain conditions would be explosive while Mg burned in air would represent a highly exothermic flash fire. The latter types are not considered in this report.

Since most fires are of the Class A type, involving cellulosic fuels, it is important to consider the different temperature zones exhibited by this type of a material since this leads to the fire environment. Based on a review by Browne,[11] described by Beall and Eichner,[12] four distinct temperature zones are given for the thermal decomposition of wood as follows:

Zone A: Below 200°C. Appearance of noncombustible gases, primarily H_2O vapor, traces of CO_2, formic and acetic acids, and glyoxal. Dehydration of sorbed water is complete.
Zone B: 200°C to 280°C. Same gases as in Zone A are produced along with greatly reduced quantities of water vapor and CO. Reactions are endothermic and products are almost entirely nonflammable.

Zone C: 280°C to 500°C. Active pyrolysis takes place under exothermic conditions leading to secondary reactions among the products. Largely combustible products, CO, CH_4, etc., and flammable tars in form of smoke particles.
Zone D: Above 500°C. Residue consists primarily of charcoal, which provides an extremely active site for secondary reactions.

The early combustion stages are similar to the pyrolysis stages, modified slightly by oxidation. These stages are categorized as follows:

Zone A: Similar to Zone A above but slightly affected by some exothermic oxidation processes.
Zone B: Primary exothermic reaction takes place without ignition.
Zone C: Combustible gases that are ignitable are produced after secondary pyrolysis. Flaming combustion can occur in the gas phase if the gases are ignited. If ignition is not induced flaming may not occur until near the end of pyrolysis when the gases cannot insulate the charcoal layer from O_2. Spontaneous ignition of charcoal takes place at a temperature lower than any of the products evolved.
Zone D: Greater than 500°C the charcoal glows and is consumed; greater than 1000° nonluminous flames are supported by the combustion of H_2 and CO.

These zones illustrate in an elementary way the complexity of cellulosic combustion processes.

In an enclosure of reasonable size one would expect an agglomeration of products from both pyrolysis and combustion. This is illustrated in the flow diagram in Fig. 1. The conductive mode of heating will induce pyrolysis at short range. This would be limited to the percolation of gases through materials that leave porous char-like residues. Alternatively, radiation and convective heat transfer are primarily responsible for flame spreading, and therefore are long-range in nature. The liquid and solid aerosol phases are also present in varying degrees.

It is important to note the distinct physical and chemical processes occurring in the zone breakdown and in the flow diagram since fire detectors are designed to respond to these differences.

Comments on Formation of the Fire Plume and Detector Response Times

The enormous number of variables that can affect a fire,[13] as well as the strong coupling between the conservation equations precludes accurate predictions of the state variables (primarily composition and temperature), in time and space, for different types and amounts of combustible materials, for all but the simplest of geometries. Thus, computed composition and temperature profiles cannot be used to facilitate an optimum positioning of a given detector within an enclosure. Nevertheless, experimental tests, such as those conducted during Operation School Burning No. 2 and by various detector manufacturers are very helpful in selection of a suitable detector with proper positioning. However, because even geometrical similarity is often not preserved in going from the reported test results to another area, one cannot be assured of similar detector behavior. What appears to be needed, is first, a detailed experimental study of detector response vs. changes in system parameters; second, a nondimensional correlation of the

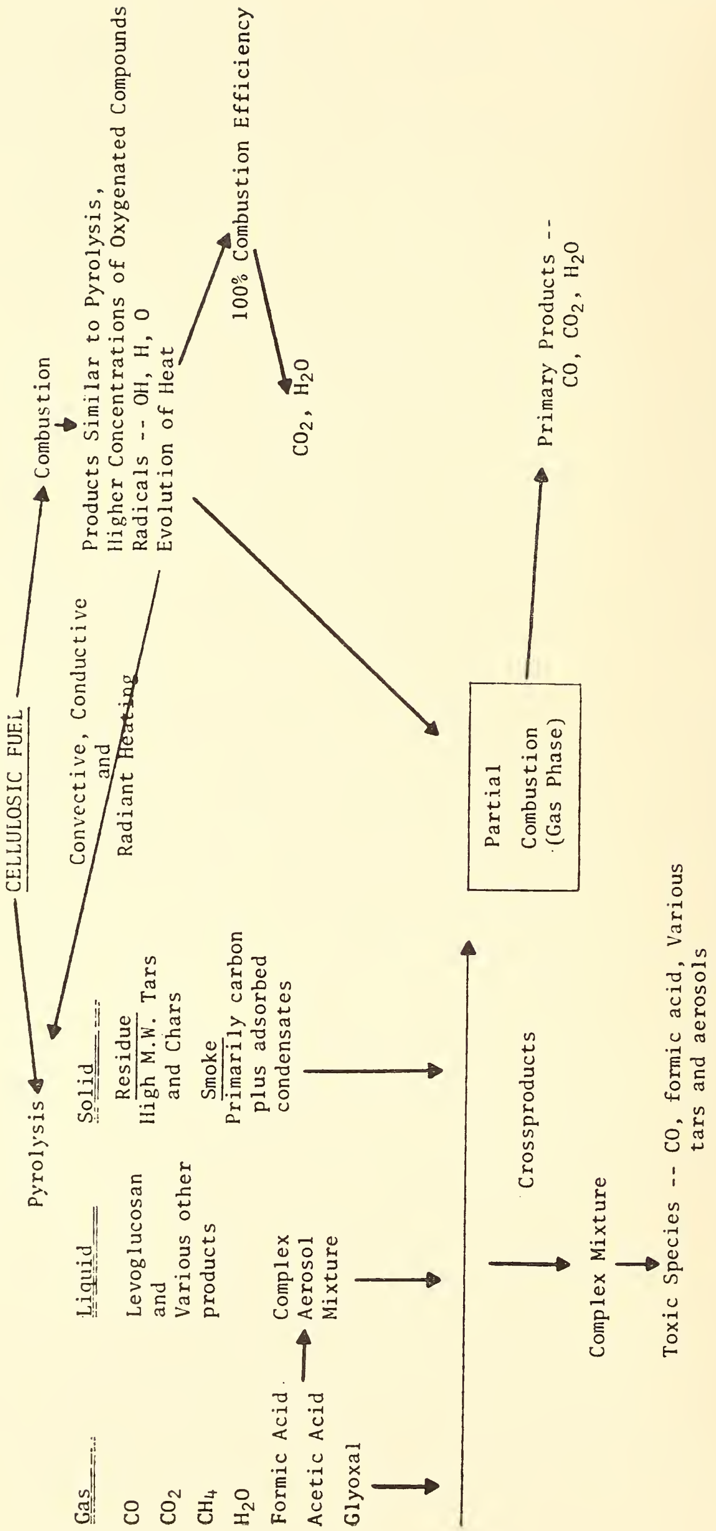

FIG. 1. Flow diagram for pyrolysis and combustion of cellulosic fuels in an enclosure.

data in a series of graphs or charts. These may be used to answer various questions which are now treated largely as an art.

Although complete modeling of a fire is an unrealistic endeavor, there are a number of interesting conditions which merit consideration. First, let us limit ourselves to the situation most often considered, namely a fire occurring on the floor of an enclosure with the detector(s) mounted in the ceiling. If the detector is of the local type, i.e., requires a sample of the combustion gas to actuate, information about the fire must be brought to the detector by turbulent (possibly laminar under ideal conditions) free convective heat and mass transfer mechanisms. An accounting of the early work for modeling and analysis of free convective processes for point and horizontal line sources is given by Taylor.[14] The important results contained in this review article were: a heated turbulent jet expands at a uniform rate with increasing height and, therefore, the jet arising from a point source will be contained in a cone, while the jet arising from a line source will be contained within a wedge. For a three dimensional jet arising from a point source Schmidt's velocities scale identically as for two dimensions; temperature also scales if one assumes that the point source was a series of short lengths. More recent published works are given in Refs. 15 and 16.

Information on fires sufficiently far off the centerline of the detector, or not contained within the wedge or cone of influence of the fire plume, can only be brought to the detector by a secondary lateral expansion along the ceiling. We need to know the time scales for both fire plume ascent and its expansion for a range of system variables. Tests reported in Operation School Burning No. 2 and also in Pyr-A-Larm News[17] illustrate the importance of knowing these times. For example, the Pyr-A-Larm tests show that in manufacturing and warehousing areas having ceiling heights ranging from 14 ft to 26 ft, a combination of ionization and infrared detectors was needed to provide the fastest detection time. This occurred even though the ionization detector has a much faster response time to a Class A fire (excluding the flash fire). Judging from the photo accompanying this result, it appears that both detectors are located directly above the fire; thus, even larger differences are conceivable for off-the-centerline fire sources. More recent studies on this problem have not appeared in the literature.

An examination of detector response times reveals a somewhat confusing picture. First, the time responses quoted in corporate brochures are invariably the fastest obtained under ideal conditions. Differences of orders of magnitude are conceivable under extreme conditions. Second, there is no standard test procedure (e.g., similar to the flammability tests for plastics[3] for testing the various detector types. Consequently, the various manufacturers quote different response times and procedures for their detectors. Because of these drawbacks, and also the limited conditions under which the more realistic tests were carried out, it is difficult to form any definite conclusions at this time. There is certainly a need for further study in this area, however. Also, the need to establish a standardized test procedure for detectors which would include the response time under predetermined conditions as well as the frequency of false alarming is quite evident.

Operational Characteristics of Detectors

Detectors may be classified according to their response to the following parameters:

a) products of combustion
b) visible smoke

c) light
d) heat
e) sound

In the following sections, the limitations and salient features of both conventional and non-conventional detectors will be outlined whenever possible.

Conventional Fire Detectors

1) Products of Combustion

a) α-Ray Ionization. This type of a detector employs a radioactive α emitter (e.g., $Ra_2{}^{226}SO_4$, Am^{241} etc.) to ionize air in a chamber between two electronic plates. In the Pyrotronics 220 V d.c. detector, only 70–80 microcuries of Am^{241} is used.[18] Other manufacturers of the products of combustion type-detectors as well as other detectors are Fenwall, Fire Alert Co., Honeywell, Ionization Detector Corp., Statitrol, and BRK Electronics Corp.

Current in the picoamp range results from production and transport of positive and negative ions to opposite poles of the plates. A decrease in the current, relative to air, is obtained when combustion products enter the chamber because of their lower effective ionic mobility, and increased absorption and scattering of the α particles by the aerosol fraction of the gas. This decrease is monitored electronically leading to the triggering of an alarm. At high sensitivity settings, aerosols such as cigarette smoke, room deodorant sprays, and dust particles will trigger false alarms. Heat sensing thermocouples are recommended for use in conjunction with an ionization detector in order to circumvent this problem.[19] The ionization detector will also not function properly in regions where there is a high radiation background.[20] Nevertheless, it responds rapidly at an early stage to a fire, and is considered the most versatile detector.

Chaffee[6] examines in considerable detail the major differences in circuitry and electronic components for ionization detectors manufactured by five different corporations. These pertain to instrument sensitivity, detector or amplifier malfunctioning, balanced detection circuits between sealed and open ionization chamber (for devices that use double ionization chambers), voltage and current requirements. He mentions because of lack of proper schematics it was not possible to make many definite statements between the operational differences of the various detectors, and also that it was impossible to determine what electronic circuitry would best complement the ionization chamber. Based on his study, it appears that one type of an ionization detector is not significantly different from another make. One often finds that the advantages a different detector has over a competitive make resulted from a tradeoff in another detector characteristic, e.g., increased sensitivity to a lower threshold level of combustion product vs. an increase in the integrated time for detection. At this stage one can only use economic judgment in distinguishing between detector types. Detector cost, which should include the cost of accessory electronic equipment and installation if necessary, the nature or state of the company, and its service reputation should all be considered before a purchase is made.

b) Laser Beam. Research at the Boreham Wood Fire Research Station in England has led to the development of a laser beam fire detection system for extended area coverage.[21] It operates on the principle of deflection of the laser beam due to differences in the index of refraction of the combustion gases vs. air. Ambient fluctuations in temperature are discriminated against by tuning an

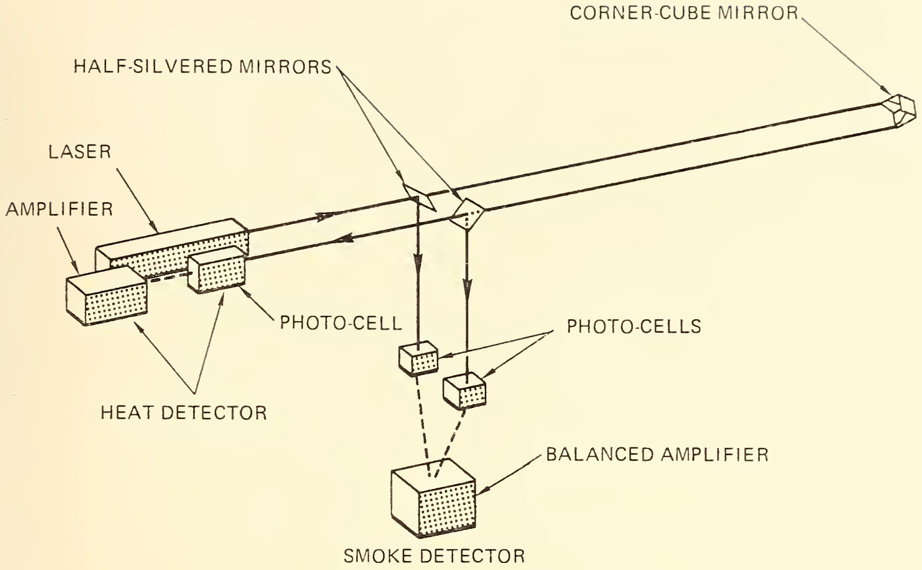

Fig. 2. System for heat and smoke detection [after Ref. 21].

amplifier to receive a frequency of 40–70 Hz. The system can be used to detect simultaneously heat and smoke (Fig. 2). The corner-cube mirror and a checkered mask for the photocell detector prevent slight changes in the reflected beam due to the mirror mounting and the laser itself, respectively, from triggering false alarms. The laser device offers tremendous potential for large room coverage, whereas, in small enclosures it probably will not be economically competitive with present devices nor more accurate.

2) Visible Smoke

The technique for determination of visible smoke relies on the principle of photometry based on Lambert's or Beer's law, or more commonly the Lambert-Beer law. Lambert's law directly relates the rate of decrease in radiant power of a monochromatic light beam with the path length of the absorbing medium to the radiant power of the beam. Beer's law states that the decrease in the radiant power is directly proportional to an increase in concentration of light absorbing species. Reflection, refraction, or diffraction of the beam are not considered in this treatment. Scattering because of some given particle-size distribution is likewise ignored. Experience has shown that provided one calibrates a photometric cell, the above complicating factors are adequately accounted for in the constant of proportionality in the Lambert–Beer law.

Basic requirements for such a fire detector are two: a light source (preferably monochromatic or nearly so) and a detector (photocell, phototube, etc.) to measure the radiant power of the light. Three different modes of operation presently used are based on the following:

a) the amount of light transmitted or absorbed by the medium
b) the amount of light reflected
c) the amount of light refracted.

In the light transmission or absorption case, a light source and detector are arranged in line at opposite extremes of the test area giving extended area coverage. When smoke crosses the beam path the radiant power reaching the detector is reduced which leads to a current reduction. This reduction can be monitored to sound an alarm at a predetermined value of light transmittance or absorbence, or perhaps more correctly in the specific optical density.[22]

Extended area coverage is also provided with the reflection technique, although in a slightly different manner. Both the light source and the detector are integrated into a single unit. A mirror (possibly a suitable arrangement of mirrors) located at some predetermined position, not necessarily on the light source axis, is used to reflect light back to the receiver.

Refraction devices contain the source and detector in a single unit but unlike the beam devices they are open to the atmosphere. Smoke particles must be present in the sensing chamber in order to refract the light beam so that it strikes the photocell. Extended area coverage is not provided with the refraction detector since the smoke contained in the sampling chamber represents a local property. Its response time is usually much slower than the other two types of photoelectric detectors.

The beam-type detectors are quite useful since they are preferred to the ionization-type in regions where there is a normal high ambient level of combustion gases or where the material protected is anticipated to produce dense heavy smoke.[23]

3) Light

Chemists, physicists, and other researchers have for some time used a number of devices to measure emission and absorption of radiant energy. The same basic devices are used in the ultraviolet, visible, and infrared portions of the spectrum with appropriate changes in the detectors and in the construction materials. The definitions of Ref. 24 will be used to summarize their operational principles:

a) Photometer. An instrument for measuring relative radiant power or some function of this quantity. The main components are a source of radiant energy, a filter to isolate a band of energy, an optical system for producing a parallel beam of filtered light for passage through an absorption cell, a detector for unabsorbed radiant energy and readout meters. The photometric principle was also used to detect smoke as previously outlined.

b) Spectrometer (Optical). An instrument with an entrance slit, a dispersing device, and one or more exit slits, with which measurements are made at selected wavelengths within the spectral range, or by scanning over the range.

c) Spectrophotometer. Gives the ratio, or function of the ratio, of the radiant power of two beams as a function of spectral wavelength. Separates the beams in time and/or space. Uses a prism or grating as a dispersing device.

Fire detectors which respond to ultraviolet radiation employ modifications of the same basic principles enumerated above. The Honeywell Model #C7037A designed to operate in the 1850 A–2500 Å region is insensitive to both sunlight and artificial light. Its cone of vision is 90°. The quoted sensitivity is a 1 sq ft flame from 15 ft. Since light intensity decreases with the square of the distance, proper positioning of the detector relative to the location of a potential fire is important. The sensing element is a gas filled, uv sensitive tube. At some threshold value of uv radiation, the gas is ionized and becomes conductive activating an alarm. Amplification is required with this device.

Fenwal's uv detector responds to uv radiation in the range 1900 Å to 2500 Å. It operates on the ionization principle similar to the Honeywell model. It has a 120° cone of vision. The response time given is 15 millisec for a propane air flame 1.75 in. high at a distance 8 in. from the flame source.

A solid-state Si C uv detector developed by Westinghouse Research produced a current proportional to intensity with a sharp peak response at 2900 Å. A 30 V power supply and transistor amplifier will drive a relay and solenoid valve.[25]

In other applications a molybdenum photocathode was used in a biplanar structure of quartz construction to produce amplification by electron multiplication in a H_2 gas discharge.[26]

Infrared detectors employ a system of optical and electronic filters which limits detection to a narrow signal wavelength of range 1–2.75 μm and frequency 4–15 Hz.[7] The Infrascan detector described in this reference has a scanning reflector which rotates at 6 rpm. When infrared radiation of the proper characteristic is reflected from it onto a sensitive cell for an uninterrupted period of 15 seconds, an alarm will sound. The radius of scan is up to 400 ft through 360° horizontally. Infrastat, a variation of Infrascan, does not employ a scanner. It is similar to a camera. A photocell is mounted inside a collimating tube protected by a quartz shield. By adjusting this tube, one can vary the angle of the cone of detection from 15° to 160°.

Both the uv and IR detectors respond rapidly to flash-type fires. One finds widespread use for these detectors in fuel storage areas and aircraft hangars.

4) Heat

Detectors responding to heat are of two general types; those employing the fixed temperature principle and those that employ the rate-of-rise principle.[3]

In the fixed temperature approach an ideal temperature level is first selected. When this is reached a temperature sensitive material will bend, expand rapidly, fuse or produce a current:

a) Bimetallic elements. Bend in such a manner as to close or open a pair of contact points with increasing or decreasing values of temperature, respectively.

b) Ampoule devices. Organic liquids that expand rapidly with temperature changes. Cause a surge in pressure which breaks a thin-walled glass ampoule.

c) Metallic devices. Certain types of eutectic solders and metals fuse or melt over a convenient temperature range. A recent description of a low-temperature thermal battery is given in Ref. 27. This device, made by pressing a piece of Li between two pieces of 60/40 Sn–Pb solder, is self-activating at around 200°C and is capable of supplying a pulse of electrical power greater than 40 watts. A high temperature device (300°F to 1000°F), for an airborne overheat hazard detection system, is given in Ref. 28. It consists of a metallic core with a glassy sheath and a thin coating of a second metal. The metals constitute the anode and cathode of the couple with the glassy sheath serving as the electrolyte.

d) Thermocouples, thermistors, and certain types of photodetector devices (see page 107) all produce a current output in response to heat.

One major disadvantage of a fixed temperature device is that the detector unit must be completely heated to the operating temperature. Low cost is the primary advantage of these devices. The response times are relatively slow for all but the thermocouples. Response times for commercial fire detector thermocouples are around a few tenths of a second. In Ref. 29 a response time as low as 50 micro-

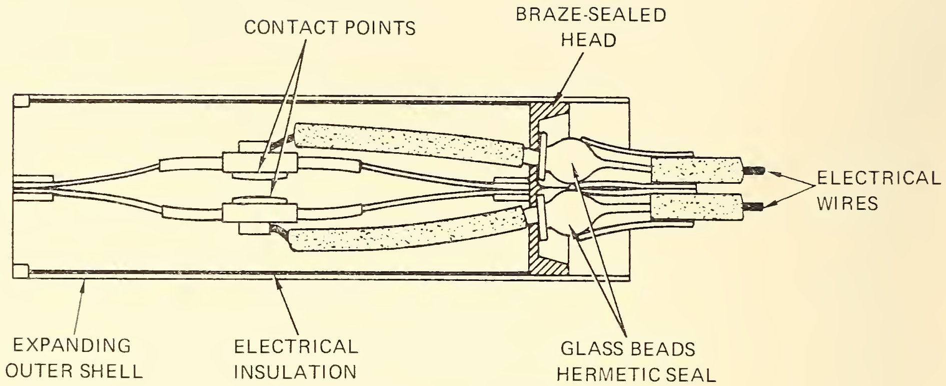

Fig. 3. Rate-compensated fire detector [after Fenwal Inc.].

seconds was obtained in liquids. This would work out roughly to 0.05 sec in a gas if one allows for a thousandfold difference in thermal conductivity.

Rate-of-rise detectors are designed to respond to changes in temperature at a rate of around 15°F/min. They are fairly reliable and will not alarm for slow increases in ambient temperature. They are not suitable for smoldering-type fires and also where rapid temperature changes are natural occurrences. Two fairly common rate-of-rise detectors are the pneumatic tube detector and an orifice-type detector. In the former device, a pressure buildup in a detector diaphragm chamber is used to close a set of contact points at some predetermined value of pressure.[3,30] The latter device relies upon pressure increases resulting from differences in flow rates of an expanding gas passing through an orifice.[6] Here sensitivity is directly related to orifice size. Hence, very small orifices which are prone to clogging are primarily limited to dust free laboratory environments.

A rate-compensated device (Fig. 3) manufactured by the Fenwal Corp. combines the fixed temperature principle with the rate of rise.[31] The key requirements are materials of different coefficients of expansion. For very low rates of rise both materials line up evenly and the device operates as a fixed temperature device. For rapid rates of rise the materials no longer expand evenly which leads to an alarm even though the fixed temperature is not reached.

*Non-Conventional Fire Detectors**

In this section several different types of detectors used in other fields that have potential use as fire detectors in either a hybrid setup (without modification) or following appropriate modifications are outlined.

1) Products of Combustion

a) β-Ray Ionization. Uses a β-ray source (e.g., Sr^{90}) to ionize the gas. Because an α particle produces around 10^3 times more ions than a β particle over the range of ionization chamber voltages (roughly 50 to 250 volts)[32] a β-ray detector would have to be operated as a proportional-type counter at a much higher voltage, around 550 volts, to produce equal ion currents. This high voltage is undesirable.

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* In the research or development stage and/or not used in the fire detection field.

Possibly a β source in the millicurie range could provide sufficient ionization to reduce the required voltage. Because of the low cost of β-ray material relative to the very high cost of α material, the development of a β-ray fire detector may prove advantageous.

b) Argon Detector. Operates on the principle of ionization of foreign molecules by collision with high energy Ar atoms leading to high concentrations of metastable Ar* of long half life (10^{-4} sec.).[33]

$$Ar+\beta \xrightarrow{-15.7\text{ev}} Ar^{+}+e$$

$$Ar^{+}+e \xrightarrow{11.6\text{ev}} Ar^{*} \qquad \text{Background}$$

$$Ar^{*}+\text{Impurities} \rightarrow Ar+M^{+}+e$$

$$Ar^{*}+\text{Combustion Gas} \rightarrow Ar+M^{+}+e+\text{Signal}$$

Either β or α radiation in the 10 to 50 millicurie range placed in an electronic chamber will provide background currents of 0 (10^{-9}–10^{-8}) amps.

Most organic compounds will be detected because their ionization potentials are in the range 9 to 11 ev; however, two important flame gases CO (Zone B) and CO_2 (Zone A) which have ionization potentials of 14.1 and 14.4 ev respectively, will not be detected. The argon detector is best suited for very small concentrations of gases. It is relatively insensitive to changes in detector body temperature.

This device could possibly be used to detect combustible organic vapors. It would complement the ionization detector because of the latter's inability to detect organic vapors.[6] Used jointly, the ionization detector could be set at high sensitivity and its output signal would be an input to the Ar detector to sample the gas. If the argon detector responded according to some predetermined level, one would have a double check on the presence of a fire. The occurrence of false alarms could be minimized with this hybrid setup.

c) Flame Ionization. A hydrogen-oxygen (or air) flame which makes up one of the electrodes, is used to induce electron emission in various types of organic and inorganic molecules having low work functions. Electrodes under imposed voltages are used to collect the resulting ions. High sensitivity, reasonable stability, moderate flow insensitivity, and linearity over a wide range are the highlights of this device.[33]

Because a continuous flow of H_2 is required to operate as a fire detector, this device is limited to a hybrid system similar to the Ar detector.

d) Thermal Conductivity. A set of heated matched metal filaments or thermistors is used to follow changes in thermal conductivity. A pure carrier gas is passed over a reference junction while the carrier gas plus a mixture eluted from a suitable column passes through the detector element. In the differential-type setup, the resistance of the detector element changes relative to the fixed junction, and is a measure of the concentration of the component in the gas stream.

It appears that with some modifications of this technique the device could function as a fire detector. With air in a thin-walled, sealed reference compartment (of high thermal conductivity metal) and with the detector element open to the atmosphere, differences in composition and temperature will lead to bridge imbalance. One could also fabricate the two compartments out of different pore-size electromesh screens. Variations in the mass throughput leading to thermal conductivity imbalances and/or in temperature in the two compartments will lead to bridge imbalance.

If the proposed device operates there are many unanswered questions pertaining to response time, the need of a separation column, etc. The latter does not appear to be necessary since we are not interested in resolving the various combustion products. Actually, some degree of separation will probably be obtained if fine electromesh screens are used. Study in this area appears warranted because this device could respond simultaneously to composition and temperature changes.

e) Catalytic Devices. Used primarily for CO detection. In the MSA-Model C portable CO detector, beds of active and inactive hopcalite surround two thermistors in a Wheatstone bridge circuit.[34] An exothermic reaction of CO to CO_2 leads to bridge imbalance and causes a proportional "upscale" meter reading thereby giving the CO concentration.

This device can be hooked up to an alarm system. Catalyst life limits its use to a toxic gas detector since ambient CO levels are fairly high during certain periods. High humidity will shorten life, and tobacco smoke will seriously impair the accuracy of this instrument.

If one develops a catalyst that could produce a physical change similar to the hopcalite material in the presence of small amounts of Zone A constituents, e.g., acetic acid, then catalyst life will not be a serious drawback since this constituent is generally not present in the atmosphere. Research would be needed to explore the feasibility of this approach.

f) Fuel Cell Devices. The operation of a fuel cell may be analogized to an electrochemical cell in that conventional fuels react at the anode while O_2 or air reacts at the cathode. The electrodes, which are usually sintered porous metals, serve as reaction sites where electrons are transferred to an external circuit. The electrodes are considered inert since they do not undergo the mass transfer exchange accompanying oxidation and reduction as in a typical electrochemical cell. The fuels most often used are hydrogen, hydrocarbons, and hydrazine.

Carbon monoxide fuel cells are unimportant in the fuel cell field. They appear to be of potential use in the fire detection area. For example, mixed electrocatalysts (e.g., $Pt{-}WO_2$) consume appreciable amounts of CO along with H_2, and alloy electrocatalysts promote selective anodic oxidation of hydrogen. An application of this principle would seem to offer promise for combustion gases. With a liquid electrolyte $5N$ H_2SO_2 and special CO sensitive electrodes appreciable voltage changes occur for small variations of % CO.[35] From a best estimate of the graphical results, an increase in CO concentration from just 1% to 3% leads to a voltage increase from 13.75 mv up to 23.8 mv. Changes of this magnitude could easily be monitored and circuitry designed to trigger an alarm. Again, a research program would be needed to explore the feasilility of adapting this procedure to the fire detector area.

2) Heat

A low-cost extended-area fire detector (similar to the gas filled device of Ref. 30) in which the sensitive element is a low-boiling liquid in a plastic tube has recently been proposed by Fristrom.[36] The movement of fluid due to volatilization at the boiling point of the liquid can be used to activate a switch or other device. Besides low cost and sensitivity at any point along its length, this device has a few more very attractive features:

a) It can be made in various colors so it can be installed inconspicuously on walls or ceilings; likewise, inside conduits or walls where fire hazards are high.

b) A grid of sensors in an X Y pattern could be used to determine the location and the extent of the fire.

c) Multiplexing to increase system reliability appears economically feasible.

Again, a study program is needed to examine this device.

A heat-sensing transmission line has been proposed by Lawson[37] as a possible method of protecting automatic warehouses from fire. It operates on the principle that an electrical pulse traveling down the line must sense a discontinuity in the characteristic impedance of the line due to the fire. The line requires characteristics which change rapidly with temperature in order to minimize response time. Experimental results are needed on the parameters associated with fire-damaged transmission lines before this device can be put into operation.

3) Sound. In Ref. 5 an ultrasonic standing wave detector is described. An ultrasonic emitter and detector set up and monitor changes in a standing wave pattern in an enclosure. When the amount of distortion produced by changes in the index of refraction due to convection currents exceeds some predetermined amount an alarm can be made to sound. This technique appears to have application in large area enclosures. Fire detectors based on this principle do not appear to be on the commercial market.

Photodetector Devices

Recent advances in semiconductor technology have increased the applicability of photodetectors. One area in which they will find increased use is in the fire detector field. A special survey article in the EEE Magazine[38] divides photodetectors into four different types—photoemissive, photovoltaic, photoconductive junction type, and photoconductive bulk effect. A summary of the operational principles and other pertinent highlights of these devices is given in Table 1.

Different photodetector devices are presently used in the uv and IR detectors and also as photocells in other detector types. Of particular interest in the fire detector field are the photovoltaic devices, which presently require some degree of amplification. One might expect future devices to respond to fires in a similar way to the RCA light sensitive monolithic IC on p. 21, Ref. 38. This device is capable of driving a lamp or relay without further amplification.

Detector Experiments

Experimental programs conducted to determine the response time of detectors to various types of fires under simulated realistic living conditions are apparently limited to the extensive test program carried out by the Los Angeles Fire Department in Operation School Burning No. 2, the recent Bloomington, Minnesota, Fire Department study[39] and other commercial test results. Other tests with very specific objectives are the laboratory tests of Chaffee, the infrared response times to flash fires described by Waters,[7] the effect of high radiation backgrounds on ionization detectors,[20] the hypobaric and hyperbaric test program under Alger,[40] the hyperbaric tests of Eggleston,[41] and the AEC sponsored tests conducted by Fenwal at du Pont's Savannah River Laboratory.[42] In a different but yet related area, the Joint Fire Research Organization examined the frequency of false alarms from automatic fire detection systems.[43]

TABLE 1

Characteristics of Different Photodetector Devices

Photoemissive—are vacuum tubes in which light impinges on a metal cathode, releasing one electron per photon of light. Photomultiplier plates are often contained in the same tube envelope. Standard for sensitivity comparison. Has poor long-term stability and high quiescent power consumption, needs high voltage power supplies, and has poor shock and vibration resistance characteristics.

Photovoltaic—absorbs light and produces an output voltage; does not need an external power supply. Most common materials are Si and Se. Se exhibits good response in the uv and is inexpensive, however, it exhibits hysteresis to light. Si photodetectors show promise in replacing Se as cost declines. Does not exhibit serious hysteresis and has microsecond response times.

The Si solar cell optimized for resistance to nuclear radiation (N junction on top), exhibits poor response in the uv, a broad band response in the visible, and a peak in the near infrared. Si photocells with enhanced blue response are now available.

Photoconductive junction type (sometimes called photosensitive)—Conductivity changes as the device absorbs light. Reverse biasing of photovoltaic junction photocells leads to operation in the photoconductive mode. Si is again the most popular material for junction photoconductive cells. For reverse biasing PIN processing is preferred to the conventional PN junction. PIN photodiodes operated with reverse bias can have response times as fast as one nanosecond. Light history effects are absent in PIN cells in either the photovoltaic or photoconductive modes.

Bulk-effect photoconductive cells—behave like resistors whose resistance decreases nonlinearly with an increase in light intensity. The usual materials are Cd and CdSe. Usually have sharp-peaked spectral responses unless they are specially compensated. Require a low voltage power supply. Major disadvantages are slow response and light hysteresis.

In the Los Angeles study, 47 different types of simulated school fires were carried out to investigate the operation of available detector types (excluding the uv and ir). It was agreed upon among industry representatives that any particular manufacturer's detector in a given generic class is representative of that class. A large percentage of the tests involved wood cribs—2′×2′×2′ of white fir, average weight of 75 lbs (approximately a 45,000 Btu/min heat release rate) and average moisture content of 18%, and much larger 340 lb cribs. Slow, medium, and fast fires were arrived at by placing combustibles beneath the crib; for example, 3 rolls of newspaper distinguish the fast type from the slow. The remaining fires were chosen to be typical of schools, e.g., wastepaper basket fires, closet fires, etc. Outdoor temperature, humidity, and wind velocity ranged between 71°–89°F, 37%–56% (for most tests, around 50%), and 4.8–6.2 mph, respectively.

The important results of this study and the discussion thereof will be limited to the two leading detectors. A summary of the highlights is as follows:

a) The ionization and photoelectric beam detectors had much faster response times than the other detectors. The response times ranged from around 7 sec to 5 min for the ionization and 1 sec to 6 min for the photoelectric detectors.

b) In many cases, particularly where the fire source was displaced roughly greater than 15 ft, the response of the beam-type detector was twice as fast as that of the ionization detector. The opposite was true for close distances from the fire source, roughly less than 10 ft, or when the fire source was outside of the primary detection zone of the light beam.

c) Increased ceiling height resulted in considerably slower response times for all detectors.

Based on these test results it is difficult for this reviewer to concur with the popular belief that the ionization detector is much better than the beam-type detector. As far as improving response times, it appears easier to do so with the beam detector than with the ionization detector. For example, the addition of a suitable mirror system could give complete room coverage to the beam detector, thus, easily offsetting any serious inadequacies. It would be difficult or impossible to do so with the ionization detector (excluding an increase in its sensitivity setting which would lead to false alarms) because it is a point source detector. A change in room conditions, such as decreasing the temperature below the 71°–89°F range would lead to an increase in the fire plume velocity and faster response times for the ionization detector (the response time of the beam detector would also be expected to increase, but not as much). The effect of increases in humidity is not well known. Because of the limited range of humidity and temperature and the use of a fairly rapid ignition source, these results are not strictly applicable in all parts of the country and also not to slow burning or smoldering types of fires. Nevertheless, these results are the present standards for comparison.

In the Bloomington study, five different types of simulated fires were conducted in a test dwelling typical of houses in that city—30 ft long by 30 ft wide, consisting of a first floor, an attic (with one bedroom), and a basement. Ionization, photoelectric smoke detectors (believed to be the refractive type) set at 0.7% obscuration, fixed temperature, and combination rate-of-rise and fixed temperature detectors were examined. Response times varied considerably for all detectors depending on their location with respect to the fire. Generalizing, the time responses for the ionization and photoelectric detectors were of the order of minutes or less (in the simulated grease fire the ionization detector responded immediately), while for the thermal devices of order 10 minutes. The overall results are in agreement with the Los Angeles study.

Chaffee examined the response times of three different detector types (Honeywell TC 14A ionization, BRK balanced bridge (a form of a combustion products sensor), and Sears (photoelectric) in a lab-sized test funnel. The test funnel is a cylinder ($17\frac{1}{2}$ in. high × 8 in. in diameter) containing essentially a side arm and two flow dampers. Here the ionization detector was far superior to the balanced bridge on an overall basis. The photoelectric detector had exceedingly poor response times in comparison with the other two types. These results show, first, that the ionization detector responds at an earlier stage to a fire than the other two types and, second, that the time scale for buoyant convection and spreading in an enclosure of small height and diameter is very short. The latter conclusion is readily seen by comparison of Chaffee's response times to the full-scale test times. In other words, detector response times obtained from studies in small enclosures are not very meaningful in large-sized rooms. This is the scaling problem mentioned previously. Other tests on unheated combustion gases and combustible vapors showed very poor or no response at all for all the detectors.

The tabulated results for the infrared detectors showed excellent response times (16 sec to 46.6 sec) to flash-type fires over distances ranging from 50 to 500 ft for several different amounts and types of fuels.[7]

The conclusions of the Los Alamos Meson Physics Facility (LAMPF) tests were that the ionization-type combustion product detector will not work in a radiation environment.[20] Also, due to ozone generation by the radiation flux, ionization detectors are likely to alarm immediately after beam turnoff.

The test program under Alger showed a number of interesting points. First, the burning of cellulose, tygon, neoprene rubber, and styrofoam in air at pressures from 50 to 150 psi, led to band reduction (particularly around 3000Å), and to an intensification of the longer wavelengths in the visible region of the spectrum. Second, the flame flicker frequency was observed to increase almost linearly with pressure for all four fuels. Time response tests on uv detectors at 150 psi showed that the detector either did not respond to certain fuels (Fenwal), or that the increased time of alarming was such that the reliability of the detector was reduced substantially (Edison).

Eggleston noted that the IR and combustion-products detectors functioned successfully and reliably following detector modifications.

In the Fenwal tests, glove box fires and explosions were studied to prevent the propagation of fires into exhaust ducts. Their detector results are summarized as follows:

a) Thermal detectors are more reliable and suitable for remote locations where maintenance and testing is difficult or not feasible.
b) Smoke detectors respond similarly to thermal detectors, but are significantly slower with solvent fires, especially of low molecular-weight alcohols.
c) Light detectors respond faster to fires, but require more maintenance and are more prone to false alarms.
d) Ionization detectors lose sensitivity in a high radiation field (this is in agreement with results of Ref. 20).

The JFRO results given in Table 2 show surprisingly high false-alarm ratios. Based on an estimated 15,000 sprinkler systems in use, this was broken down to mean that there would be only one false call from each system every three years. Although this may be acceptable to those relying on an automatic detection, it is unacceptable to the Fire Service. Projected estimates for the year 1977 show that these statistics will lead to around 125,000 false alarms a year. This will impose

TABLE 2

Summary of calls received

Type of system	Number of fire calls by system installed	Number of false calls	Ratio of false calls: fire calls
All types	489	5441	11.1:1
Heat	193	2146	11.1:1
Smoke	101	1429	14.1:1
Heat and smoke	18	410	22.8:1
Sprinkler	101	1048	10.4:1
Manual	55	243	4.4:1
Mixed	18	137	7.6:1
Unspecified	3	27	9.0:1

Note: the total number of false calls includes one false call from gas detector equipment.

TABLE 3

Reasons for false calls

Reason for false calls	Totals (all types of equipment) Number	Totals (all types of equipment) Per cent
Total (all reasons)	5441	100
Ambient conditions	1410	26
Mechanical and electrical	2507	46
Communication	901	17
Unspecified and unknown	623	11

an enormous burden on the Fire Service unless some or most of the reasons for the false alarms (Table 3) are resolved. Statistical data based on a similar type of study for the U. S. or other countries are apparently not available.

Conclusions

The important conclusions of this study may be summarized as follows:

a) A standardized or interrelated test procedure, is needed whereby one can rate the various detector types according to response time and frequency of false alarming. The problem is complicated by the operational differences in the detectors and the numerous types of fires.
b) There is need for an increased research and development effort on fire detectors.
c) In assessing or comparing detector response times the complete fire environment must be considered. Small-scale laboratory tests are not representative of actual room-size tests. If laboratory test results are to be used, then at least the dependence of fire plume velocity and spreading on height should be known.
d) There is no universally applicable fire detector, i.e., one which responds uniformly and accurately to all types of fires.

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ABSTRACTS AND REVIEWS

A. Prevention of Fires and Fire Safety Measures

Fittes, D. W., Griffiths, D. J., and Nash, P. (Joint Fire Research Organization, Boreham Wood, England) "The Use of Light Water for Major Aircraft Fires," *Fire Technology* **5,** 284 (1969)

Section: A
Subjects: Aircraft fires; Extinguishing agents; Light Water

Abstract by *Editor of Fire Technology.* Reprinted by permission

In comparison with regular protein foam, Light Water foam was generally up to twice as effective in controlling major aircraft fires, i.e., it required about half the weight of fire-fighting solution to control the same fire, when both agents were applied at their most economic rate. Similarly, a fortified protein based foam was about 25 percent more effective than regular protein foam.

Light Water was, in general, found to be proportionately more effective than protein foam in achieving a rapid initial reduction of heat radiation from the fire, although there were notably exceptions to this, possibly due to defective exploitation of its potential.

The resistance of Light Water to the re-establishment of the fire, once a sizeable area of flame has been reopened, was only about one-third that of protein based foams. This could be of importance where backup equipment is not available, e.g., far from fire-fighting base facilities.

Gerhards, C. G. (Forest Products Laboratory, U. S. Forest Service, Madison, Wisconsin) "Effect of Fire-Retardant Treatment on Bending Strength of Wood," *U. S. Forest Service Research Paper FPL-145* (December 1970)

Section: A
Subjects: Bending strength of wood; Fire-retardant effects

Author's Summary

Since fire-retardant-treated wood is gaining more acceptance year by year, it is desirable that its strength properties be known, particularly for structural applications. This paper summarizes the results of several studies conducted at the Forest

Products Laboratory and elsewhere on the bending properties of air-dried and kiln-dried fire-retardant-treated wood. Collectively the studies indicate that modulus of rupture and work to maximum load in bending were reduced by varying amounts depending on species and type of fire retardant. In general, the reductions are consistent with the 10 percent reduction in design stresses recommended for fire-retardant-treated lumber.

Hafer, C. A. and Yuill, C. H. (Southwest Research Institute, San Antonio, Texas) "Characterization of Bedding and Upholstery Fires," *Final Report under Contract No. CST-792-5-69 for National Bureau of Standards* (March 31, 1970)

Sections: A, K
Subjects: Fire hazards, bedding, upholstery, toxicity, smoke

Authors' Summary

Many accidental deaths are attributed to fires started from smoking in bed or in upholstered chairs. Frequently, the victims die as a result of exposure to smoke, heat, or noxious fumes that develop as materials burn rather than from skin burns. The objective of this program was to conduct full-scale tests using bedding and upholstered furniture to determine the life hazards that may be present during fires starting with a small ignition source.

Thirty individual tests were conducted using various combinations of materials. The ease of ignition of bedding and upholstery was demonstrated and the pattern of development of smoke, heat, noxious gases, and oxygen depletion was recorded.

Lawson, D. I. (Joint Fire Research Organization, Boreham Wood, England) "Intumescent Matrices as Fire Resistant Partitions," *Joint Fire Research Organization Fire Research Note No. 859* (February 1971)

Sections: A, E
Subjects: Fire-resistant partitions; Intumescent paint

Author's Summary

The application of intumescent paint to honeycombs provides a lightweight fire resisting partition which may be made of paper and board. The painted honeycomb itself has the property of being perforate under normal conditions and will close once a fire occurs. It may therefore have application in ventilation ducts to stop the spread of fire and for suspended ceilings to prevent fire attacking lighting fitments and services.

Martin, S. B. (Stanford Research Institute, Menlo Park, California) "Civil Defense Test Design and Support of Operation FLAMBEAU-Type Fires," *Annual Report, August 1969–August 1970, under Contract No. DAHC20-70-C-0219 for Office of Civil Defense* (August 1970)

Sections: A, L
Subjects: Fire-data reduction; Test design

Author's Summary

This report describes annual progress in a continuing program to review and appraise potential opportunities for mass-fire tests and other sources of field-test data relevant to the civil defense fire problem and to provide objective and technically sound advice in such matters as required by the Support Systems Division of OCD, Research.

Progress for the year is summarized in the following subject-area categories:

1. Review of reports on FLAMBEAU-type fires
2. Investigation of new sources of data
3. Conduct Annual OCD Fire Research Contractors Conference
4. Participation in the writing of a Handbook on Forest Thermal Effects.

Plans for the coming year are also presented.

Ramsay, H. T., Hinsley, R. S., and Waterhouse, D. (Safety in Mines Research Establishment, Sheffield, England) "The Design and Development of a Triggered Barrier System at SMRE," *The Mining Engineer* (March 1971)

Section: A
Subject: Explosion protection systems

Authors' Summary

Stone-dust and water barriers of the tipping type have been studied for some time in the SMRE large explosion gallery, and stone-dust barriers are used in all

British mines. However, this type of barrier has some practical limitations which appear to be absent from the triggered barrier systems. In a triggered barrier the functions of detecting the explosion and of suppressing it are separated. The explosion is detected by one or more "sensors" (usually flame sensors); the suppressing mechanism is usually a dust disperser. This arrangement allows some choice, for example, the timing, duration, and mode of dispersion of the suppressant material. The paper describes a triggered barrier system which consists of a thermocouple flame sensor and a compressed gas-powered water disperser. A complete mine prototype is under construction.

Syska, A. D. (Forest Products Laboratory, Madison, Wisconsin) "Fire-Retardant Treatment of Particleboard," *U. S. Forest Service Research Note FPL-0201* (August 1969)

Section: A
Subjects: Fire-retardant treatment of particleboard; Materials testing

Author's Summary

Douglas-fir and aspen flake-type particleboards made with combinations of common fire-retardant chemicals applied in several ways are evaluated for flammability and mechanical strength and dimensional stability.

National Bureau of Standards (Washington, D. C.) "The Flammable Fabrics Program, 1968–1969," *U. S. Department of Commerce Report of Activities under the Flammable Fabrics Act, 1968–1969; National Bureau of Standards Technical Note 525* (April 1970)

Section: A
Subjects: Education and training; Fireproofing methods; Flammability of materials; Test methods

Author's Summary

This report describes the work carried out during 1968 and 1969, by the Department of Commerce to fulfill the responsibilities delegated to that Department under Section 14(b) of the Flammable Fabrics Act as amended (81 Stat. 568) December 14, 1967. This section of the Act states:

"Sec. 14(b) In cooperation with appropriate public and private agencies, the Secretary of Commerce is authorized to—

(1) Conduct research into the flammability of products, fabrics, and materials;
(2) conduct feasibility studies on reduction of flammability of products, fabrics, and materials;
(3) develop flammability test methods and testing devices; and
(4) offer appropriate training in the use of flammability test methods and testing devices.

The Secretary shall annually report the results of these activities to the Congress."

This report describes the activities carried out under the above responsibilities and in addition describes cooperation with public and private agencies.

1. *Under Research into the Flammability of Products, Fabrics, and Materials, Sec. 14(b)(1)*, work is described on seven projects being carried out in-house, and on three projects carried out under contract with outside research organizations.

In-house research is being carried out on the following items:

1.1 *Products of combustion*—This project is to learn the amounts and nature of combustion products (some of which are toxic) to be expected from fabrics during normal burning. The study is directed primarily at interior furnishings. Fires from such furnishings often are dangerous because of the toxic products produced.

1.2 *Calorimetry*—The amount of heat released from a burning fabric, and the rate at which it is released are basic in determining the hazard from the fabric. It is important to know these quantities when designing new and meaningful standards. In addition, these quantities are important to the nature of the flammability of fabrics.

1.3 *Full Scale Garment Burning*—This research effort is an attempt to reproduce in the laboratory what happens in actual accidents. Measurements of such quantities as ease of ignition, heat transferred to the body, and the temperatures developed, with various garment configurations and with various materials, are important in determining the hazards from apparel fabrics. This information is necessary to develop meaningful test methods and reasonable and appropriate standards.

1.4 *Analysis of Burn Case Data*—A significant effort has been devoted to the analysis of burn case data supplied to NBS by the Department of Health, Education, and Welfare, as well as to the testing of garments recovered by that Department from some of the cases investigated. This analysis has been used to substantiate in part a finding of probable need for a new standard for apparel published on October 23, 1968. A finding of probable need for certain items of children's apparel, published on January 24, 1970, (shortly after the close of the reporting period) was also based on the analysis. In addition, the results of tests on the recovered garments, and the relationships of these results to the accident cases have yielded important information about what constitutes meaningful apparel standards.

1.5 *Analysis of Data from Outside Laboratories*—Data on the testing of carpets and rugs using the present Federal purchase specification DDD-C-95 were provided to NBS by Consumers Union, an organization located in Mount Vernon, New York, specializing in the testing of consumer products. After analysis, these data were used to substantiate in part a finding of probable need for standards for carpets and rugs published December 3, 1968.

1.6 *Investigation of the Mechanism of Flame Retardants*—One of the most important means of reducing the flammability of fabrics is by the addition of flame retardants. These are presently available for cellulosic fabrics, but are useful only for certain types and constructions. This effort is to understand the means by which the flammability is reduced.

Contract Research was carried out in the following three areas:

1.7 *Characterization of Actual Hazards from Interior Furnishings Fires*—Full-scale assemblies of beds were burned in a normal sized room, and temperature increase, smoke, and toxic gas concentrations were measured. These were related to the bedding materials and the means of ignition. Similar studies were carried out with upholstered chairs. The work was carried out by the Southwest Research Institute in San Antonio, Texas.

1.8 *Heat Transfer from Burning Fabrics*—Heat transferred from a burning fabric to the body, and the rate at which it is transferred are what ultimately cause injury in apparel fires. To determine the important factors in determining this heat transfer, a contract was funded at the Cornell Aeronautical Laboratory in Buffalo, New York.

1.9 *Sampling Plan and Model Questionnaire*—Data on burn statistics are important in assessing unreasonable risk. A project to develop a system to obtain such data was funded under contract with the Denver Research Institute of the University of Denver, in Denver, Colorado. This is expected to be completed in early 1970.

2. The activities carried out under *Feasibility Studies, Sec. 14(b)(2)*, were all carried out in-house. These are grouped under the following headings:

2.1 *Pyrolysis Products*—A study of the pyrolysis products is a way of determining the manner in which flame-retardants act, and thus of improving present flame-retardant treatments, and aiding in the development of new flame retardants. This project was begun late in 1969.

2.2 *Industry and Other Government Developments*—Considerable effort has gone into keeping abreast of outside efforts in this area, for these efforts are important in determining what standards are reasonable.

2.3 *Evaluation of Durability of Existing Treatments*—Considerable effort has gone into the evaluation of the durability to laundering and drying existing treated fabrics. Some treatments were found to be quite durable.

3. The activities carried out in *Test Method Development, Sec. 14(b)(3)*, were all carried out in-house. These activities were as follows:

3.1 *Development of a Standard for Carpets and Rugs*—A test method and standard based on the Federal purchase specification DDD-C-95 was developed and published as a proposed standard on December 18, 1969. Comments on this standard were being received at the end of 1969.

3.2 *Revision of Apparatus in CS 191–53*—The present mandatory standard for flammable fabrics has several technical deficiencies. Foremost among these are the inability to distinguish between time to ignition and rate of burning. To correct this, an ignition test and a rate of burn test were developed.

3.3 *Vertical Test Method*—The vertical test is the most stringent of those in present use, and is used for those special circumstances when maximum protection is required and other considerations are secondary. Considerable work was done with this test method.

3.4 *Tests on Bed Materials*—A program was begun during 1969, to develop methods for testing the flammability of bed materials. Mattresses are receiving considerable attention, using cigarettes as a source of ignition.

3.5 *Heat Release Test*—No present test method measures the heat released by a burning fabric, despite the importance of this quantity in determining the hazard from the fabric. Work was begun in 1969, to develop a test for measurement of heat released during burning.

4. Activities under *Training, Sec. 14(b)(4)*, were carried out in these ways:

4.1 *Research Associates*—The Research Associate program of NBS is a direct means of providing training. One Research Associate (from Consumers Union) was on board during part of the reporting period, and discussions for others were held with various interested organizations.

4.2 *Bibliographies and Information Center*—Three bibliographies, quoting pertinent literature references in the areas of Wearing Apparel, Fabrics Used on Beds, and Carpets and Rugs were completed during 1969, and were scheduled to be published early in 1970. Other bibliographies are scheduled for preparation, and an information center for flammable fabrics has been set up at NBS.

In addition to the above, there have been numerous formal and informal contacts with outside organizations and individuals, either by talks given by Department of Commerce personnel or visits by interested parties.

B. Ignition of Fires

Hillstrom, W. W. (U. S. Army Ballistic Research Laboratories, Aberdeen Proving Ground, Aberdeen, Maryland) "Ignition and Combustion of Unconfined Liquid Fuel on Water," *Ballistic Research Laboratories Memorandum Report No. 2076* (November 1970)

Section: B
Subject: Ignition of liquid fuel on water

Author's Summary

Burning of unconfined oil layers on water is an area from which techniques could be developed to improve flame weapons or to remove accidental oil spills. A method is presented by which most petroleum-based liquids can be burned to completion when spilled onto water.

Activated charcoal was shown to promote ignition and continued burning of lenses of high flash point fuels on water. The charcoal-fuel lens held its original shape during burning. The residue in most cases was a dry powder cake which could be easily collected and reused. Several model compounds and fuels were burned in laboratory experiments using this method. Large-scale field tests have not been carried out, but there are not any foreseeable problems in application of the method to burn off large oil spills in remote locations. The residue remaining after burning may be left to the elements to eventually sink to the sea bottom, or it may be collected for reuse.

C. Detection of Fires

Kerlin, D. J. and McDaniel, D. E. (U. S. Coast Guard Shipboard Fire and Safety Testing Facility, Mobile, Alabama) "Machinery-Space Fire Detecting Tests, Phase I," *Report of U. S. Coast Guard Office of Research and Development* (August 19, 1970)

Sections: C, N
Subjects: Detection of shipboard fires; Detectors; Fires

Authors' Summary

A series of small-scale fire tests were undertaken at the U. S. Coast Guard sponsored Shipboard Fire and Safety Testing Facility, Mobile, Alabama. These tests were intended to measure the response time of various types of fire detecting devices, at various locations in the machinery space of the test ship, RHODE ISLAND. Seventy-three individual devices, of nine different types were installed. The fire locations and ventilation conditions were varied to indicate differences in response time due to these factors. Because of limited instrumentation capability it was necessary to define the general area in which the fire would originate. The tests demonstrate the importance of environmental conditions on placement of various types of detection devices and indicate, from a detection capability standpoint only, that several types of devices may give satisfactory indication of a small machinery space fire. Some information on detector placement is developed.

D. Propagation of Fires

Cochran, T. H., Petrash, D. A., Andracchio, C. R., and Sotos, R. G. (Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio) "Burning of Teflon-Insulated Wires in Supercritical Oxygen at Normal and Zero Gravities," *National Aeronautics and Space Administration Technical Memorandum NASA TM X-2174* (February 1971)

Section: D, I
Subjects: Combustion of Teflon-insulated wires; Supercritical oxygen; Zero gravity

Authors' Summary

An experimental program was conducted to investigate the burning characteristics of Teflon-insulated nickel wires in supercritical oxygen in normal and zero gravities. The zero-gravity environment was obtained in a drop tower which made available 5 seconds of test time. The results indicate that the Teflon burned in both normal and zero gravities. However, the flame propagation rate in zero gravity was smaller than in normal gravity.

Vodvarka, F. J. (IIT Research Institute, Chicago, Illinois) "Full-Scale Burns in Urban Areas. Part I. Fire Spread between Structures," *Final Report, April 1968–June 1969, under Contract No. N00228-68-C-2368 for Office of Civil Defense* (June 1969)

Sections: D, F, I
Subjects: Blast damage; Burning tests of structures; Firebrands; Heat flux

Author's Summary

Four residential structures were free-burned and measurements made of time-dependent radiant heat fluxes, CO and CO_2 gas concentrations in the basements, the flame areas of the burning structures, and the firebrands produced by the fire. The first two buildings were blasted to simulate damage from an overpressure of 1 to 1.5 psi. The blast damaged structures burned in one-third to one-half the time of undamaged structures and produced larger relative flame areas. Gas compositions were found to be extremely sensitive to location. Firebrand production varied from fire to fire.

Laboratory experiments were performed with tungsten-lamp radiation source programmed to duplicate the time variation of radiant energy emitted by the burning buildings. The results indicated that a muslin sheet over a mattress exposed to the irradiance of one fire would have ignited spontaneously if within 37 ft of the burning structure. The corresponding distance for folded newsprint was 29 ft, and for muslin sheet alone was 13.5 ft.

Woods, F. J. and Johnson, J. E. (Naval Research Laboratory, Washington, D. C.) "Flammability in Unusual Atmospheres. Part 2. Selected Materials in Oxygen-Nitrogen and Oxygen-Helium Mixtures at Pressures up to 315 psia," *Naval Research Laboratory Report 6606* (September 22, 1967)*
Section: D
Subjects: Controlled atmospheres; Flammability of fabrics; Hyperbaric atmospheres; Oxygen-enriched atmospheres

Authors' Summary

The Naval Research Laboratory has been investigating the flammability of materials under unusual atmospheric conditions. Ignition and flame spread of

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* See Part 1. *FRAR 9,* 188–193 (1967).

several fabrics and paper were measured at pressures from 315 psia down to the limiting pressures for ignition. The minimum total pressure limit for the standard filter paper used was much lower at 41% O_2 than at 21% O_2 in O_2/N_2 mixtures. Also, the partial pressure of O_2 required for ignition at 41% was much lower than at 21% O_2. Although, in general, materials have a faster burning rate in helium mixtures than in nitrogen mixtures, there are some significant exceptions to this finding. The nature of the material has been shown to have a marked influence on the effect that variables, such as pressure, oxygen content, and diluent, have on the rate of burning.

F. Fire Damage and Salvage

Christian, W. J. and Waterman, T. E. (IIT Research Institute, Chicago, Illinois) "Fire Behavior of Interior Finish Materials," *Fire Technology* 6(3), 165–178 (1970)

Sections: F, G
Subjects: Effects of fires; Fire tests; Heat; Smoke; Temperature fields

Reviewed by J. Wagner

In this experimental study the outputs of fully developed real occupancy fires—smoke, heat, and gases—are measured. In addition, an assessment of the contributions from combustible finish materials placed on walls or ceiling in either the room of fire origin or in an adjacent corridor is made.

The test facility was a room of dimensions 30 ft × 15 ft with 16 ft high ceiling. This was subdivided into a primary burn room 10 ft by 15 ft with an 8 ft high ceiling with double doors leading to a corridor 6 ft wide, 8 ft high and 50 ft long. Air is inducted along the corridor into the primary burn room, while the combustion products pass through the upper corridor space to an attached laboratory for analysis. A prefabricated closet could also be installed in the doorway between the primary burn room and the corridor as an option. Temperature, heat flux, smoke concentration, air flow, and gas composition were measured at selected locations during the fire.

Fires of types A, B, and C with code names real, reference, and finish were examined. Five occupancies—bedroom, linen room, kitchen, office, and storeroom—were chosen to define approximately the upper limit of severity for fully involved room spaces. The closet option was also included.

For the real fires temperatures approached their maximum values in roughly four minutes. Temperatures in the mid-corridor tests ranged from around 400° to 700°F, while for the room-ceiling tests values from around 1000° to 1400°F were obtained. The fires in both types of tests were in the bedroom, the storeroom, and the linen room. The light transmission curve was nearly perfectly V-shaped over the first five minutes for the bedroom fire, while an orderly decrease was obtained for the storeroom and the linen room fires.

In the reference fires propane burners were used as the fuel source. High and low intensity room fires and closet reference fires were examined. Here the reference fire is characterized by the heat flux intensity imposed on the adjacent corridor and its heat contribution to the total system. Heat releases ranged from 34,000 Btu/min up to 165,000 Btu/min. Temperatures increased rather abruptly to their maximum values of around 400° to 1400°F.

Four locations, seven interior finish materials, and bare asbestos-cement board were chosen for the type C tests. The various interior finishes represented combinations of high, medium, and low flame spread, and smoke numbers. The times required for the flame to spread approximately 19 ft down the corridor were used to represent flame spread in the full-scale facility. These times were compared with flame spread rating numbers obtained in the standard test based on spread over 19½ ft of the sample. Here none of the materials tested burned the entire length of the corridor when exposed to the closet fire although all ignited. However, when exposed to the high intensity room fire, all the materials burned the fuel 19 ft within 20 min. It was noted that materials with increasing tunnel test flame-spread ratings do not quite correspond to increasing flame-spread rate, or decreasing time, in the full-scale corridor.

Smoke production was measured by passing a collimated light beam through the exhausting smoke. Relative positioning of materials according to their smoke production changed drastically with location and fire intensity.

Comparisons are made between the standard light absorption tunnel test and a more exact optical density of Gross *et al.*[1] for smoke numbers of 100, 427, and 460. Differences between the smoke produced for the two highest smoke numbers only amounted to 7½% for the standard test while a 50% difference was obtained from the optical density curves. A series of tunnel and full-scale test comparisons show the same relative order of smoke production for the integrated optical density even though different curves were obtained for each fire size and material location.

The authors point out that materials could possibly be placed in a proper relative hazard order as pertains to flame spread provided the tunnel test flame spread number is used in conjunction with some function of material properties, such as thickness, ignition temperature, and thermal diffusivity. Also, no single smoke rating number can adequately define the relative smoke hazards of interior finish materials.

Reference

1. Gross, D., Loftus, J. J., and Robertson, A. F.: "Method for Measuring Smoke from Burning Materials," *STP-442, American Society for Testing and Materials* (1967)

Vodvarka, F. J. (IIT Research Institute, Chicago, Illinois) "Firebrand Field Studies," *Report under Contract No. N00228-68-C-2686 for Office of Civil Defense* (September 1969)

Section: F
Subjects: Burning tests of structures; Firebrands

Author's Summary

Five residential structures were burned and their firebrand production was sampled by distributing plastic sheets downwind from the structures. Hot brands melted the plastic to leave holes showing their profiles in the sheet. The holes were then traced onto paper and their areas measured with a planimeter.

Three of the structures were standard frame construction with wood siding. The fourth was asphalt siding applied over sheet rock which covered the original shiplap. The fifth structure was a brick veneer over a wood frame. All five structures were burned under light and variable wind conditions.

The firebrand production was greatest at the time of roof collapse. The firebrands captured ranged from smaller than match-head size to about 15 in.^{2} They were classified by fractions of the standard "C" brand used for testing roof flammability. Tentative brand densities for distances to 300 ft were determined.

Concurrently with the experimental phase, attempts were made to obtain firebrand data from accidental fires as reported by IITRI's fire consultants. Only four fires were reported, of which only two were unwanted fires. The other two were set to dispose of the buildings.

A firebrand field study questionnaire was sent to the chiefs of approximately 1600 United States communities with populations over 12,000. Almost 500 replies were received, of which 268 provided detailed information.

Geographically, the mountain states provided the fewest replies and those indicated the least difficulty with firebrands. The remainder of the country all indicated about the same degree of occurrence of firebrands.

G. Combustion Engineering

Heselden, A. J. M. (Joint Fire Research Organization, Boreham Wood, England) "Smoke Travel in Shopping Malls. Experiments in Co-operation with Glasgow Fire Brigade. Part 2.," *Joint Fire Research Organization Fire Research Note No. 854* (December 1970)*

Section: G
Subjects: Smoke spread; Temperature; Visibility

Author's Summary

Following an earlier report which dealt with measurements of the rate of smoke spread and the depth of the smoke layer in experimental fires in a disused railway

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* See Part 1. *FRAR 12*, 234 (1970).

tunnel representing a pedestrian mall, data are now given for the temperature and opacity of the smoke layer.

The fall of temperature of the smoke layer as it passed along the tunnel could be accounted for entirely by convection and radiation transfer to the walls and floor of the tunnel so that there seems to have been little mixing of the layer with the cold air underneath, a factor which could also lead to a fall in temperature along the tunnel.

One smoke test was made outside the tunnel under a canopy. This emphasized the dependence of smoke spread on the wind conditions and showed that smoke logging to a low level could occur even when the smoke was not completely confined.

Values can be derived for the optical density of the smoke produced by burning a given weight of kerosine in a given volume, enabling an estimate of the visibility to be derived in other comparable situations where the burning rate and mixing conditions are known. The values obtained exhibit substantial variation so that the precision of an estimate of visibility is low, though sufficient for the present purpose. Such variation has a bearing on the problem of relating the behavior of materials in a smoke test to some assumed real fire situation, a problem which itself falls outside the scope of this report.

Beér, J. M. and Howarth, C. R. (University of Sheffield, Sheffield, England) "Radiation from Flames in Furnaces," *Twelfth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania* (1969)

Section: G
Subjects: Furnaces; Heat flux

Authors' Summary

Theoretical and experimental research on the radiative transport from flames in furnaces is reviewed. A "flow chart" of the procedure of solving a radiative transfer problem is presented. Banded and continuous emission in furnace flames is considered. Emission from particulate clouds is discussed in three groups according to the value of the Mie parameter $X=\pi d/\lambda$: for $X \ll 1$ (soot in flames) where scattering is negligible, and calculated and measured optical constants are available, for $X \approx 1$ (cenospheres in flames) where scattering by individual particles is taken into account, and for $X \gg 1$ (pulverized coal flames) where the scattering is multiple and anisotropic. Simplified furnace calculations: the well-stirred and the plug-flow furnace models and the zone method of analysis are discussed, together with approximate methods for the solutions of the transport equation when allowance has to be made for multiple scattering.

The experimental information surveyed is presented in two groups:

(a) Radiometric measurements on industrial size flames, and
(b) Physical measurements of radiative properties of absorbing-emitting-scattering media

The experimental research reviewed includes data of radiant emittance and emissivity of flames as a function of design and operational input variables obtained at IJmuiden and discussions on the correlation of values of absorption coefficients determined from flame measurements with results of theoretical studies.

Further research is required on methods of predicting temperatures, gas- and soot-concentration distributions in flames from input parameters; on the radiative properties of soots at flame temperatures, and of scattering characteristics of particles that are large compared with the wavelength of the incident radiation. Approximate methods for the solution of the transport equation for scattering media need checking experimentally.

Cottle, T. H. and Bailey, T. A. (Cardiff Fire Brigade) and **Butcher, E. G. and Shore, C.** (Joint Fire Research Organization, Boreham Wood, England) "Smoke Tests in the Pressurized Stairs and Lobbies in a 26 Storey Office Building," *Joint Fire Research Organization Fire Research Note No. 850* (November 1970)

Section: G
Subjects: Multi-storey buildings; Pressurization; Smoke movement

Authors' Summary

Smoke tests carried out in a 26 storey office building which had pressurization installed on its stairs and lobbies showed that the system satisfactorily prevented any smoke from entering the protected spaces.

H. Chemical Aspects of Fires

Lipska, Anne E. (Stanford Research Institute, Menlo Park, California) "The Effect of Flame Retardants on Thermal Degradation of α-Cellulose in Nitrogen," *Annual Report, August 1969–August 1970 under Contract No. DAHC-70-C0219 for Office of Civil Defense* (August 1970)

Section: H
Subjects: α-cellulose; Flame retardants; Pyrolysis

Author's Summary

Measurements for use in assessing the Parker-Lipska model for decomposition of cellulose are reported. These include changes in molecular weight during isothermal pyrolysis and increases in char yield and weight-loss rate due to retardant treatment. These experiments also investigated the role of 1,5-anhydro-2,2-deoxy-β-D-pent-2-enofuranose (a major product of thermally degraded cellulose and levoglucosan) in the char-formation process of fire-retarded cellulose. The isolated furanose derivative, both in the neat form and in the presence of $NH_4H_2PO_4$, was pyrolyzed and its degradation products were analyzed by means of a gas chromatograph.

At 276°C, initial pyrolysis of α-cellulose results in an abrupt decrease in average molecular weight and is followed by a linear decrease over a prolonged period of heating. Increased yields of char and rates of degradation due to the basic and neutral retardants were found to be in quantitative agreement with the predictions of the Parker-Lipska model for decomposition of cellulose. Effects of the acidic retardants, however, were not in agreement with the prediction. These results suggest that some modification of the model are in order. The results of the pyrolysis experiments on the furanose derivative support the contention that the excess yield of char in retardant-treated cellulose is due to the degradation of secondary products of cellulose decomposition rather than of the cellulose molecule itself.

Woolley, W. D. and Wadley, Ann I. (Joint Fire Research Organization, Boreham Wood, England) "The Thermal Decomposition Products of Phenol-Formaldehyde Laminates. Part 1. The Production of Phenol and Related Materials," *Joint Fire Research Organization Fire Research Note No. 851* (December 1970)

Section: H
Subjects: Phenol-formaldehyde resins; Pyrolysis

Authors' Summary

The phenolic products from the thermal decomposition of phenol-formaldehyde laminates have been studied by gas chromatography and mass spectrometry at temperatures between 300° and 550°C in nitrogen and air. The main phenolic components have been identified as phenol, *o*- and *p*-cresols, 2:4- and 2:6-xylenols and 2:4:6-trimethyl phenol. The maximum yields of the phenols are obtained at 460°C in nitrogen. The presence of air greatly reduces the quantities of the phenolic products. It is shown that in fires the phenolic laminates could, under certain conditions, generate hazardous amounts of phenolic products.

The results of three experimental fire tests are recorded to show that the concentrations of phenol and cresols appear to be lower than expected and, in these tests, not hazardous in comparison with the carbon monoxide.

Woolley, W. D. and Wadley, Ann I. (Joint Fire Research Organization, Boreham Wood, England) "The Thermal Decomposition Products of Phenol-Formaldehyde Laminates. Part 2. The Production of Carbon Monoxide and Carbon Dioxide," *Joint Fire Research Organization Fire Research Note No. 852* (December 1970)

Section: H
Subjects: Carbon dioxide; Carbon monoxide; Phenol-formaldehyde; Pyrolysis

Authors' Summary

The production of formaldehyde has been studied by gas chromatography during the thermal and thermal-oxidative decomposition of two commercial phenol-formaldehyde laminates between 200° and 500°C. Formaldehyde has only been detected between 400° and 500°C. In nitrogen the maximum formaldehyde yield is 0.85 mg/g which increases to 1.63 mg/g in air.

The release of carbon monoxide and carbon dioxide from one laminate only has been monitored between 250° and 550°C. In nitrogen, the maximum recorded yield of carbon monoxide is 76.0 mg/g at 550°C which increases to 240 mg/g at 450°C in air.

A toxic evaluation of the products is given to show that the toxic hazard of formaldehyde in the decomposition gases is small in comparison with carbon monoxide and phenolic products. The phenols, monitored in Part 1 of this report, appear to be the main toxic hazard of the thermal and thermal oxidative decomposition products.

Kanury, A. Murty (Factory Mutual Research Corporation, Norwood, Massachusetts) "Thermal Decomposition Kinetics of Charring Polymeric Solids," *Factory Mutual Research Corporation Serial No. 19721–4* (January 7, 1971)

Section: H
Subjects: Kinetics of thermal decomposition; Polymers; Pyrolysis; X-ray density measurements

Author's Summary

Solution of the equations of energy and mass conservation describing the thermal response of charring polymeric solid fuels exposed to a fire environment requires a knowledge of the pyrolysis rate equations. Because the results of conventional thermogravimetric experiments (static or dynamic) or small samples are speculated in the literature to be inapplicable to large samples in real fire situation due to the influence of composition, catalysis and autocatalysis, physical structure of the solid, gradients of temperature and density, etc., an *in situ* measurement technique

is needed to deduce the "overall" kinetics of pyrolysis of large samples. In this paper, a novel x-ray photographic technique is described to measure the density profiles in the pyrolyzing solid which when combined with the temperature profiles measured with thermocouples yield the kinetics. Sample radiographs of pyrolyzing α-cellulose to illustrate (a) the success of the technique and (b) the method of deducing the kinetic information are presented. In the main, the findings include that a first-order Arrhenius-type rate equation (with an activation energy of 19,000 cal/mole and a preexponential frequency factor of 10^6/min) satisfactorily describes the pyrolysis rate. The nature of the internal temperature profiles is demonstrated to be of crucial importance in the use of such a rate equation to predict the burning rate of wood-like fuels.

I. Physical Aspects of Fires

Blackshear, P. L., Jr., Wood, B. D., Alvares, N. J., Matthews, J. W., and Barsic, N. J. (University of Minnesota, Minneapolis, Minnesota) "Fire Research—A Collection of Papers Representing Research Completed during the Year Ending October 15, 1969," *Combustion Laboratory Technical Report No. 7 under Contract No. N00228-69-C-1172 for the Office of Civil Defense* (November 1969)

Sections: I, H, J
Subjects: α-cellulose; Atmospheric diffusion; Fire spread; Heat transfer; Mass transfer; Pyrolysis

Authors' Summary

Mass Fire Model

A sand-filled pan burner is used to study the heat and mass transfer phenomena during various phases of the burning episode for large turbulent fire plumes. The total heat fluxes and radiant heat fluxes to the fuel surface are given for luminous and nonluminous flames as well as fire plume mean optical depths for axially symmetric plumes and fire plumes with fire whirls.

Fire Spread

Heat transfer and burning rates are given for vertically hanging cotton cloth panels as a function of distance from an isothermal wall. The maximum burning rate, radiant heat transfer, and convection heat transfer occurred at 3, 1.5, and 0.75 in., respectively.

Thermal Decomposition

Combustion of pure α-cellulose cylinders treated with KBr are studied to obtain the effects of size, KBr concentration and heat flux on ignition, mass loss rates, temperature profiles, and mode of burning. It is suggested that the effectiveness of fire inhibitor compounds may be limited to a given burning geometry.

Atmospheric Diffusion

A literature review is given for mass coefficients for large sources as they are influenced by atmospheric phenomena.

Bowes, P. C. (Joint Fire Research Organization, Boreham Wood, England) "Thermal Explosion in Rectangular Parallelepipeds," *Joint Fire Research Organization Fire Research Note No. 842* (November 1970)

Section: I
Subjects: Self-heating; Thermal explosions

Author's Summary

The Frank–Kamenetskii thermal explosion parameter, δ_c, is calculated for rectangular parallelepipeds with sides in the ratio of $1:p:q$. It is given by:

$$\delta_c = 0.873(1+1/p^2+1/q^2)$$

The coefficient includes a small correction to give agreement to within 1% of existing values of δ_c for the extreme configurations, i.e., the cube when $p=q=1$ and the infinite plane slab when $p=q=\infty$.

Butler, C. P. (Stanford Research Institute, Menlo Park, California) "Measurements of the Dynamics of Structural Fires," *Annual Report, August 1969–August 1970 under Contract No. DAHC20-70-C-0219 for Office of Civil Defense* (August 1970)

Sections: I, M
Subjects: Fire dynamics; Propagation rates; Radiant flux; Scaling

Author's Summary

A major effort has begun to evaluate experimentally the dynamic behavior of structural fires in the context of civil defense implications following nuclear attack.

This report describes the accomplishments of the first year's effort which included (1) experimental measurements of the dynamic characteristics of fires in one-story wooden buildings, (2) methods used for correlating and interpreting the resulting data, and (3) attempts at reduced-scale modeling of such fires.

For the most part, tests were conducted in single, uncollapsed structures in which fires were started in a single room at one end of the structure. In one full-scale test, a structure was partially collapsed to simulate moderate blast damage, and in another series, two long, parallel structures were burned simultaneously to observe effects of interactions.

Measurements included weight-loss rate, energy-release rates, radiant fluxes, rates of fire propagation through structures, fire-induced inflow winds, CO and CO_2 production, oxygen depletion, optical attenuation by smoke, and ignition of nearby fuel specimens. In spite of substantial differences in the conditions of tests, notably those due to weather variables, many consistencies in fire behavior characteristics and associated environmental factors were found.

Radiometric measurements were shown to be a practical means for characterizing the burning rate of test fires in such structures. The pulse of radiant flux with time as measured at a distance in a suitably chosen direction correlates well with rate of weight loss as a function of time. Maximum burning rates in full-scale barracks sections occurred from 16 to 26 min after ignition with corresponding energy release rates of about 2×10^9 to 4×10^9 cal min^{-1}. Fire appeared to spread through these buildings in a more nearly linear than exponential fashion. Rates of spread were estimated to be 12 ft min^{-1}. To the extent that the data can be represented by exponential growth of volume involved in fire, the doubling time was estimated to be only about 2.5 min. Whichever method is used to express the rate of spread, the values clearly reflect the highly combustible construction of the test buildings. The dynamic characteristics in partially collapsed structures appear to be substantially different than those of their undamaged counterparts.

Carbon monoxide was found to be the major life hazard insofar as atmospheric composition is concerned. Measurements of CO concentration were translated into escape restraint times ranging from as short as 5 min in open rooms to no more than 21 min in a simulated subgrade shelter.

Measured inflow winds were quite modest for all tests. Velocities ranged from 2 to 8 mph at a height of 6 ft above grade and a distance of 10 ft from the outside walls.

The relatively unsophisticated models employed in the study to date exhibit dynamic fire characteristics that are encouragingly similar to those of the full-scale counterparts. The development of small-scale models, however, must be regarded as preliminary.

Graves, K. W. (Cornell Aeronautical Laboratory, Inc., Buffalo, New York) "Fire Fighter's Exposure Study," *Technical Report AGFSRS 71–2 under Contract No. F33615-70-C-1715 for Aircraft Ground Fire Suppression and Rescue SPO, Wright-Patterson Air Force Base, Ohio* (December 1970)

Sections: I, K
Subjects: Design of protective clothing; Evaluation of protective clothing; Heating rates; Pool fires; Radiation flux

Author's Summary

Experimental fires from pools of burning aircraft fuels were instrumented with heat meters to determine heat flux distributions for application to the design of protective clothing for fire-fighting personnel. The spectral distribution of infrared radiation emitted by fires was also measured. Conditions affecting the fires and the resulting heat effects that were studied were wind velocity, fuel pool area, time of burning, orientation around the fire relative to wind direction, distance from fire, and an extraneous object in a fire. Heating rates within the fire were found to be a maximum of 8.0 cal/cm^2-sec. Because this imposes an extreme and impractical restriction upon clothing design and because the convective heating mode was significant only in a downwind direction from fires, it was concluded that radiative heating was the predominant mode that determines clothing design requirements for fire proximity. The maximum value of this heating that would be encountered for a fire of large extent was estimated at 1.9 cal/cm^2-sec. A means by which evaluation of reflective clothing can be made is described.

Torrance, K. E., Orloff, L., and Rockett, J. A. (Factory Mutual Research Corporation Research Associates at the National Bureau of Standards, Washington, D. C.) "Experiments on Natural Convection in Enclosures with Localized Heating from Below," *J. Fluid Mechanics* **36**, Part 1, 21–31 (1969)

Section: I
Subjects: Convection; Steady-state

Reviewed by J. Wagner

The objective of this experimental report was to investigate systematically the steady-state free-convective flow patterns, arising from a uniform heat source on the floor of enclosures. Besides being an initial effort to study air movements in enclosures under simulated fire conditions this report is also of practical significance. Most early-warning fire detectors depend on free or natural convection to carry evidence of the fire to the detector.

The test chambers, made out of acrylic plastics, were of rectangular (height, a, floor $2a$ by a) and cylindrical (height equal to radius) geometries. The conventional light beam/dust particle technique was used to visualize and photograph metaldehyde (polymerized acetaldehyde) particles. Either three 500 W tungsten iodide lamps or a single 1000 W carbon arc, for the smallest chamber, were used as the light source. High speed (ASA 3000) film was used in a 10.2×12.7 cm plate camera with an $f/3.5$ lens of 12 cm focal length to photograph the illuminated particles. The particles were introduced into the chamber through a trapdoor in the floor. The larger particles settled out leaving those less than 1 mm in diameter floating in the air. The heat source on the floor was a uniform-temperature disk with a radius of about one-tenth of the enclosure height. Chromel-alumel thermocouples of 0.32 mm diameter were placed at selected locations on the floor, on the heated disk, and on the walls of the enclosure. For low Grashof numbers it was necessary to control the temperature difference between opposing pairs of walls to better than 0.03°C in order to avoid spurious effects on the flow.

Photographs are presented for a range of Grashof numbers in the rectangular and cylindrical chambers. Here the Grashof number is defined as

$$\mathrm{Gr} = g\beta\Delta T a^3/\nu^2$$

where a is the height of the chamber, g is the acceleration of gravity, β is the volume expansion coefficient, ν is the viscosity of air, and ΔT is the thermal driving force equal to $\Delta T = T_h - T_0$. T_h and T_0 are the uniform temperatures of the heat source and the cold walls, respectively. Both β and ν are evaluated at T_0.

For the rectangular chamber with an illuminated plane area of 15.2×30.5 cm photographs are presented for Grashof numbers equal to 4×10^6, 8×10^6, 4×10^7, and 1.4×10^8. The corresponding ΔT's are 8, 16, 77, and 292°C. A column of heated air is observed to rise above the hot spot and spread out radially along the ceiling; upon reaching the vertical wall it turns downward. Air then turns inward and moves toward the center where it is again entrained in the rising column. The vortex motion thereby set up is symmetrical.

When the illuminated plane was 15.2×15.2 cm three-dimensional effects became apparent for $\Delta T > 60$°C. For ΔT less than this value, the flow patterns along the axes of the rectangular chamber were very similar.

The effect of superimposed heating of one wall (15.2×15.2 cm) to 5°C above the remaining five faces was examined for Grashof numbers equal to 0, 4×10^6, 1×10^7 and 1.5×10^8. The ΔT's are 0, 8, 20 and 300°C. Here non-symmetrical flow patterns are evident in all tests.

For the circular cylindrical chambers the Grashof numbers were 8×10^5, 4×10^6, 4×10^7, 3×10^8, and 1×10^{10}. Both enclosure height and driving force were varied in order to obtain the wide range of Gr. The driving force ΔT was as high as 752°C. Turbulence was observed for Grashof numbers above 1.2×10^9. The flow patterns in the laminar regime are similar to those obtained on the rectangular chamber with the 15.2×30.5 cm illuminated plane area. An analytical study by the authors[1] showed good agreement between calculated streamlines and the present laminar flow patterns.

The authors caution the reader not to move too rapidly to "more realistic" configurations because of the complexity of the flows obtained at the higher Grashof numbers for even simple geometry.

Reference

1. Torrance, K. E. and Rockett, J. A.: "Numerical Study of Natural Convection in an Enclosure with Localized Heating from Below-Creeping Flow to the Onset of Laminar Instability," *J. Fluid Mechanics 36,* p. 33 (1969)

K. Physiological and Psychological Problems from Fires

Bertrand, A. L., Heffernan, W. D., Welch, G. D., and O'Carroll, J. P. (Louisiana Agricultural Experiment Station) "Attitudinal Patterns Prevalent in a Forest Area with High Incendiarism," *Louisiana Agricultural Experiment Station Bulletin 648* (1970)

Section: K
Subject: Opinion surveys

Authors' Summary

Interviews with heads of 259 households in an area in western Louisiana revealed a moderately favorable attitude toward forestry agencies; the area's fire record appeared to be the work of a small number of individuals.

L. Operations Research, Mathematical Methods, and Statistics

Baldwin, R. and Fardell, Lynda G. (Joint Fire Research Organization, Boreham Wood, England) "Statistical Analysis of Fire Spread in Buildings," *Joint Fire Research Organization Fire Research Note 848* (November 1970)

Sections: L, D
Subjects: Fire spread; Fire statistics

Authors' Summary

Fire statistics are analyzed to estimate the influence of various factors on the spread of fire in buildings. The spread of fire beyond the room of origin is considerably less likely in modern buildings, particularly in multi-storey buildings, and

spread is much more likely at nighttime, probably because of delays in discovery. Early attendance by the brigade over the range of these data has no measurable influence on this chance of spread, probably because of the wide range of variation in the size of fire confronting the brigade.

Chandler, S. E. (Joint Fire Research Organization, Boreham Wood, England) "Deaths in Fires Attended by Fire Brigades in 1969," *Joint Fire Research Organization Fire Research Technical Paper No. 26* (August 1970)

Section: L
Subjects: Fatalities; Fire statistics, U.K.

Author's Summary

This report analyzes all deaths in fires attended by fire brigades in the United Kingdom in 1969. It shows that there were 861 deaths, of which 710 were in England and Wales, 128 in Scotland, and 23 in Northern Ireland. Deaths in fires in buildings numbered 783 of which 688 were in dwellings. There were 86 multiple death fires, 67 being in England and Wales, 16 in Scotland, and three in Northern Ireland.

The report shows that there are more fire deaths in terraced houses and houses converted into flats than in other dwellings, and there is a strong tendency for the buildings to be old ones.

The most important known sources of ignition were smoking materials, fires in grates and oil and electric heaters. Apart from electric space heating, all these causes, and also "children with fire," were major sources of ignition in multiple death fires.

The worst fire in the year occurred at an hotel in Saffron Walden which resulted in 11 deaths.

Chandler, S. E. (Joint Fire Research Organization, Boreham Wood, England) "Fire Deaths in the Third Quarter of 1970," *Joint Fire Research Organization Fire Research Note No. 849* (November 1970)

Section: L
Subjects: Fatalities; Fire statistics, U. K.

Author's Summary

A preliminary survey shows that 88 persons died in fires in the third quarter of 1970. Of those, 79 were in England and Wales, 8 in Scotland, and one in Northern Ireland.

The worst incidents in this quarter were a road traffic accident in Birkenhead (7 deaths) and a multiple occupancy house in Wembley (6 deaths).

Davies, T. W., Beér, J. M., and Siddall, R. G. (University of Sheffield, Sheffield, England) "The Use of a Mathematical Model for the Prediction of the Burn Out of Char Suspensions," *Chemical Engineering Science* **24,** 1553 (1969)

Section: L
Subject: Burn out of char suspensions

Authors' Summary

A simple one-dimensional mathematical model is developed which is used to calculate the burn away of char suspensions. The model consists of a rate equation for the combustion of a single carbon sphere, derived from boundary layer diffusion and kinetic theory, which is combined with an approximation to the size distribution of a suspension permitting the calculation of the instantaneous combustion rate of the whole cloud. To allow the calculations to proceed in time, balance equations are set up, from which the time dependent parameters of the rate equation can be calculated as the computations proceed.

The model is used to investigate the relative importance of the parameters involved in the rate equation in determining the burn out of a suspension. The model is then tested by comparing predicted burn out curves with those obtained experimentally under unidimensional conditions.

Fry, J. F, (Joint Fire Research Organization, Boreham Wood, England) "Fires in Flats and Maisonettes," *Municipal and Public Services Journal* (July 24, 1970)

Section: L
Subject: Fire statistics, U. K.

Author's Summary

Reports of fires in postwar multi-storey flats in inner London reveal that the fire incidence rates are lower than those in dwellings in general, if rubbish-chute fires are discounted; that fires start most frequently in kitchens; that fires in common

service areas are frequently associated with accumulations of rubbish; and that most fires spreading beyond one room are confined to the flat or maisonette in which they start.

Main, W. A. (North Central Forest Experiment Station, U. S. Forest Service, St. Paul, Minnesota) "Computer Calculation of Fire Danger," *U. S. Forest Service Research Note NC-79*

Section: L, J
Subject: Computation of National Fire Danger Rating Index

Author's Summary

This paper describes a computer program that calculates National Fire Danger Rating Indexes. Fuel moisture, buildup index, and drying factor are also available. The program is written in FORTRAN and is usable on even the smallest compiler.

Weisbecker, L. W. and Lee, Hong (Stanford Research Institute, Menlo Park, California) "Evaluation of Systems of Fire Development," *Report under Contract No. DAHC-20-67-C-0116 for Office of Civil Defense* (August 1970)

Sections: L, D
Subjects: Fire spread models; Urban configurations

Authors' Summary

This report compares three fire spread models, recently developed for the Office of Civil Defense, for utility, accuracy, and efficiency when applied to civil defense fire information requirements. The fire spread modeling was essentially limited to the radiation fire spread mechanism. All three models provided procedures for calculating fire spread under a limited range of conditions, but all suffered to some degree from inadequate modeling of urban configurations and the fire parameters associated with urban structures that significantly affect fire spread mechanisms.

It is recommended that a "reference" fire spread model be structured for evolutionary development. Although none of the models considered could provide a sufficiently broad base upon which a "reference" model could be built, parts and

concepts from all three models could be incorporated. The "reference" model should be structured in terms of fire spread mechanisms by developing fire spread submodels that are then analyzed at the most basic level and subsequently, systematically broadened in scope. Models for specific purposes and having predictable characteristics can be derived from the "reference" model by making appropriate simplifying assumptions. Fire spread modeling approaches and concepts are also suggested.

National Aeronautics and Space Administration (Lewis Research Center, Cleveland, Ohio) "The Reaction Kinetics Ablation Program (REKAP)," *Report of work under Contract with General Electric Co.* (*F. E. Schultz*), *NASA Technical Brief 66-10426* (1966)*

Section: L
Subjects: Ablation; Computer simulation

NASA Brief Summary

The Reaction Kinetics Ablation Program (REKAP) developed to simulate ablation of various materials, provides mathematical formulations for computer programs which can simulate certain industrial processes. The programs are based on the use of nonsymmetrical difference equations that are employed to solve systems of complex partial differential equations.

The REKAP program can be generally adapted to the simulation of processes involving heat and mass transfer by substituting specific parameters into the basic equations. In the kiln drying of lumber, for example, profiles of temperature, humidity, and drying time for woods of different types can be simulated to predict minimum process cost and loss of material.

The REKAP program could also be adapted to the simulation of the manufacture of ceramics, the casting of large concrete structures, and the propagation of forest fires (to determine optimum methods of control).

* Copies available at National Technical Information Service, Operations Division, Springfield, Virginia 22151

M. Model Studies and Scaling Laws

Lee, B. T. (Stanford Research Institute, Menlo Park, California) "Laboratory Scaling of the Fluid Mechanical Aspects of Mass Fires," *Annual Report, August 1969–August 1970 under Contract No. DAHC20-70-C-0219 for Office of Civil Defense* (August 1970)

Section: M
Subjects: Fluid mechanics; Scaling

Author's Summary

The effective application of a practical modeling technique in the study of the gross flow features of a mass fire requires more knowledge of the essential scaling laws than has hitherto been available. As the technique rests upon the assumption of negligible viscous forces, i.e., fully developed turbulent flow in the fire and convection column, there is thus some lower limit on the size of a mass fire model operating under ambient conditions. Furthermore, owing to boundary layer buildup, some uncertainty exists as to how close to the ground in a mass fire it is possible to scale the flow field.

Two electrical models—one 2 ft×2 ft and the other 4 ft×4 ft—and a 4 ft×4 ft gas flame model employing methane jets were utilized in an endeavor to provide more information concerning the areas of interest. When model and prototype geometries and heat release rates are scaled, velocities and temperatures should theoretically scale at homologous locations over the fires. Velocity histories recorded at elevations from 7 to 70 ft along the sides of and within a square-shaped, 30 acre fire, and temperatures at elevations from $3\frac{1}{2}$ to 50 ft within the same fire were used as prototype data for comparison with model data. Also used were the temperature measurements at elevations from $\frac{1}{2}$ to 5 ft within a 44 acre, also square-shaped fire.

Field measurements of velocity from the 30 acre prototype fire were found to agree well with values scaled from the model results, thus demonstrating the feasibility of laboratory scaling of the flow aspects of the low altitude environment in mass fires. Furthermore, good scalability between velocities from the models at elevations as high as one model diameter, the highest elevation considered in the investigation, also suggests possible similar scalability of the flow at homologous points above a large mass fire.

Temperatures from the two prototype fires were also found to agree well with the values from the electrical models. However, modeling of the temperature fields at low elevations with the gas model failed owing to the nonscaling of radiative heating of the surface.

The further application of the modeling technique to the flow field about the detailed individual components of mass fires, e.g., a single burning structure, appears to be promising. Preliminary study with 1/16-scaled model buildings suggests the practicality of the method. Use of the technique for the study of wind interaction with the flow environments within the mass fire as well as about individual structures also appears to have potential.

Byram, G. M. and Nelson, R, M., Jr. (Southeastern Forest Experiment Station, U. S. Forest Service) "The Modeling of Pulsating Fires," *Fire Technology* 6(2), 102–110 (1970)

Section: M
Subjects: Pulsating fires; Scaling laws

Reviewed by J. Wagner

The authors employ dimensional analysis for the development of a scaling law for modeling a pulsating fire. Experiments were carried out in the laboratory to check the functional relationship of their analysis.

The geometry considered is a circular perimeter of diameter D that encloses the burning area over which the rate of convective heat output per unit area is assumed constant and equal to a steady-state value I_a. It is furthermore assumed that the atmosphere is an isothermal, incompressible fluid with the same coefficient of thermal expansion, specific heat, c_p, and density, ρ, as the actual atmosphere. In the absence of viscous forces two dimensionless groups

$$\pi_1 = \tau(g/D)^{1/2}$$

and

$$\pi_2 = I_a/(gD)^{1/2}\rho c_p T$$

where τ is the pulsation period, g the acceleration of gravity, and T the temperature of ambient air characterize the pulsation phenomena. Here π_1 is regarded as a dimensionless time and π_2 is a buoyancy number. According to the Buckingham π theorem, $\pi_1 = \phi(\pi_2)$ where $\phi(\pi_2)$ is some unknown function of π_2. When solved for τ this becomes

$$\tau = (D/g)^{1/2}\phi[I_a/(gD)^{1/2}\rho c_p T] \qquad (1)$$

On logarithmic co-ordinates, any series of scaled fires would be represented by a curve formed by the intersection of the τ surface with a plane parallel to the log $\tau - \log D$ plane. The curve of intersection is a straight line with a slope equal to one-half. If viscous forces were considered this would introduce the dimensionless group

$$\pi_3 = gD^3/\nu^2$$

where ν is the kinematic viscosity of ambient air. Here π_3 is a modified Grashof number.

The experiments were carried out in two series of fires using 95% ethanol as the fuel. The first series consisted of five circular pool fires having diameters of 0.5, 1.02, 2.0, 4.0, and 8.0 ft. The second series was identical to the first except that a fire 0.25 ft in diameter was added. Shallow metal pan burners, filled to the top of the rim to reduce heat conduction from the fuel to the metal burner, were used in all the tests with the exception of the 8 ft fire. The 8 ft burner, a level cylindrical metal ring, was mounted about five inches deep in clay soil of a smooth, level terrain. Average burning rates for the 8 ft and 4 ft fires were determined from the time required for a given depth of fuel to burn. Weight loss obtained on a top loading balance was used to obtain the burning rates for all other fires. A high-speed movie camera was used to count pulsation frequencies for the fires less than 1 ft in diameter. The low roaring sounds that accompanied the pulsations were used to obtain the frequencies for the larger fires.

The fires exhibited three stages of burning: a heat-up period for the fuel approximately one-third of the burning time, a steady-state period during which the burning rate maintained a constant maximum value, and a falling-rate period caused by uneven burnout in the bottom of the burner. Since it was noted that the ratio of the drop in fuel level to burner diameter was much greater for the small fires than for the large ones the data on frequency and burning rate were taken during the fuel heat-up period, 2 min after ignition. The data for all the fires are given in Table form. Values of $\nu = 1.69 \times 10^{-4}$ ft²/sec and $\rho c_p T = 9.40$ Btu/ft³ were used in calculating the dimensionless groups; π_3 is also included in the Table although disregarded in the analysis. For the $D = 0.50$ ft to $D = 8.00$ ft diameter fire π_1 and π_2 varied from only 2.28 to 2.00 and 0.574 to 0.224, respectively, while π_3 varied from 1.40×10^8 to 5.74×10^{11}. For the 0.25 ft burner π_1, π_2, and π_3 were 1.72, 0.896, and 1.75×10^7, respectively. The π_1 vs. π_2 data, with the exception of the 0.25 ft fire, could be fit by a simple exponential equation. A straight line with slope equal to one-half was obtained on a log–log plot of pulsation period τ vs. burner diameter D.

The authors point out that π_2 does not appear to have a pronounced effect on the period of a pulsating fire, but that its value could determine whether the fire will pulsate at all. When π_2 is too large fires will not pulsate. This was observed on a kerosene fire in the 8 ft burner.

Roberts, A. F. (Safety in Mines Research Establishment, Sheffield, England) "Fires in the Timber Lining of Mine Roadways—A Comparison of Data from Reduced-Scale and Large-Scale Experiments," *Safety in Mines Research Establishment Report 263*

Sections: M, I
Subject: Fires; Mine roadway fires; Scaling laws

Author's Summary

The study of any type of combustion system by means of reduced-scale experiments presents problems, since a change in scale can produce major changes in the relative importance of the various physical processes occurring in the system. This paper is concerned with the development of scaling laws based on a simplified mathematical model of the development of fires in the timber linings of mine roadways. The application of these laws to data obtained in reduced-scale experiments predicted that, given a strong enough igniting source, e.g., burning mineral oil, and a continuous timber lining, a previously unreported type of roadway fire could occur, in which all the oxygen in the ventilating air is consumed in the fire. A series of large-scale experiments confirmed this prediction. In addition, where detailed comparisons could be made the relationships between data from large-scale and small-scale experiments were in agreement with the formulated scaling laws.

BOOKS

Fire Service Hydraulics (Second Edition) Edited by James F. Casey. The Reuben H. Donnelley Corporation, New York, N. Y. (1970)

Reviewed by J. Wagner

This book is intended for the beginner and the advanced student in the fire protection field and also for the fire fighter. It is divided into four parts: Theory, Water, Practice, and Foam. Five authors, in addition to the editor, have written the various sections of the book. There appear to be no prerequisites, with perhaps the exception of elementary physics, for an understanding of the material covered. Sample problems with answers are provided to familiarize the reader with a number of basic working equations. Numerous illustrative figures are given throughout the book. Brief selected reference lists are included after several of the chapters. An Appendix of useful tables is provided.

Part I—Theory (70 pages) first deals with the fundamentals of Hydrostatics and Hydrokinetics (Chapter 1). Attention is then given to the pumping, transport through hoses, and the discharging of water from nozzles under typical fighting conditions (Chapter 2).

Part II—Water (pp. 74 to 224) is divided into Water Distribution Systems and Fire Service Pumps. A rather comprehensive treatment along with numerous figures are given for both topics. Practical applications are again emphasized.

Part III—Practice (pp. 226 to 341) is divided into four short chapters—Friction Loss Calculations (pp. 226–238), Fire Streams (pp. 293–307), Standpipe Systems (pp. 308–323), Automatic Sprinkler Systems (pp. 324–341) and a lengthy one on Engine and Nozzle Pressures (pp. 239–292). The reviewer believes that the *friction loss calculations* would be better suited as a small section in Part I. The coarse description of friction and the need to refer the reader to Chapter 2 (Part 1) could thereby be avoided. If further consolidation is desirable, Standpipe Systems could be included in Chapter 3 since it is a specific type of a Water Distribution System.

Part IV—Foam (pp. 344 to 391) is titled Fire Fighting Foams and Foam Systems. The excellent treatment of Foam given here greatly enlarges the perspective of this book. In this final chapter the reader receives an initial comprehensive treatment of a chemical type of extinguishing agent.

In addition to the objections mentioned previously the reviewer finds a few minor faults in terminology: e.g., the use of Hydrokinetics (which implies a rate of attainment of equilibrium for some process in a flowing fluid) as the study of liquids in motion instead of Hydrodynamics; the use of conductor for a conduit or a pipe. In addition, there are some errors and inconsistencies. A particularly conspicuous one is seen in the statement on page 62, "Friction loss under laminar flow in straight pipe or hose is strictly due to viscosity," (Should be friction loss is a function of Reynolds number) while on page 64 an equation for friction loss depends on hose length, volumetric flow rate, hose diameter, and a constant but not on the viscosity.

Overall the book is judged to be a success and should be welcomed by the fire community. The subject matter covered is very broad in scope but is well written. In attempting to appeal to a diverse audience one encounters enormous difficulties, however, this reviewer believes that the interests of the beginning student and the fire fighter are more than satisfied. The reviewer doubts that the advanced student would find all of the chapters particularly enlightening.

PERIODICALS

Fire Control Notes. Published quarterly by the U. S. Department of Agriculture, Forest Service*

Contents

Volume 31, No. 4 (Fall 1970)
- *Fire Control Notes* Offers Its Services—R. Headley
- Contributor's Information—Here's How:
- Prescribed Nighttime Burns Bring Benefits—S. S. Sackett and D. D. Wade
- Excess-Flow Check Valves Prevent Propane Accidents—L. L. Downey
- Mass Fire Phenomenon in Sundance Fire
- Fire Reports System
- Teletype Maps Display Predicted Burning Index Using Overlay—R. E. Lynott and H. E. Graham
- Testing Service Rates Wetting Agents—R. W. Johansen and J. E. Deeming
- The Silent Tracker—D. B. Bradshaw

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Volume 32, No. 1 (Winter 1971)
  1970 Fire Season Statistics: November 30
  Thinning Slash Contributes to Eastside Cascade Wildfires—J. D. Dell and D. E. Franks
  Fire Occurrence Mapped by Computer—A. T. Altobellis, C. L. Shilling, and M. M. Pickard
  Diammonium Phosphate Prevents Roadside Fires—J. B. Davis
  Air Horn Helpful in Fire Emergencies—A. G. Bell
  ℞ for Burning on Apache National Forest—B. Buck
  Flexible Plates for Simulators Found Feasible—H. P. Gibson
  1970 Author Index
  1970 Subject Index
  Black Wednesday in Arkansas and Oklahoma—R. T. Davis and R. M. Ogden

TRANSLATIONS

Baskakov, A. P. and Kirnos, I. V. (Sverdlovsk, USSR) "Study of the Combustion of a Gas-Air Mixture in a Fluidized Bed of Fine–Grain Material," *Physics of Combustion and Explosion* 5(4), 549–554 (1969)

Subject: Combustion in fluidized beds.

Translated by L. Holtschlag

The large number of papers devoted to the study of ignition of a gaseous fuel in a fluidized bed of inert or active fine-grain material[1,2] is due primarily to the broad use made of the latter in the various branches of industry and, in particular, to the highly promising future of furnaces with a fluidized bed for heating and thermal processing of metals.[4] Of greatest interest for non-oxidative and non-decarbonizing heating is the combustion of rich fuel-air mixtures with a coefficient of oxidizer consumption (α) considerably less than unity. A theoretical analysis and the experimental data show that the combustion products in thermodynamic equilibrium at temperatures above 800°–900°C do not oxidize a metal whose oxide has an isobaric potential greater than the standard isobaric potential of CO if the coefficient of oxidizer consumption is

$$\alpha_{\mathrm{Me}}/\alpha_c \le 1+(n-l)^{-1}\{[0.5m/(kk_5+1)]+[n/(k_5+1)]\}. \qquad (1)$$

Here n, m, l are the atomic fractions of carbon, hydrogen, and oxygen in a fuel with the empirical formula $C_nH_mO_lN_g$; k and k_5 are the equilibrium constants of the reactions $CO+H_2O=CO_2+H_2$ and $CO_2+Me=MeO+CO$; α_c is the coefficient of oxidizer consumption below which it is thermodynamically impossible to avoid the formation of carbon black. When $T > 850°C$

$$\alpha_c = n - l/(0.5m + 2n - l). \quad (2)$$

Upon the ignition of methane-air mixtures ($\alpha_c = 0.25$), when $\alpha \geq 0.5 - 0.55$, a medium non-oxidative to iron is obtained and when $a \leq 0.25 - 0.3$, the medium is non-decarbonizing.

A fluidized bed is of theoretical interest because owing to its tremendous thermal conductivity, which is due to the intense mixing of the pseudo-liquefying particles, combustion takes place under vigorously isothermal conditions, especially when $\alpha < 1$ (Table 1). Small temperature deviations were observed only in the immediate neighborhood of the gas-distributing grate and in the zone where secondary blowing takes place. Even upon the ignition of a stoichiometric mixture, when huge quantities of heat are evolved in the immediate vicinity of the grate, the temperature in this zone is usually only 20°–30°C greater than that in the rest of the layer.

The results presented in the following were obtained chiefly in the experimental apparatus shown in the right-hand corner of Fig. 1. A gas-air mixture with $\alpha < 1$ is fed into the tube (inner tube in Fig. 1) filled with a fine-grain material, pseudo-liquefies it and burns in the fluidized bed. In order to ignite the products of incomplete combustion, secondary air is supplied to the upper part of the bed (the splash zone). Owing to the intense mixing of particles, the combustion heat is transferred into the lower portion of the bed, resulting in rather high temperatures at very low values of α. In order to expand the range of the experimental conditions, the tube was placed in a unique constant-temperature heater with a fluidized bed and an independent gas-air mixture supply system. The heater itself serves as a large-diameter test apparatus when the inner tube is removed from it. The results given in the table were obtained in this type of pilot-plant apparatus with a diameter of 250 mm without the inner tube.

First of all, it should be noted that the mechanism and burning rate are essentially dependent on the coefficient of ozidizer consumption α. When $\alpha \geq 1$, methane (natural gas) burns stably and practically without a residue in a fluidized bed of inert fine-grain material at a temperature above 800°–850°C and a propane-butane mixture with $T \geq 750°–800°C$, at the same time, when $\alpha_c < \alpha < 1$ the methane is

TABLE 1

Temperature Distribution Over the Height of a Furnace With a Fluidized Bed of Active Grog (Particles 0.63 mm–1.00 mm) during the Combustion of a Methane-Air Mixture.

Distance from the point of introduction of the gas-air mixture (mm)	Temperature (°C)	
	Experiment 1	Experiment 2
0	—	927
100	900	935
200	900	935
300	900	935
400	901	935
500	901	945
600	910	945

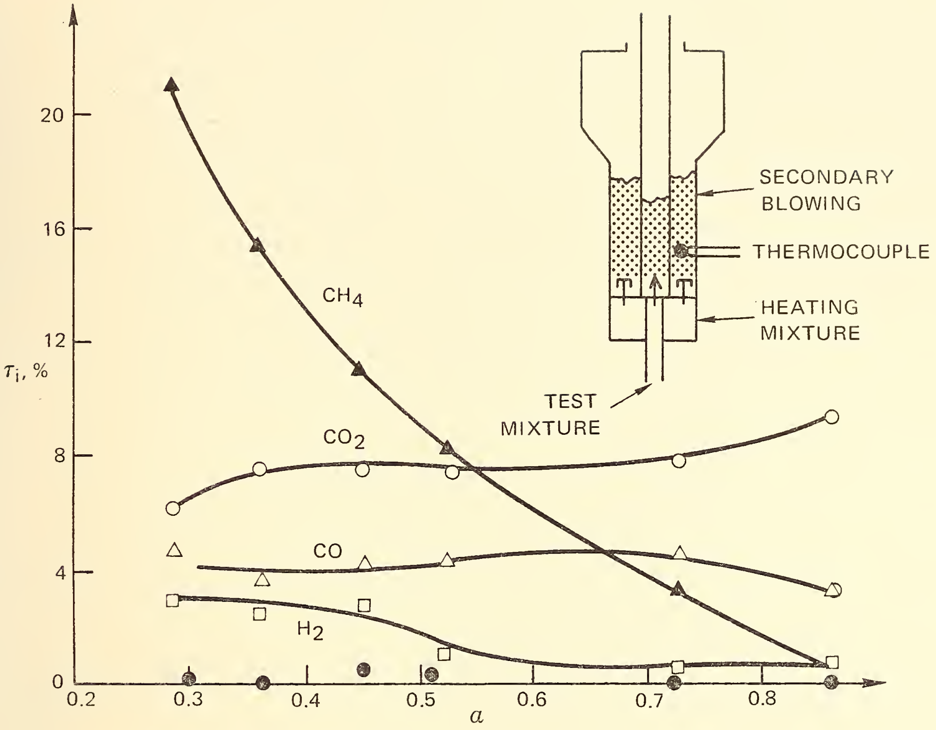

FIG. 1. Dependence of the composition of the combustion products on the coefficient of air consumption during the burning of natural gas in a fluidized bed of inert corundum; $w=0.15$ m/sec, $h_{\text{tube}}=200$ mm; $T=900°C$. (A diagram of the experimental apparatus is shown in the upper right-hand corner.)

consumed much more slowly. From Fig. 1 it can be seen that the content of undecomposed methane in the combustion products sample from the fluidized bed is several orders of magnitude greater than the thermodynamic-equilibrium content even at 900°C, and when $\alpha > \alpha_c$ it turns out to be greater than for a smaller α. Here it should be emphasized that beginning with the height at which almost all the oxygen is absorbed (100 mm–150 mm from the grate) the composition of the combustion products remains essentially unchanged.

In the literature the idea has already been advanced[3] that the combustion of hydrogen fuels takes place in two "visible" stages: first the fuel reacts with oxygen forming H_2O and CO_2, and then the products of complete combustion react with the still unreacted fuel, forming CO and H_2; the first stage proceeds considerably faster than the second. Finally, each of these stages is the result of complex chain reactions, whose mechanism is still far from being known.

Confirming such a two-stage process are the large concentrations of CO_2, which, when $\alpha < 0.6$, are considerably greater than the equilibrium concentrations, and the small concentrations of H_2 and CO. The rates of the two stages differ so greatly that for $\alpha \geq 1$, when the second state is absent, the methane vanishes at a distance of 30 mm–100 mm from the grid at a velocity of better than 0.5 m/sec, whereas when $\alpha = 0.4$ and the velocity is 0.15 m/sec, the combustion products contain more than 10% methane (Fig. 1); the methane concentrations at a distance of 100 mm and 500 mm from the grid differ by no more than 1%–2%, i.e., the methane almost does not react in this section.

The high content of CO_2 and H_2O in the combustion products leads to their oxidation of iron even at very low values of α. In order to get a non-oxidative medium, it is necessary to speed up the second stage of the process, which at the given temperature can be done only by means of a catalyst.

A nickel catalyst was used in two variants. In the first variant it was applied to porous grog particles (0.65 mm–1.0 mm), impregnated in the fluidized bed. In the

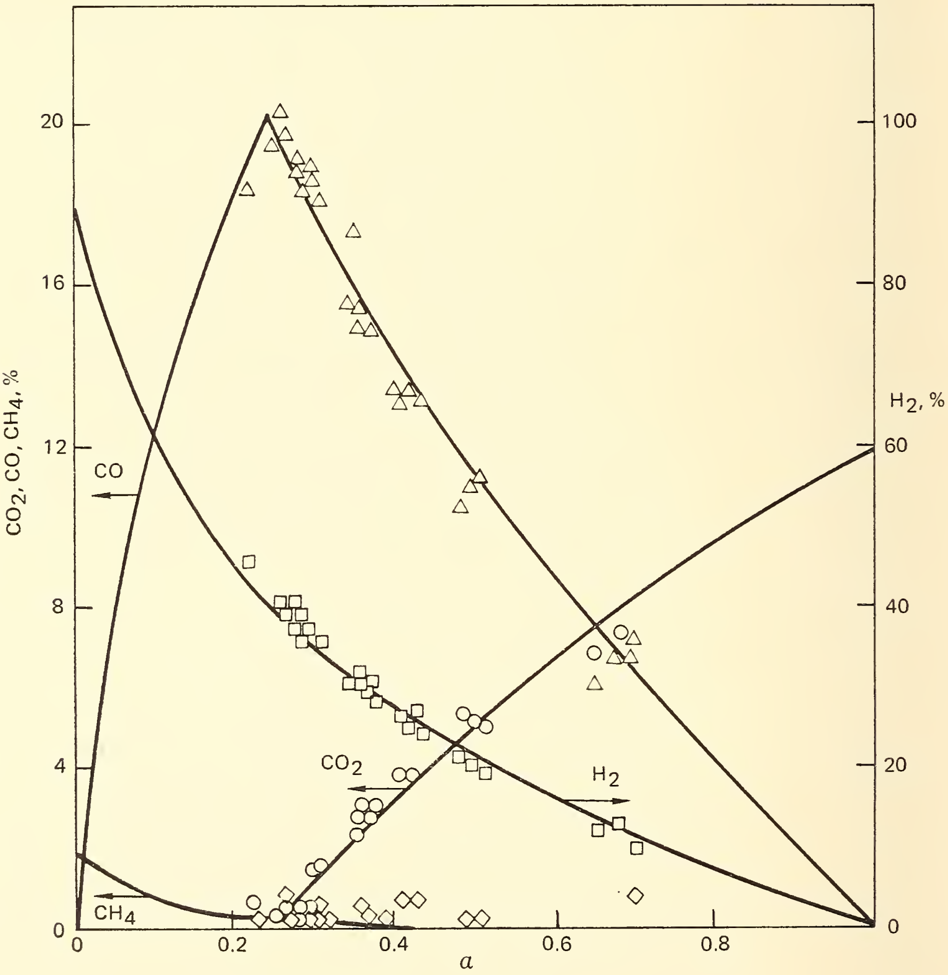

FIG. 2. Dependence of the composition of the combustion products on the coefficient of air consumption during the combustion of natural gas in a fluidized bed of active grog; $w = 0.3$ m/sec; $h_{\text{tube}} = 300$ mm; $T = 900°C$. The solid lines give the dependence of the thermodynamic-equilibrium composition of the combustion products on α; the plots represent the experimental data.

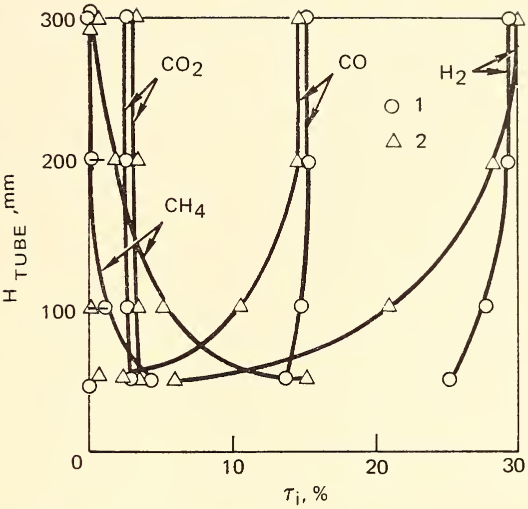

FIG. 3. Distribution of the concentrations of components over the chamber height; $w=0.285$ m/sec, $\alpha=0.35$; temperature (1) =850°C (2) =950°C.

second variant, a fixed bed of high-temperature industrial catalyst HIAP-3, produced in the form of cylinders about 10 mm in length and diameter, was deposited in the test chamber. The fine-grain material (various fractions of corundum, usually 0.32 or 0.4) was fluidized in the pores between the particles by the particles of catalyst. Special investigations showed that such a fluidized bed, impregnated in a fixed bed, turns out to be extremely homogeneous without the flare-ups and pressure pulsations characteristic of the usual fluidized bed. At bulk stresses over the methane-air mixture of less than 2,500 $N/m^2 \cdot hr$, an essentially equilibrium composition of the combustion products was obtained above the catalytic bed.

When active fluidized grog particles are used, the bulk composition of the combustion products above the reaction zone in the range $\alpha_c < \alpha < 1$ was almost indistinguishable from the equilibrium composition (Figs. 2, 3): a noticeable increase in bulk content of methane above the equilibrium content was observed when $\alpha < \alpha_c$. An analysis of the experimental data shows that the two-stage nature of the process is preserved in the presence of a catalyst: the CO_2 concentration increases as the oxygen concentration decreases, and then decreases to equilibrium. But the entire process terminated considerably faster.

As was to be expected, the height of the stabilization zone at which the combustion products became essentially equilibrium products decreases with increasing temperature of the fluidized bed (Fig. 2) and decreasing velocity of the gas-air mixture. In the indicated temperature range the equilibrium composition of the combustion products varies weakly with the temperature. The use of a catalyst, applied to the fluidized particles, in conjunction with two-step air supply has a feature which is interesting both insofar as application and theory is concerned. It is well known that the separation of carbon black during the burning process leads to gradual carbonization of the catalyst and to complete loss of its effectiveness. Therefore, rather extended experiments with a fixed catalyst for $\alpha<\alpha_c$ are impossible. If fluidized particles are used as the catalyst, the carbon deposited on them in the lower part of the bed burns up when these particles reach the zone of secondary air supply; as a result, carbon does not accumulate in the bed. For example, when $\alpha=0.184$, which is less than α_c ($=0.25$), and the temperature is 930°C, the composition of the gas does not change during the entire experiment, lasting about 50 hours. It is interesting that combustion of the carbon in the secondary blowing zone is not accompanied, apparently, by appreciable oxidation of the nickel-catalyst, since if it were, its activity should decrease with time. In a practical sense such conditions are promising for the steel hardening process. In a theoretical sense such an organization of the process is interesting in that it permits us to study the stationary process of incomplete burning with the formation of carbon black at sufficiently high temperatures. It should be noted that the presence of carbon black in the layer appreciably changes the burning mechanism, especially upon burning without a catalyst. The newly formed carbon is extremely reactive; it combines actively with oxygen, carbon dioxide, and water vapor.

Shown in Fig. 4 are the results of experiments on the burning of natural gas without a catalyst in a precarbonized bed of inert (corundum) particles. The bed was precarbonized while being operated for some time in pure gas. All the oxidizer is used up for the formation of CO (primarily from carbon black) and at a sufficient distance from the point of introduction of the mixture the medium is characterized by high contents of CO and H_2. From the figure it can be seen that the CO content over the height of the retort remains practically unchanged; the hydrogen concentration increases as a result of thermal decomposition of the methane. The CO and H_2 content decreases as the carbon burns.

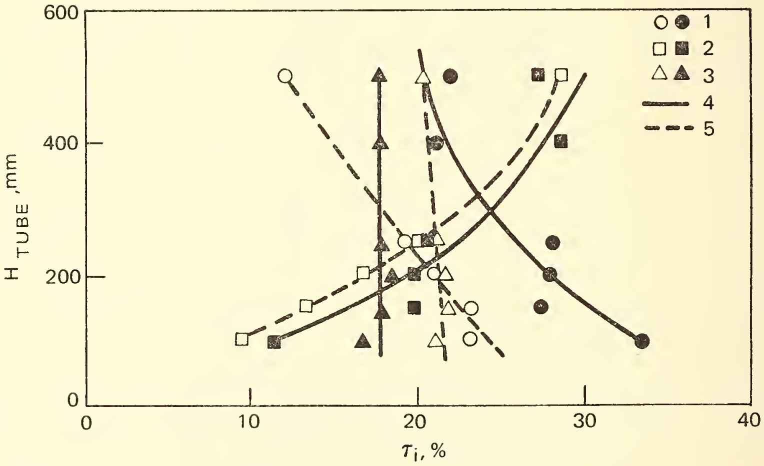

FIG. 4. Distribution of the composition of combustion products over the height of the reactor upon the burning of natural gas in a precarbonized bed of fluidized corundum: $T=900°C$, $w=0.2$ m/sec. 1—CH_4; 2—H_2; 3—CO; 4—$\alpha=0.125$; 5—$\alpha=0.176$.

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MEETINGS

Symposium on Movement of Smoke on Escape Routes in Buildings—Watford College of Technology, Watford, England (April 9–10, 1969) Proceedings published by H. M. Stationery Office, 1971)

Organized and Sponsored by: Fire Research Station, Boreham Wood, England
Purpose: As buildings become taller the problems facing the designer in his plans to ensure a safe escape route for the occupants become more and more complex, since in many cases the traditional principles of limiting travel distance and ventilating to the open air become almost impossible to follow without introducing severe and expensive restrictions to floor layout.

The Fire Research Station has for some years been actively concerned with a research program to show that a mechanical ventilation system designed to pressurize selected parts of a building can be successfully and economically used to control the movement of smoke in a building.

The papers presented at the Symposium and the discussions which they inspired represent a collection of information which should be of considerable help to designers who are required to provide safe escape routes for buildings.

Contents of Proceedings

A critical look at some current problems of escape route planning and a glimpse of the future—A. Silcock, Fire Research Station
Canadian studies on control of smoke in tall buildings—N. B. Hutcheon, National Research Council of Canada, Ottawa
Design problems that arise from the control of smoke spread in buildings—W. J. Smith, Greater London Council
Present methods of smoke control which rely on natural ventilation—W. A. Coggan
Pressurization as a means of controlling the movement of smoke and toxic gases on escape routes—E. G. Butcher and P. J. Fardell, Fire Research Station and J. Clarke, City of Glasgow Fire Brigade

Public Buildings Service International Conference on Firesafety in High-Rise Buildings—Airlie House, Warrenton, Virginia (April 12–16, 1971)

With the participation of: Building Research Advisory Board, National Academy of Sciences; National Fire Protection Association; Building Research Division, National Bureau of Standards; Building Owners' and Managers' Association; Federal Fire Council

Sponsored by: Public Buildings Service of the General Services Administration

Purpose: To bring together approximately 70 experts to undertake a concentrated interdisciplinary effort to systematically explore new or revised approaches to solving the problems of fire safety in high-rise buildings.

Contents of Report

REVIEWERS

THOMAS C. ADAMSON, JR.
University of Michigan

GEORGE A. AGOSTON
Paris, France

JOHN J. AHERN
General Motors Corporation

THOMAS P. ANDERSON
University of Iowa

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THE NATIONAL ACADEMY OF SCIENCES is a private, honorary organization of more than 700 scientists and engineers elected on the basis of outstanding contributions to knowledge. Established by a Congressional Act of Incorporation signed by Abraham Lincoln on March 3, 1863, and supported by private and public funds, the Academy works to further science and its use for the general welfare by bringing together the most qualified individuals to deal with scientific and technological problems of broad significance.

Under the terms of its Congressional charter, the Academy is also called upon to act as an official—yet independent—adviser to the Federal Government in any matter of science and technology. This provision accounts for the close ties that have always existed between the Academy and the Government, although the Academy is not a governmental agency and its activities are not limited to those on behalf of the Government.

THE NATIONAL ACADEMY OF ENGINEERING was established on December 5, 1964. On that date the Council of the National Academy of Sciences, under the authority of its Act of Incorporation, adopted Articles of Organization bringing the National Academy of Engineering into being, independent and autonomous in its organization and the election of its members, and closely coordinated with the National Academy of Sciences in its advisory activities. The two Academies join in the furtherance of science and engineering and share the responsibility of advising the Federal Government, upon request, on any subject of science or technology.

THE NATIONAL RESEARCH COUNCIL was organized as an agency of the National Academy of Sciences in 1916, at the request of President Wilson, to enable the broad community of U.S. scientists and engineers to associate their efforts with the limited membership of the Academy in service to science and the nation. Its members, who receive their appointments from the President of the National Academy of Sciences, are drawn from academic, industrial and government organizations throughout the country. The National Research Council serves both Academies in the discharge of their responsibilities.

Supported by private and public contributions, grants, and contracts, and voluntary contributions of time and effort by several thousand of the nation's leading scientists and engineers, the Academies and their Research Council thus work to serve the national interest, to foster the sound development of science and engineering, and to promote their effective application for the benefit of society.

THE DIVISION OF ENGINEERING is one of the eight major Divisions into which the National Research Council is organized for the conduct of its work. Its membership includes representatives of the nation's leading technical societies as well as a number of members-at-large. Its Chairman is appointed by the Council of the Academy of Sciences upon nomination by the Council of the Academy of Engineering.

THE COMMITTEE ON FIRE RESEARCH functions within the Division of Engineering to stimulate and advise on research directed toward the development of new knowledge and new techniques that may aid in preventing or controlling wartime and peacetime fires. The Committee was established in December of 1955 at the request of the Federal Civil Defense Administration. 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.

Volume 13 1971 Number 3

Fire Research Abstracts and Reviews

Clayton Huggett

National Academy of Sciences

FIRE RESEARCH ABSTRACTS AND REVIEWS

Robert M. Fristrom, Editor

Geraldine A. Fristrom and Girard L. Ordway, Associate Editors

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.

Editor: Robert M. Fristrom, Applied Physics Laboratory
The Johns Hopkins University, Silver Spring, Maryland

Editorial Staff: Geraldine Fristrom, Joan M. Macdonald

Volume 13 Number 3

Fire Research Abstracts and Reviews

Committee on Fire Research
Division of Engineering
National Research Council

NATIONAL ACADEMY OF SCIENCES
Washington, D. C.
1971

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FOREWORD

It is with regret that your editor must report the death of Mrs. Emma Jane Whipple, Staff Associate to the Committee on Fire Research. Mrs. Whipple has been with the Committee since its inception. She has enthusiastically served the Committee and the entire fire research field through many tasks: the editing of the *Biannual Directory of Fire Research*; editorial assistance on *Fire Research Abstracts and Reviews* and the multitude of details which arose in the arranging and editing of the various symposia. She was always helpful and above all, enthusiastic. Those of us who have worked with her will miss her pleasant, cheerful manner and sharp eye for detail which has made the publications of the Committee a source of pride to us.

The National Commission on Fire Prevention and Control has begun a series of public hearings. They are scheduled in Washington, D.C., February 15–17; in Dallas, Texas, April 25–26; in Los Angeles, California, June 27–28; in San Francisco, California, June 29, and finally in Washington, D.C., June 13, 1973. These hearings provide an excellent forum and as many of you as possible should plan to attend the hearings. If you feel that you have testimony of interest to the commission you should contact:

Mr. Clayton Willis
Director of Public Affairs and Congressional Relations
National Commission on Fire Prevention and Control
1730 K Street, N.W.
Washington, D.C. 20006

This issue begins with a series of papers from the Symposium held by the Committee on the "Role of Chemistry in Fire Problems." This interesting series provided an excellent summary of the contributions to the Fire Field from the area of chemistry. We also have a French article on Forest Fires translated by Dr. G. Ordway.

In the next issue, we plan to begin a series of articles describing multidisciplinary programs in the area of fire. We solicit short communications to acquaint our readers with the Fire Research Programs which exist in this and other countries and the objectives and specialties which they have.

ROBERT M. FRISTROM, *Editor*

NOTICE

The study reported herein was undertaken under the aegis of the National Academy of Sciences/National Research Council with the express approval of the Governing Board of the NRC. Such approval indicated that the Board considered that the problem is of national significance; that elucidation and solution of the problem required scientific or technical competence and that the resources of NRC were particularly suitable to the conduct of the project. The institutional responsibilities of the NRC were then discharged in the following manner:

The members of the study committee were selected for their individual scholarly competence and judgment with due consideration for the balance and breadth of disciplines. Responsibility for all aspects of this report rests with the study committee, to whom sincere appreciation is expressed.

Although the reports of study committees are not submitted for approval to the Academy membership or to the Council, each report is reviewed by a second group of scientists according to procedures established and monitored by the Academy's Report Review Committee. Such reviews are intended to determine, *inter alia,* whether the major questions and relevant points of view have been addressed and whether the reported findings, conclusions and recommendations arose from the available data and information. Distribution of the report is permitted only after satisfactory completion of this review process.

CONTENTS

Volume 13 Number 3

PAPERS PRESENTED AT FIRE RESEARCH COMMITTEE SYMPOSIUM—Role of Chemistry in Fire Problems.

ABSTRACTS AND REVIEWS

A. Prevention of Fires and Fire Safety Measures

B. Ignition of Fires

C. Detection of Fires

D. Propagation of Fires

E. Suppression of Fires

F. Fire Damage and Salvage

G. Combustion Engineering

H. Chemical Aspects of Fires

I. Physical Aspects of Fires

J. Meteorological Aspects of Fires

K. Physiological and Psychological Problems from Fires

L. Operations Research, Mathematical Methods and Statistics

M. Model Studies and Scaling Laws

N. Instrumentation and Fire Equipment

O. Miscellaneous

BOOKS

PERIODICALS

TRANSLATION

MEETINGS

AN INTRODUCTION TO COMBUSTION CHEMISTRY

W. G. BERL

Applied Physics Laboratory, The Johns Hopkins University

Introduction

The question we are asked to discuss is: What major contributions to reducing fire losses and protection costs have come and can be expected to come from insights into the *chemical* aspects of fires? Also implied in this question is a corollary: if areas of ignorance exist, should they be cleared up by the fire research community or can one expect their solution to come from elsewhere? I raise this point because only a small fraction of the research on the physical and chemical principles of fires has been directly supported thus far by sources concerned with fire suppression. For example, what is known about the structure of premixed flames was obtained largely in support of jet engine development; understanding of ignition of materials by radiation was a consequence of work on defense against nuclear attacks; and the characterization of materials with respect to their behavior in fires is largely the responsibility of chemical manufacturers.

Five participants will address themselves in some detail to specific chemical aspects of fires. My purpose is to stress what one might achieve in practice with an organized, close look at "Fire Research" topics, particularly those related to urban/industrial circumstances. Understanding of principles, one feels, is essential in order to permit prediction of risks; to assess the adequacy of responses and to compare their effectiveness with what is theoretically required; to minimize unnecessary losses or ineffective prevention expenses; to reduce the scale of the counterattack in extinguishment; and, not least, to permit operations with reasonable safety in environments that are potentially hazardous.

Fire problems are largely chemical-engineering in nature. The basic phenomenon is a chemical reaction, strongly coupled with physical (fluid and heat flow) interactions which often may be dominant in determining the course of the fire. Since so many chemical substances, simple and complex, qualify as fuels, an enormous variety of special situations exist. However, the goals of a research effort are common, i.e., to develop principles of prediction (how will a fire develop?); to explore principles of initiation and suppression (how can a fire be prevented or extinguished?); and to set down design criteria that will lower fire risks and fire damage.

Added to these science/engineering-oriented problems are other important facets concerned with (1) the analysis of the fire services operations; (2) the training of professionals and the education of the public; (3) the economics of alternate solutions; (4) the acquisition and evaluation of meaningful statistics. Each topic represents an essential support to the ultimate goal of more rational control of fires. Being closely related to actual fire situations, they deserve detailed attention.

Combustion Reactions

I will describe, on the basis of a model fire situation, where chemical influences play a significant role and where physical effects predominate. The question I want to ask is: Is it possible to *predict* the time history of a fire from information that might be found in an appropriate design handbook?

I want first, however, to place fires into the more general context of reactions grouped together under the terms "Combustion and Oxidation." One cannot help but be astonished by the extraordinary subtleties which nature (and man) has discovered to convert carbon/hydrogen compounds into (mostly) H_2O and CO_2 and to utilize the energy liberated in this process for useful purposes.

Most basic (and chemically most complex) is the process of "respiration" in plants and animals by which carbon/hydrogen containing substances (proteins, carbohydrates, fats) are ultimately converted to carbon dioxide and water (and a small number of "waste products") while simultaneously generating heat and an untold number of compounds of essential use to the living organisms. This oxidation, taking place efficiently only near room temperature, represents the largest chemical conversion process on earth and is still several orders of magnitude larger than the controlled and uncontrolled chemical combustion reactions that occur at higher temperatures.

In these metabolic reactions the fuel substrates are converted by numerous small interlocked steps, with oxygen addition and water elimination, into simple carbonyl-containing organic acids, 3–6 carbon atoms in length. Carbon dioxide is eliminated with the help of specific enzymes from some of these acids (mainly the β-keto acids) and replaced, in turn, by acetate, a common product of the "in vivo" degradation of carbohydrates, fats or proteins. The oxygen, in turn, is reduced to H_2O in a number of steps involving iron in various valence states, bound to coenzymes. The energy liberated in this set of reactions is, in turn, transferred to the fuel degradation reactions which require it in a number of endothermic steps. This set of reactions in living organisms leads to the same products as the combustion reactions, but the detailed pathway bears no resemblance whatever.[1]

At more elevated temperature (a few degrees above room temperature for the highly reactive boron hydrides, and a few hundred degrees for hydrocarbons) a new oxidation regime exists in which reactions proceed at reasonable rates, accompanied by "wave" phenomena in which flow processes and chemical reactions couple. In such "cool" flames the emphasis is still predominantly on complex chemical reaction pathways, although they are much less intricate than respiration. In the past 40 years, insights into these oxidation pathways of hydrocarbons have grown substantially (thanks, in large part, to the development of refined analytical techniques) so that the interlocked reactions and product distributions are becoming reasonably well understood. The reactions are still so varied and interwoven (74 products having been identified in the oxidation of 3-methyl pentane[2]) that a prediction of rates of product formation from first principles is not possible. It should be noted that the final products, although containing some $CO_2/CO/H_2O$, are far removed from the thermochemically most stable chemical equilibrium state.

One may wonder about the practical value of such studies. They have had a profound effect on the large-scale synthesis of many chemical compounds by partial oxidation from hydrocarbon raw material. Quite unexpectedly, they have also given insight into air pollution problems from the incomplete oxidation of hydrocarbons in practical devices since several of the reaction products will, with oxygen, react further photochemically to form "smog."

A gap of several hundred degrees exists between "hot" flames in which oxidation reactions go essentially to completion and the "cool" flames just described. This is due to experimental difficulties which do not permit sufficiently rapid heating and cooling to study the behavior of complex systems under isothermal conditions, although shock tube investigations are beginning to fill the gap.[3]

In the regime of "hot" flame reactions we distinguish two pathways for transforming reactants into products: In "premixed" systems in which fuel and oxidizer are mixed on a molecular scale (or, as in monopropellants, exists in the same molecule) flame propagation is made possible in a steep temperature and composition gradient by an elegant combination of heat flow and diffusion from the hot combustion products into the unreacted mixture, coupled with chemical reactions within the combustion wave. The pathways are fewer in number and complexity compared to the "cool" flames where small changes in condition can have profound effects on product distribution.

Premixing need not be confined to the molecular level. Nonhomogeneities comparable in size with the reaction zone thickness will behave similar to the homogeneous case. As the "unmixedness" of fuel and oxidizer increases and, an added complication, when liquid or solid fuel phases are involved, then mixing, heat transfer and radiation contributions become an increasingly important part of the reaction and frequently dominate the rate of the combustion process. In most fire situations we deal with such coarsely distributed fuel–oxidizer mixtures. As a consequence, in normal fires the chemical reactions do not control the rate of the overall conversion. Thus, many of the phenomena of on-going fires (particularly their propagation and steady-state burning rates) are only weakly coupled with the chemistry of the conversion reaction and depend instead on the intrinsic nature of the reactants, their thermochemical properties, the mixing and heat transfer conditions, the degree of subdivision, etc. We will deal with specific examples in the next section.

Fire Situation

The fire situation I want to discuss consists of a compartment that contains:

(1) A relatively easily ignited fuel source (which may be a liquid fuel in a pan; or a continuous array of solids, such as paper strips; a discontinuous array of solids, such as vertical fibers; or interconnected solids as exemplified by wood cribs);
(2) A flat ceiling of a combustible material (wood);
(3) A floor of similar material (fireproofed by a chemical treatment).

The compartment has windows and ventilation ducts. It is equipped with fire detecting devices, contains a supply of fire inhibitors (chemical or water) and a living organism. A fire in such systems would have the following history: An energy input of adequate size near the fuel–air interface initiates a flame. This flame will propagate across the fuel source. After reaching the fuel boundary a steady-state fire situation will result. The products of combustion will leave the fuel source, forming a convection column. This column will interact with the combustible ceiling, be deflected and ignite the ceiling material. A flame will be formed under the ceiling which, in turn, can ignite the combustible floor.

The rates of fuel consumption, the nature of the combustion products and the pattern of gas flow will be influenced by the wall openings, the dimensions of the structure and the fuel source, which, in turn, affect the effectiveness of the countermeasures.

The questions I want to explore are: What can be said about the speed of progress of a fire in such a situation? Can effects of changes in fuel arrays be predicted? How do variations in compartment dimensions affect fire progress? Can the temperatures and the gas compositions inside the compartment be predicted? What are the effects of a fire on the organism?

It will be no surprise to learn that an overall analysis is not possible, neither now nor very soon. A promising beginning has been made on some of the individual steps. But many design parameters are missing as well as knowledge of the interactions among the various steps. I will summarize where work has been done or is in progress on the component parts of the problem and emphasize those aspects where chemical parameters appear to be important or dominant.

Ignition

Ignition energy requirements for homogeneous gas mixtures are known for a variety of conditions as are radiant energy requirements for the ignition of solids.[4] While the detailed chemical and physical principles responsible for the establishment of a propagating combustion "wave" are only moderately clear (for example, the steps in the ignition of a radiation-ignited solid are not even qualitatively understood), the energy requirements are well known. Thus, much information on minimum electric spark or radiation ignition requirements is on hand and techniques for measuring them are well established although little has been published about energy requirements in the presence of combustion inhibitors or retardants. If ignition is due to convective or conductive heat transfer, the available design information is much more limited.

In view of the convenience of direct measurement, no strong motivation exists to pursue a "first principles" approach in order to solve practical ignition problems. However, since the chemical characteristics of the fuel (and of the oxidizer) enter strongly into the ignition energy requirements and the ignition limits beyond which no self-sustaining reactions are possible no matter what the size of the ignition source, a better understanding of the ignition process would provide a useful guide for the selection of effective inhibitors or fire retardants.

Propagation

The rate of flame propagation across a liquid surface or a solid fuel array is a complex phenomenon in which chemical parameters play by-and-large a secondary role (except in the case of propagation for liquids of sufficiently high vapor pressure that provide mixtures within the flammability range of the fuel). In the common cases, flame propagation rates are controlled by convective or radiant heat transfer processes, which determine fuel evaporation from liquids and fuel generation from solids.

Detailed analyses of the propagation of laminar diffusion flames across solids have been made by McAlevy, by Tarifa and by de Ris.[5] The analysis for propagation across thin and thick fuel slabs is based on the assumption that the gas phase chemical reaction is not rate limiting except near and at the propagation limits. Generation of combustible gases from the solid is caused by heat transfer in front of the diffusion flame which introduces conductive heat transfer, radiation, fuel vaporization, the thermal properties of the fuel and the temperature of the flame into the analysis. With liquids an additional flow process of convective mixing of heated fuel with cold liquid occurs ahead of the flame[6] which influences the vapor generation rate. No analysis of more complex fuel arrays (such as solid fuel cribs) has as yet been made, but chemical reactions appear adequately fast and do not set the limit on the rate of flame propagation, as long as the system is situated well within the flammability regime. As in the ignition case or the steady-state burning (next section) near the propagation limit, chemical factors can play a very important role.

Steady-State Burning

The burning of liquid fuel pools and of solid structures, once flame has spread from a localized ignition source to the fuel boundary, accounts for the bulk of the heat generation and the nature of the combustion products in typical fire situations. The studies of Blinov and Khudiakov on the rate of burning of liquid fuel pools have recently been extended and reanalyzed.[7] There is little doubt that, in the region where burning proceeds the chemical processes are too rapid to be rate limiting. Fuel generation and the mixing of fuel vapor and air determine the overall fuel consumption rates. Scale effects are pronounced since transitions from laminar to turbulent flow affecting the mixing of fuel and oxidizer, set in with pan dimensions of practical sizes. Also, the heat transfer mechanism to the fuel bed changes from convection to mixed convection-radiation with increase in scale due to changes in the optical thickness of the radiating gas column.

If combustion takes place within an enclosure containing a limited amount of air but which communicates with an unlimited air supply via flow-limiting openings (windows or ducts) the burning rates will be strongly affected by the "ventilation rate" as set by these constrictions.[8] Very pronounced effects on burning rates, gas composition and circulation within the enclosure have been qualitatively observed.

While the fluid dynamic and heat transfer effects play a dominant role in most situations of common fire experience one should not lose sight of the fact that such fires can be extinguished by interfering with the evaporation process (by cooling), by lowering the oxygen partial pressure (by inert gas admixture or lowering of total pressure) or by the addition of inhibiting chemicals. The two last interferences clearly affect the chemical reaction rates by modifying the balance of heat generation in the gas phase and heat transfer to the fuel.

These limit conditions, so important in the practical extinguishment of fires, are not now amenable to analysis nor will there be a guide to further development unless the mechanism of combustion limits (including the dominant mechanisms in the absence and presence of chemical inhibitors) are understood. The availability of counterflow diffusion flames[9] has opened up a promising avenue for such studies leading to extinguishment under realistic conditions. It has already been demonstrated that diffusion flames can be extinguished either by thermal quenching in the presence of a heat sink or due to chemical limitations on the combustion rate. Those interesting studies could readily be extended to investigate the influence of chemical inhibitors and, thus, lead to a much better understanding of the events taking place at or near the limits of flame propagation.

Convection Column

In the absence of confining walls, the properties of turbulent buoyant columns above a source of heat are reasonably well understood. Similarly, the composition and temperature profiles of convection columns above burning fuels have also been adequately analyzed.[10]

An interesting problem in fire propagation arises if the combustion takes place inside an enclosure. The flow of hot gases under a potentially combustible ceiling of the enclosure has an important bearing on two important items: it determines the response of devices installed to detect the presence of fires in the enclosure; it also determines how rapidly ignition of the ceiling due to convective heating will take place.

Preliminary studies are being made[11] on the time–temperature and velocity of buoyant plumes impinging on horizontal surfaces. This is normally an aerodynamic process, without chemical inputs. However, as soon as the ceiling material begins to decompose the processes leading to eventual ignition are strongly affected by the chemical properties of the ceiling, and by the chemical composition of the buoyant plume.

Ceiling Fires

A steady flame, burning below a horizontal combustible ceiling, is a diffusion flame in which fluid dynamics and heat transfer to the fuel determine the burning rate, although limits on chemical rate may be responsible for extinction.[12] Such ceiling fires have been investigated by de Ris who presents good evidence that turbulent free convection from the flame to the fuel is responsible for burning rates, which are set by the mass-transfer driving force that characterizes the heat flow from the combustion gases to the fuel source, taking into consideration the effect of mass addition from the decomposing ceiling on the transport properties. Such a flame is a source of radiation which may lead to further fire spread on surfaces (floor, side wall) which, in turn, will undergo thermal decomposition and ignition. Ignition at a distance is commonly observed (flashover) and may be initiated either by flame propagation in the gas phase if sufficient combustible gases accumulate in the enclosure or may be caused by ignition at or near the heated surfaces as products from thermal decomposition mix with the ambient atmosphere.

Detectors

A large number of detector designs are conceivable and have been built and tested. Those that depend on measurements of physical constants such as temperature, temperature gradients, light emission, are, of course, uninfluenced by the chemistry of the combustion reaction. In view of the presence of large amounts of CO in most fire situations, its detection is a good clue of potential fire hazards and is applicable in situations where direct physical measurements of flame properties are impractical. This is particularly true for large buildings with many interconnected cubicles, making use of a common air supply. Other chemically-related indications of fires are based on the detection of smoke or of odors typical of thermal decomposition products of common building materials.

Inhibition and Extinction

Existing fire can be brought under control if ignition and propagation are prevented. In the present example this can occur in several ways and by several modes. The effect of water is predominantly through its interference with the gasification of solid fuels. It also can affect the temperature of the fire convection column and, thereby, interfere with the ignition of ceilings or walls by convection. Water droplets, in addition, may reduce radiant energy transfer from flames to unignited fuels. It is doubtful that water vapor has a substantial specific effect on the chemical reactions in the gas-phase combustion zone.

Chemical inhibitors, on the other hand, exhibit their influence largely by interfering with the chemical reaction in the gas phase[13] and may also interact with the reaction mechanism in the solid fuel as it decomposes. The behavior of fire retardants is still poorly understood. Some exert their influence in the gas phase to which they are transported with the combustible constituents of the fuel.[14] Others produce a physical barrier that alters the heat flow to the fuel. The effects are predominantly chemical in nature.

Chemical Effect of Fires on Living Beings

Exposure of living beings to hot gases can be lethal or produce serious burn injuries. Many fatalities or severe sicknesses can also be produced by exposure to the chemical products of combustion. The state of knowledge in this field is rudimentary. While the toxic effects of carbon monoxide are well established, the possible injurious effects of other products of combustion are not well documented. This is, in part, due to the difficulty to specify the chemical compositions of the products of combustion of thermally decomposing (but not burning) solids, or of complex fuels burning in oxygen-limited atmospheres, particularly under conditions where the chemical reactions do not reach equilibrium temperatures and compositions.

Conclusions

What conclusions can we reach? "Normal" fire behavior is strongly affected by the fluid dynamics and heat flow parameters of the combustion, by the physical properties of the fuels and by the dimensions of the fire and of the structure within which it is contained. Propagation across surfaces,[5] in ducts,[15] across arrays of various sizes and subdivisions,[16] fall into this category, as do the properties of convection columns, the influence of windows, etc. Chemical reactions in the gas phase are too rapid to have any limiting effect on the overall process.

However, flame initiation (ignition) and termination (suppression) are strongly affected by the nature and rates of chemical reactions. Similarly, the nature and generation of combustible gases from solids is strongly influenced by chemical factors. Their unquestioned complexity makes it a difficult task to elucidate their effects. However, they should be pursued if the goal of fire research is to minimize fire occurrences and to maximize the effectiveness of fire suppression and retardation.

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CHEMICAL THERMODYNAMICS AND FIRE PROBLEMS

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Introduction

Throughout history there has been a continuing struggle to subordinate fire to the service of man, but the mastery is incomplete. The usual concept of a fire is the union of a fuel with oxygen, but in its most general aspect, we must regard fire as a chemical reaction. The study of chemical reactions is a relatively recent activity of man that has provided many benefits, but again the mastery is incomplete, since we still experience reactions that rage out of control. A fire is a special kind of reaction; it is spontaneous, it evolves heat, it is not reversible, and the reaction products are generally smaller molecules and of greater number than are the reactant molecules.

The past few centuries have witnessed a continually accelerating growth of chemical manufacturing, and of the study of chemical reactions. Thus, for millions of years fires involved the combustion of natural materials: grass, wood, oils, fibers, foodstuffs, and the like. Chemical manufacturing introduced chemical fires feeding on man made chemicals and resulting in a larger number of fire types and generating a wider range of fire problems. For example, the combustion of wood in air has happened often enough so that there is a reasonable body of experience available to aid in extinguishing such a blaze. On the other hand, a leak in an iron pipeline transporting chlorine under pressure has been known to result in a fire which generates copious clouds of ferric chloride as the pipe burns away. In this case, experience in extinguishing such a blaze is limited. The corrosiveness of the reaction products raises some new problems for the first time.

The world of today witnesses an increasing variety of fires involving both natural and man made materials in combinations that are increasingly complex. The job of the modern fire fighter involves something more than soaking the blaze with water to cool it below the ignition temperature. It is necessary to know what materials are burning in order to properly extinguish a complex fire. It is necessary to have some idea of the degree of reactivity of the reactants so the fire fighter can do his work at close range or maintain a safe distance if the reactants may detonate. It is necessary to know if the products of the fire are toxic, or present some unhealthy condition to the humans who are exposed.

Society must also decide how much safety it is willing to pay for, because it costs money to fight fires and bring them under control. After all, fires or chemical reactions proceed according to natural laws, most of which are known, but have not yet been applied in sufficient detail. It is my belief that this is one area where progress can be made and the rate of progress will be related to the amount of national treasure directed at this problem.

The Significance of Thermochemistry

The word THERMODYNAMICS denotes the dynamic or mechanical action of heat, while the word THERMOCHEMISTRY expresses the relations existing between chemical action and heat. The laws of thermodynamics and thermochemistry are linked together and govern the behavior of all the tangible material in the universe. The first and second laws of thermodynamics were developed and proven during the nineteenth century while the laws of thermochemistry are a development of the twentieth century[1] which partially accounts for the fact that they have not been as widely applied as is fully warranted. Thermochemistry is a quantitative science in which a man of action can have the satisfaction of doing something no one else has done, and of making a true contribution to world knowledge. The work area is the frontier where what is known meets that which is not known. It is on this frontier that new knowledge can be put to work, and where problem-solving takes place. As new experimental thermochemical data are generated, new insight is brought to the fields studied. Note too, that thermochemistry rests on the measurement of heat and that calorimetry has been adequately developed to meet our current needs.

The Basic Thermodynamic Properties

The basic thermodynamic properties are: energy E, entropy S, pressure P, absolute temperature T, and volume V. The forces between the atoms that compose any kind of matter are related to the energy, while the arrangement of those same atoms is related to the entropy. Quantitative information on the behavior and stability of a chemical substance can be obtained by linking the energy and entropy with the absolute temperature, while these three properties can be derived entirely from well known laboratory measurements.[2] These thermodynamic quantities are related thus: The Gibbs energy (G) is defined as

$$G \equiv E + PV - TS, \tag{1}$$

while the enthalpy or heat content (H) is defined as

$$H \equiv E + PV; \tag{2}$$

hence,

$$G = H - TS. \tag{3}$$

When the reactants and products of a constant temperature reaction are in their standard states, we can write

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ. \tag{4}$$

A general reaction at equilibrium can be symbolized

$$aA + bB \rightleftarrows cC + dD \tag{5}$$

where A, B, C, and D represent the thermodynamic concentrations of the components, and a, b, c, and d indicate the number of moles present at equilibrium. The equilibrium constant (K) for this reaction is given by

$$K = \frac{(\text{activity of } C)^c(\text{activity of } D)^d}{(\text{activity of } A)^a(\text{activity of } B)^b}. \tag{6}$$

This equilibrium constant K for the reaction is related to the standard Gibbs energy change by

$$-RT \ln K = \Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ, \tag{7}$$

where R is the universal gas constant. Rearranging, we have

$$\ln K = -\Delta H^\circ / RT + \Delta S^\circ / R. \tag{8}$$

This relationship shows that the atoms present in a reaction will prefer the molecular configurations in which the entropy is maximized and in which the energy is algebraically minimized.

Maximum entropy is achieved by the molecular configurations with the largest number of states available to the system, thus providing more "freedom" for the system. Minimum energy is achieved by the molecular structures in which the atoms are most strongly bound to each other, thus providing the maximum "stability" for the system. In evaluating the equilibrium constant K for a reaction, the result is a compromise between these two opposing factors: stability and freedom. The stability term ΔH° is more dominant at low temperatures, but at high temperatures the equilibrium is more heavily influenced by the freedom term ΔS°. Application of these thermochemical principles to real problems requires the thermodynamic data for the substances involved in the problem.

Rapid Computation of Chemical Equilibria

The past two decades have been marked by the very active development of electronic digital computers. Their present state of development permits the detailed solution of many problems that were formerly regarded as too extensive to contemplate. Today, lengthy computations of reaction equilibria based upon chemical thermodynamic data are commonplace.[3] Costs of such calculations are low enough to permit widespread employment of this technology. A description of the capabilities of a specific computer procedure will give a better idea of what can be accomplished.

In a specific chemical equilibrium problem, the reactants interact to form the natural products which at equilibrium will turn out to be those products possessing the largest Gibbs energy change from the reactants. The input to the computer consists of

(a) the number and kind of atoms in each mole of reactant,
(b) the heat of formation for each reactant,
(c) the quantity of each reactant present,
(d) the pressure and temperature where the equilibria are to be calculated, or the maximum temperature that the reactants can achieve,
(e) an estimate of the maximum temperature reached ($T_{\max}$), and
(f) the name of each reactant.

Stored in the computer is a massive list[4] of possible products with a complete tabulation of thermodynamic properties of each product. The computer matches the elements in each reactant against the elements in each product species in the stored product list and discards the species having elements not in the input reactant set. The remainder constitute a list of possible reaction products, which are then ordered according to the Gibbs energy at $T_{\max}$. The computer then selects the most stable products at T_{max} and balances the stoichiometry of the reactants and products. Once the product composition is established, the enthalpy of the products from 298°K to T_{max} is compared with the enthalpy of the reaction. If these two enthalpies are unequal, the computer selects a new T_{max} and continues iterating until these two enthalpies are equal. From the final equilibrium composition at 1 atm total pressure, the final number of moles can be calculated, together with the enthalpy and entropy change of the reaction, and the pressure developed by compressing the products from 1 mole of reactants into 1 molar volume at T_{max}. This is one single set of options that can be calculated by a versatile program at a cost commensurate to one-tenth of a man hour of time.

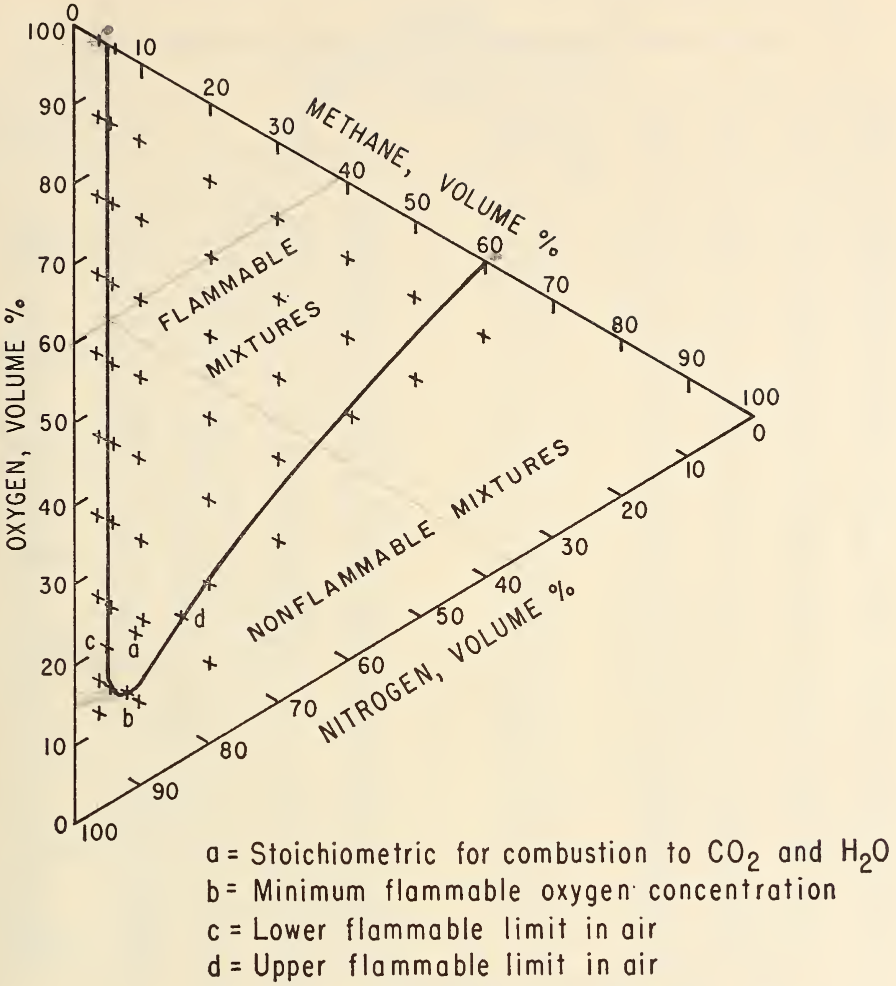
The Methane–Nitrogen–Oxygen System

As an example, detailed calculations of the methane–nitrogen–oxygen system were calculated. Figure 1 shows the flammability diagram for the system at 26°C, 1 atm pressure, and delineates the compositions which are flammable. The series of compositions given in Table I were input to the computer with the instructions to calculate T_{max} and the enthalpy generated for each composition. Figure 2 is a plot of the calculated adiabatic equilibrium flame temperatures; the dotted line indicates the experimental boundary between the flammable and nonflammable mixtures. Note the steep temperature–methane concentration gradients; 200° is equivalent to a change of 1 mole % methane concentration. A lean-limit flame temperature of 1675°K±200°K will define the boundary between flammable and nonflammable compositions. This is in agreement with the temperature found by Fenn and Calcote[5] in their kinetic studies. They have shown that this lean-limit boundary is related so closely to the activation energy for methane combustion that practical activation energies for combustion can be derived from the observed adiabatic equilibrium flame temperature of the lean-limit mixture. This is a very important relationship between kinetics and thermodynamics. Figure 3 shows the calculated heat in kcal/100 grams released by equilibrium combustion of the compositions in the methane–nitrogen–oxygen system. The highest heat releases occur along the methane–oxygen binary as expected.

The Vinyl Chloride–Air System

Chlorinated hydrocarbons are widely used for many purposes and are shipped in tank-car quantities. At about 2:45 P.M., Thursday, September 11, 1969,[6] near Glendora, Mississippi, there was a railway wreck in which 15 cars were derailed. Eight of these were tank cars containing vinyl chloride, one of which was ruptured and was reported to be leaking at 8 P.M., but there was no fire. At about 9 P.M. the vinyl chloride became ignited from sparks caused by a Mississippi utilities crew trying to remove three limbs from nearby power lines. At 6:45 A.M., Friday, one car of vinyl chloride exploded, causing another car to be ruptured and ignited.

Due to some erroneous information (that burning vinyl chloride would produce phosgene) approximately thirty thousand people were evacuated from their homes unnecessarily. Mississippi National Guard troops were called in and martial law was put in force in the area. A special Army Team from Ft. McClelland, Alabama, Chemical School reported finding *no* phosgene in the area, and informed the



FROM: M. G. ZABETAKIS, U.S. BUR. MINES BULL. 627, (1965).

FIG. 1. Flammability diagram for the system methane, nitrogen, oxygen at atmospheric pressure, 26°C.

Mississippi National Guard that a phosgene hazard did not exist. In the vicinity of the wreck, some livestock were found dead by returning residents. However, a report issued later indicated that the livestock deaths were not phosgene-connected. After all fires were extinguished, of the eight vinyl chloride cars involved, one exploded, two burned, and five remained intact and were recovered.

The vinyl chloride–air system was studied over the whole combustion range. First, vinyl chloride was equilibrated with its thermodynamically most stable products from 300° to 1500°C. The thermal decomposition of vinyl chloride takes

TABLE I

Temperature and enthalpy generated by flammable compositions in the methane–nitrogen–oxygen system

CH_4 (mole)	N_2 (mole)	O_2 (mole)	T_{max} (°K)	Enthalpy (kcal/100 g)	CH_4 (mole)	N_2 (mole)	O_2 (mole)	T_{max} (°K)	Enthalpy (kcal/100 g)
0.040	0.000	0.960	1237	−24.5	0.200	0.000	0.800	2863	−94.3
0.040	0.100	0.860	1341	−24.8	0.200	0.100	0.700	2858	−95.0
0.040	0.200	0.760	1245	−25.1	0.200	0.200	0.600	2855	−95.7
0.040	0.300	0.660	1250	−25.4	0.200	0.300	0.500	2847	−96.3
0.040	0.400	0.560	1254	−25.7	0.200	0.400	0.400	2814	−95.8
0.040	0.500	0.460	1259	−26.1	0.200	0.500	0.300	2619	−88.2
0.040	0.600	0.360	1264	−26.4	0.200	0.600	0.200	1700	−51.5
0.040	0.700	0.260	1269	−26.8	0.200	0.700	0.100	889	−20.7
0.040	0.800	0.160	1274	−27.2	0.300	0.000	0.700	3033	−117.6
0.040	0.900	0.060	983	−18.9	0.300	0.100	0.600	3009	−117.6
0.060	0.000	0.940	1637	−37.0	0.300	0.200	0.500	2956	−116.1
0.060	0.100	0.840	1640	−37.4	0.300	0.300	0.400	2774	−108.3
0.060	0.200	0.740	1645	−37.8	0.300	0.400	0.300	2129	−78.6
0.060	0.300	0.640	1650	−38.3	0.300	0.500	0.200	1127	−34.4
0.060	0.400	0.540	1656	−38.8	0.400	0.000	0.600	3031	−135.7
0.060	0.500	0.440	1662	−39.4	0.400	0.100	0.500	2869	−128.1
0.060	0.600	0.340	1669	−39.9	0.400	0.200	0.400	2425	−105.0
0.060	0.700	0.240	1677	−40.5	0.400	0.300	0.300	1596	−62.6
0.060	0.800	0.140	1686	−41.2	0.400	0.400	0.200	981	−32.0
0.060	0.840	0.100	1410	−32.5	0.500	0.000	0.500	2615	−130.2
0.100	0.000	0.900	2274	−60.4	0.500	0.100	0.400	1971	−92.7
0.100	0.100	0.800	2268	−60.7	0.500	0.200	0.300	1134	−45.7
0.100	0.200	0.700	2272	−61.4	0.600	0.000	0.400	1524	−75.8
0.100	0.300	0.600	2278	−62.2	0.600	0.100	0.300	1028	−44.2
0.100	0.400	0.500	2286	−63.0	0.700	0.000	0.300	1000	−47.8
0.100	0.500	0.400	2296	−63.9	0.095	0.715	0.190	2223	−62.2[a]
0.100	0.600	0.300	2307	−64.9	0.086	0.793	0.121	1503	−36.9[b]
0.100	0.700	0.200	2282	−64.6	0.050	0.751	0.200	1481	−33.9[c]
0.100	0.800	0.100	1128	−25.5	0.150	0.672	0.179	1774	−50.6[d]

[a] Stoichiometric for combustion to CO_2 and H_2O.
[b] Minimum flammable oxygen concentration.
[c] Lower flammable limit in air.
[d] Upper flammable limit in air.

the following pattern as the temperature is raised:

$$2\,H_2C{=}CHCl \rightarrow 2\,HCl+CH_4+3\,C.$$

At the higher temperatures, the methane cracks

$$CH_4 \rightarrow CH_3+H \rightarrow C+2\,H_2,$$

forming methyl groups, atomic hydrogen, diatomic hydrogen, and graphite, and the

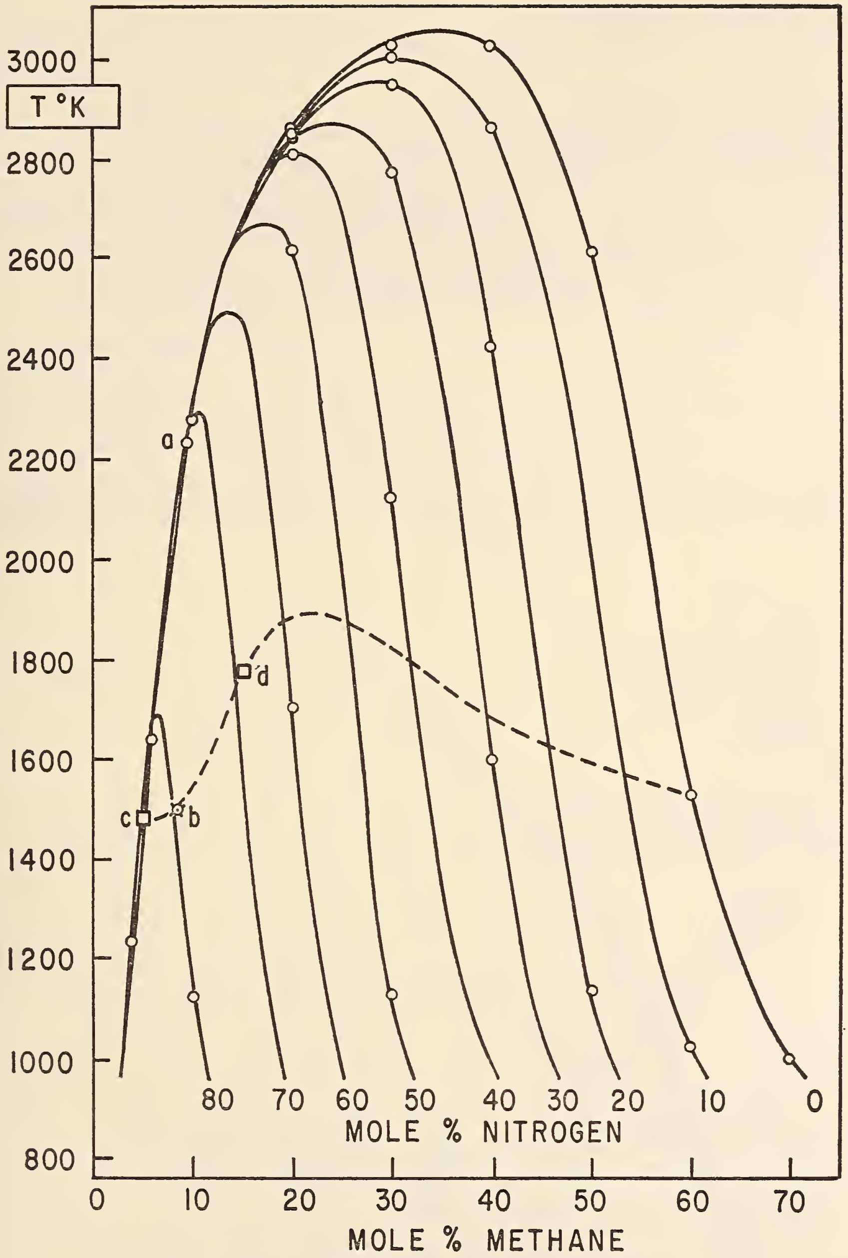


FIG. 2. Flame temperatures for the system CH_4–N_2–O_2.

hydrogen chloride decomposes to

$$HCl \rightarrow H+Cl,$$

forming atomic hydrogen and chlorine.

These relationships are shown graphically in Figure 4. Note that at no time is free diatomic chlorine formed in the presence of hydrogen. Atomic chlorine and atomic hydrogen are formed in equal amounts from the decomposition of hydrogen chloride and reach 1 ppm at 1000°C, 10 ppm at 1200°C. The decomposition of methane into solid graphite, and hydrogen and methyl radicals is also clearly shown.

Combustion of vinyl chloride with stoichiometric air requires enough air to contain 2.5 moles of oxygen, which is accompanied by 10.0 moles of nitrogen.

$$H_2C=CHCl+[2.5\ O_2+10.0\ N_2] \rightarrow HCl+2\ CO_2+H_2O+10.0\ N_2$$

This five-element (C, H, Cl, O, N) system is much more complex, but is readily solved by the computer for the products that are thermodynamically the most stable, and are shown over the temperature range 300° to 1500°C in Figure 5. With excess oxygen, the major products are indeed nitrogen, water, carbon dioxide, and hydrogen chloride. There are trace amounts of diatomic hydrogen (10 to 30 ppm),

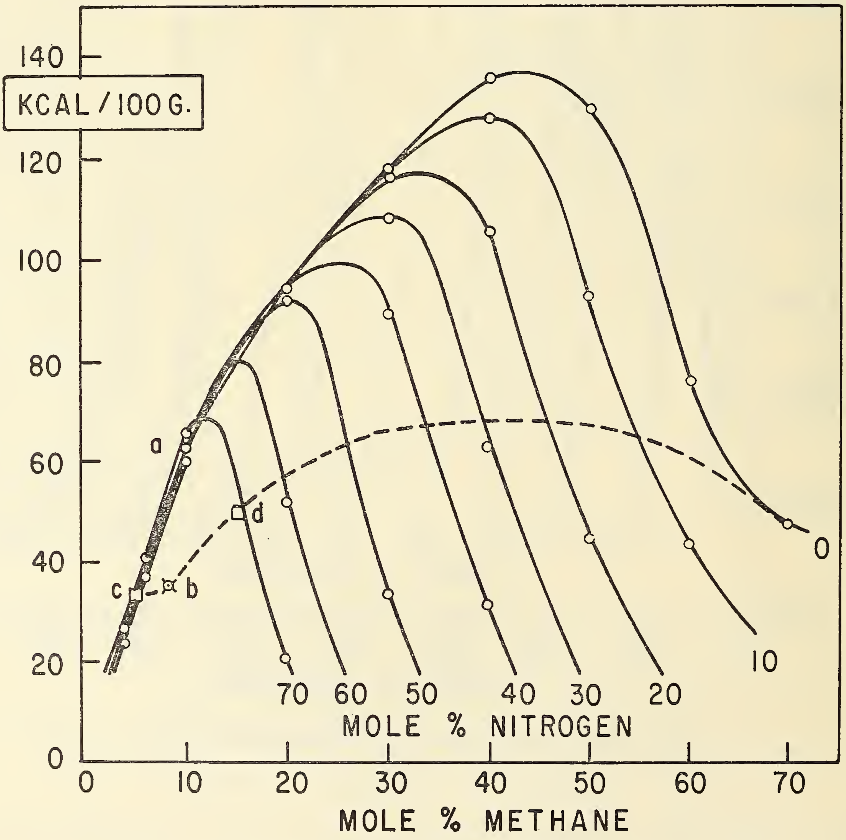


FIG. 3. Heat released by the system CH_4–N_2–O_2.

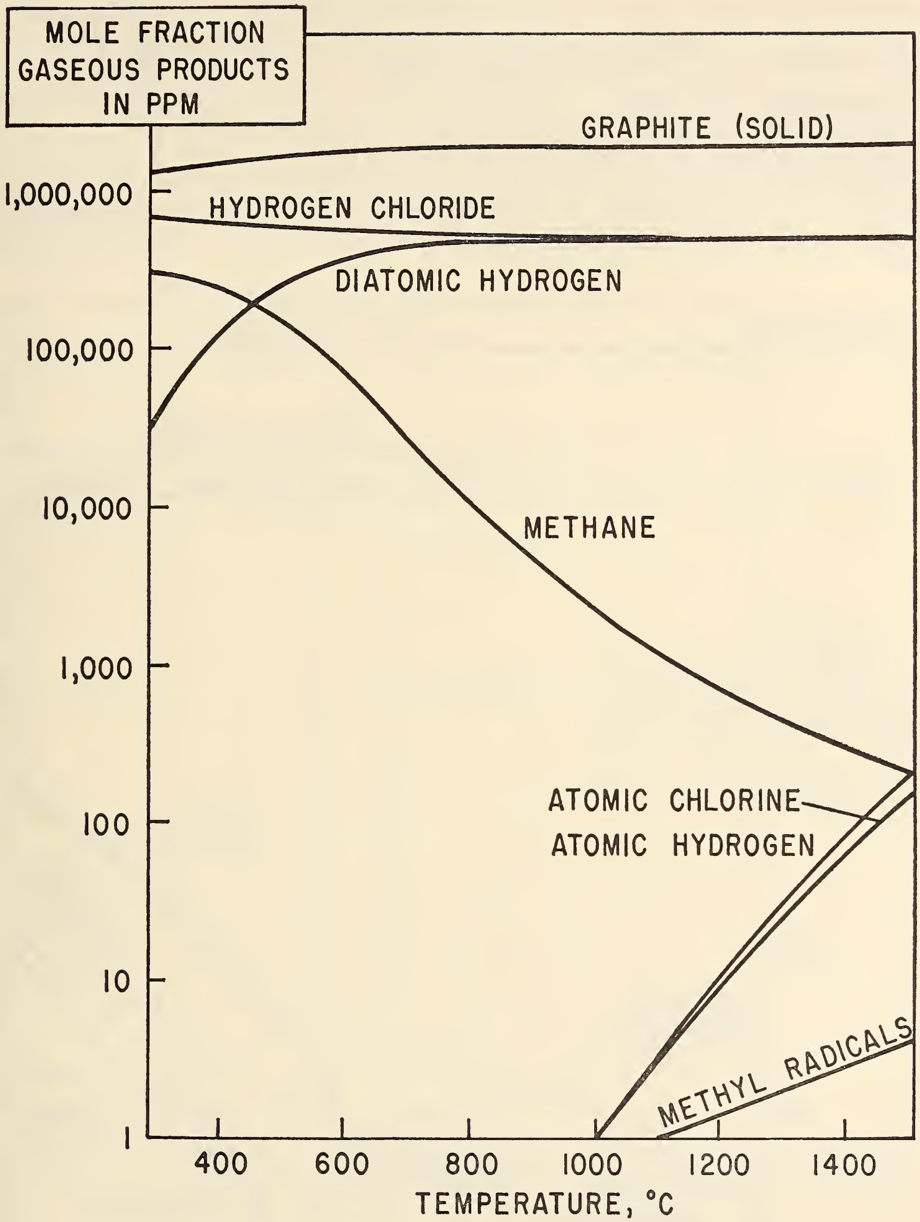


FIG. 4. Thermodynamically calculated decomposition of vinyl chloride.

and carbon monoxide (1 to 30 ppm) below 800°C, which increase in concentration as the temperature is raised; at higher temperatures, there are trace amounts of atomic chlorine (1 to 1000 ppm), diatomic chlorine (1 to 18 ppm), diatomic oxygen (1 to 300 ppm), nitric oxide (1 to 150 ppm) and hydroxyl (1 to 100 ppm). The system does form some phosgene, but it is of the order of 0.1 ppm.

Calculations were also made for underoxidized conditions containing 0.25, 0.50, and 0.75 stoichiometric air. The results for the species present at concentrations of 1 ppm or greater are given on seven figures tracing the separate constituents for clarity. Figure 6 shows how the concentration of solid graphite decreases as the air

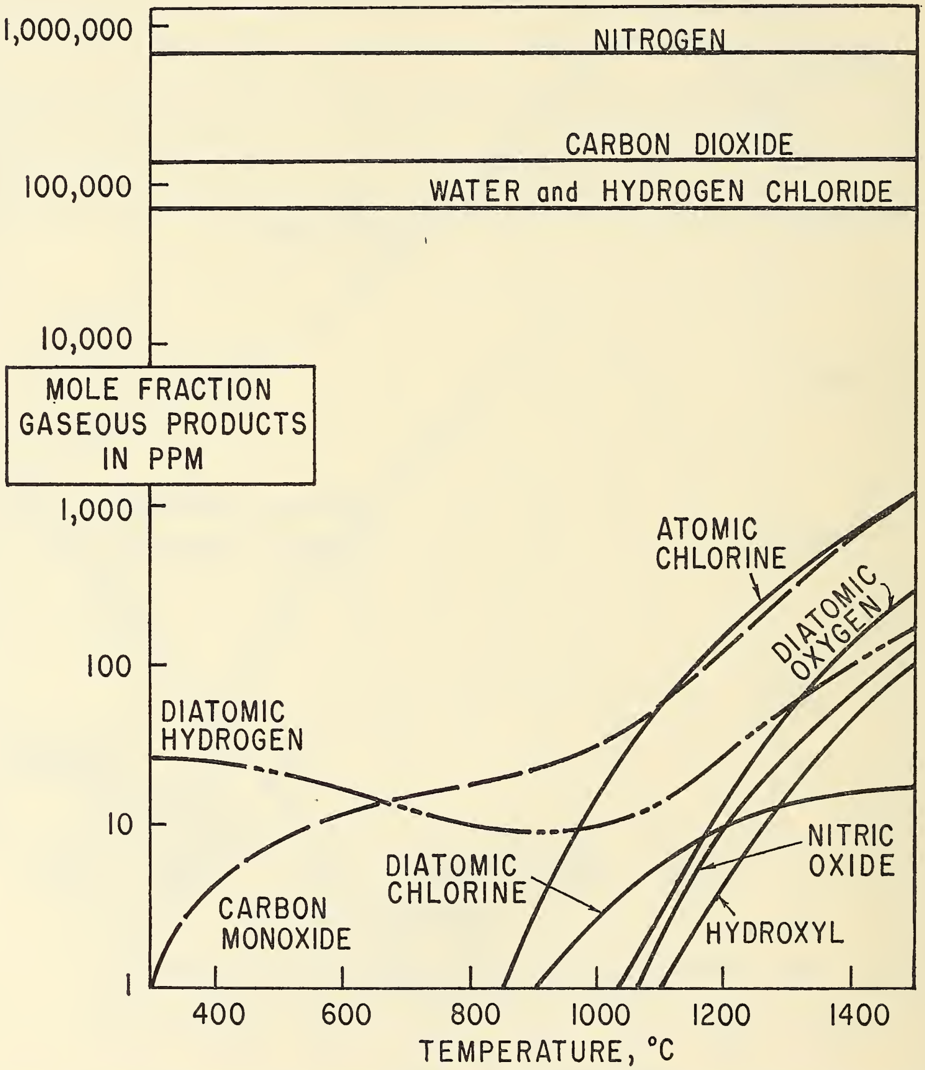


FIG. 5. Thermodynamically calculated combustion of vinyl chloride with stoichiometric air.

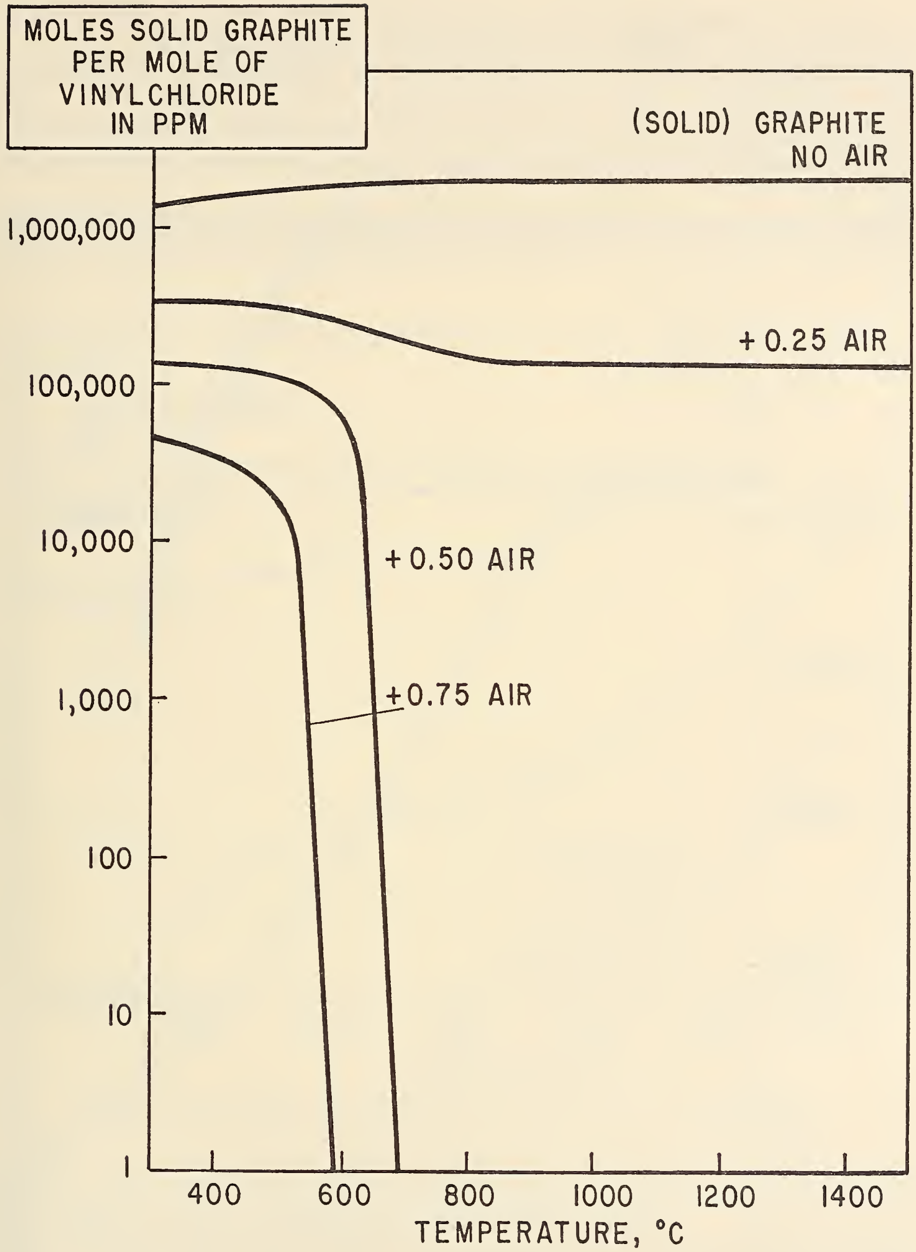


FIG. 6. Thermodynamically calculated vinyl chloride–air equilibria.

is increased. With stoichiometric air, the graphite is all oxidized to carbon dioxide and there is no soot. Absence of soot thus means complete combustion.

Figure 7 shows the increase of carbon dioxide as the quantity of air rises to the stoichiometric amount. Figure 8 shows the decrease of carbon monoxide as the air increases, reaching its lowest value at the stoichiometric point. Also included is the increase of the hydroxyl radical as the concentration of air rises to the stoichiometric point.

Figure 9 shows the expected rise in the nitrogen concentration as the air increases. Also shown is the decrease in methane concentration as the air rises to the stoi-

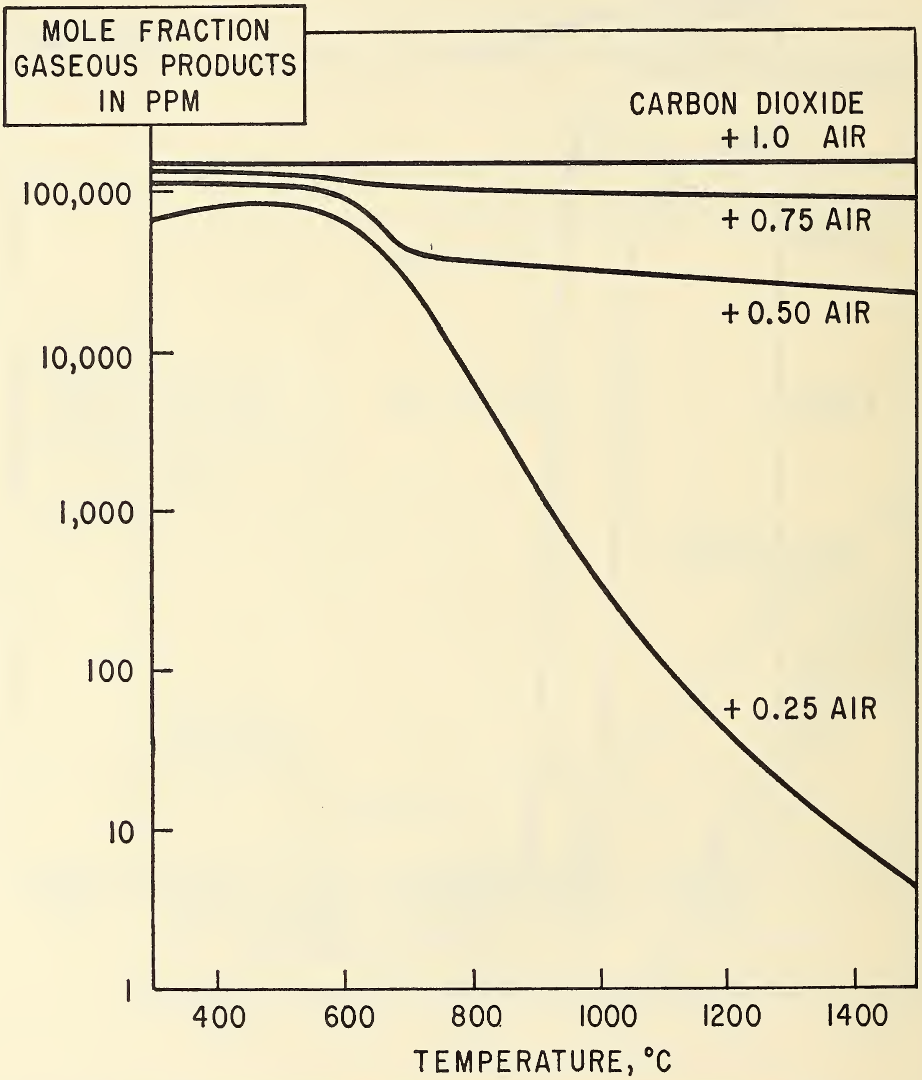


Fig. 7. Thermodynamically calculated vinyl chloride–air equilibria.

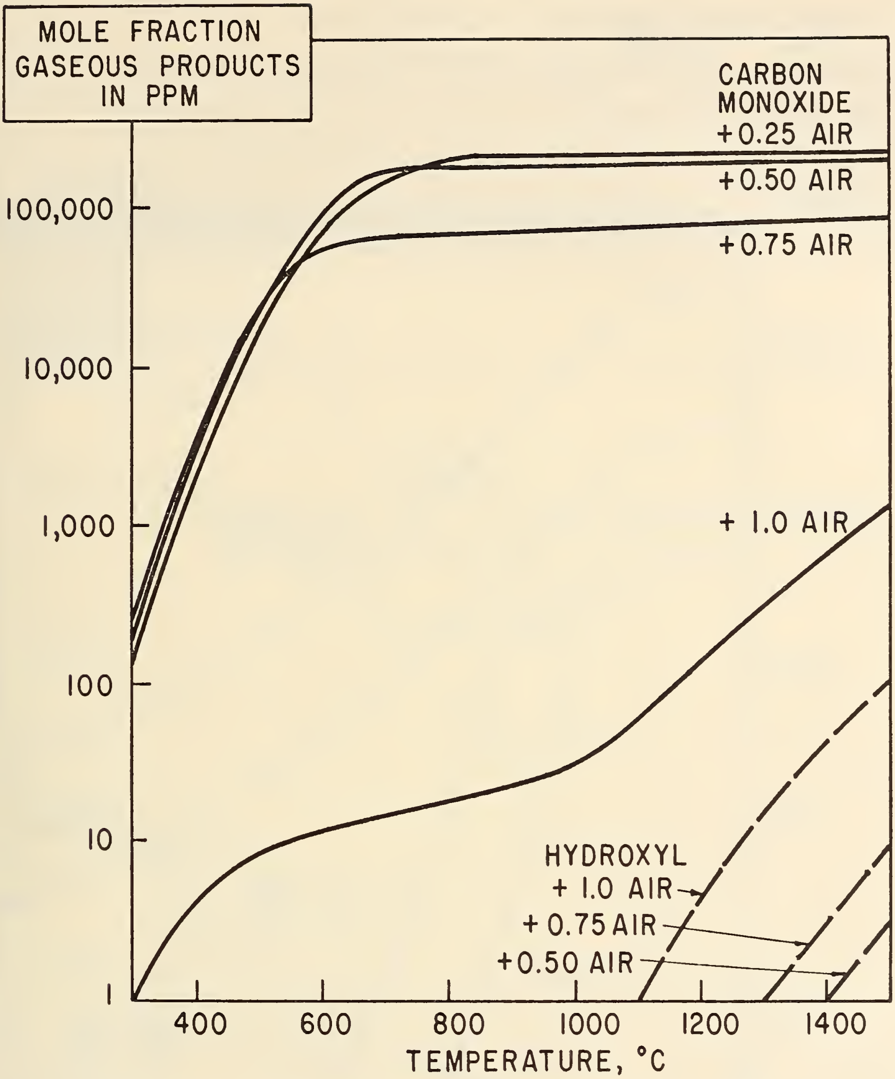


FIG. 8. Thermodynamically calculated vinyl chloride–air equilibria.

chiometric point. With the methane is also shown the high temperature methyl radical, which of course parallels the methane concentration.

Figure 10 shows the rise of water concentration as the concentration of oxygen increases. Since the system contains nitrogen and hydrogen, the concentrations of ammonia are shown and reach a maximum at about 400°C. Hydrocyanic acid synthesized at high temperatures by the reaction

$$CH_4+NH_3+1.5\ O_2 \rightarrow 3\ H_2O+HCN$$

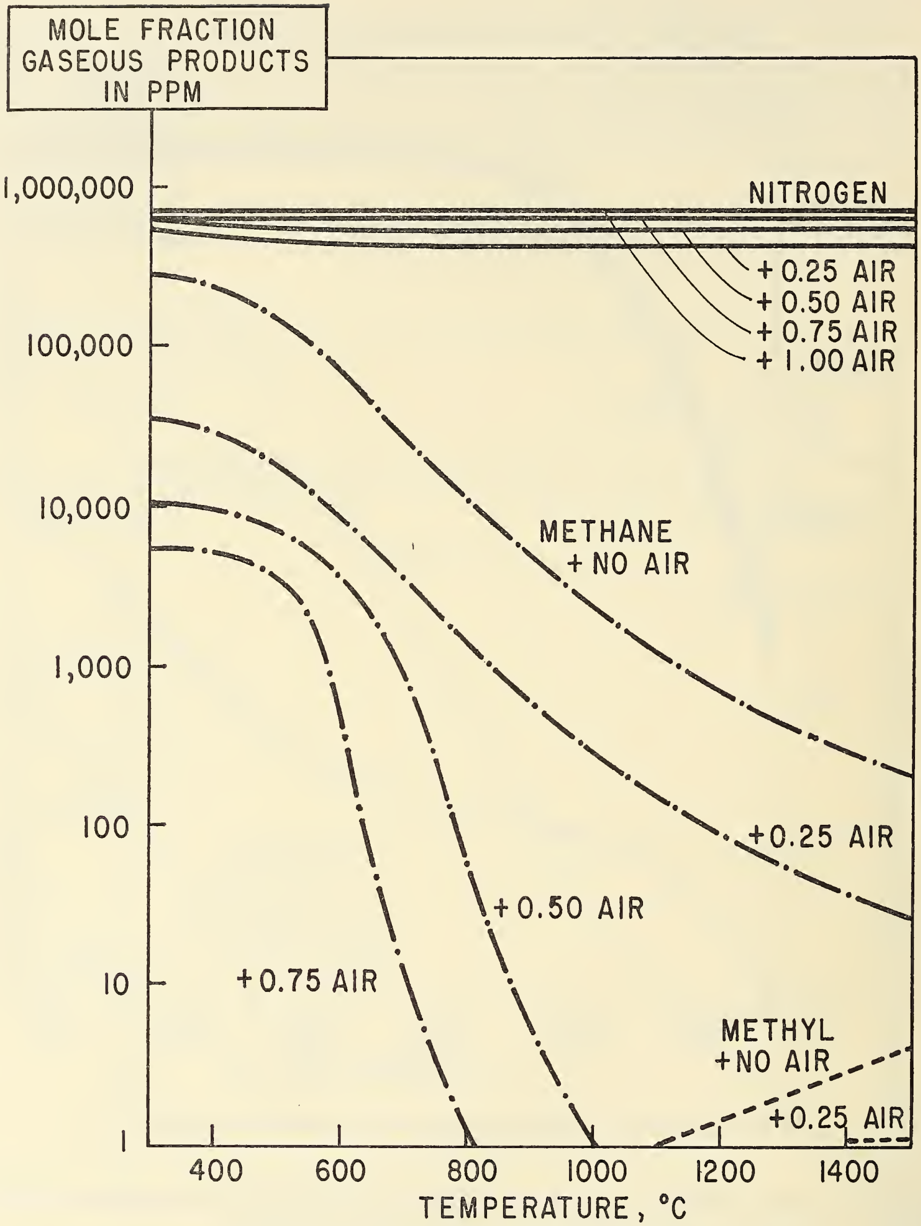


FIG. 9. Thermodynamically calculated vinyl chloride–air equilibria.

is present in the 0.25 and 0.50 air calculations. At stoichiometric air, nitric oxide is also formed.

Figure 11 shows the concentrations of both atomic and diatomic hydrogen, and how they decrease as the air rises in concentration. Figure 12 shows the concentrations of hydrogen chloride, and how they decrease as air is added. Also shown is the concentration of atomic chlorine, and how it decreases as air is added. Note, too, that with stoichiometric air, diatomic chlorine is formed (1 to 18 ppm).

Further study will show why phosgene is not found in these equilibrium mixtures at concentrations above about 0.1 ppm. Figure 13 shows the thermodynamically

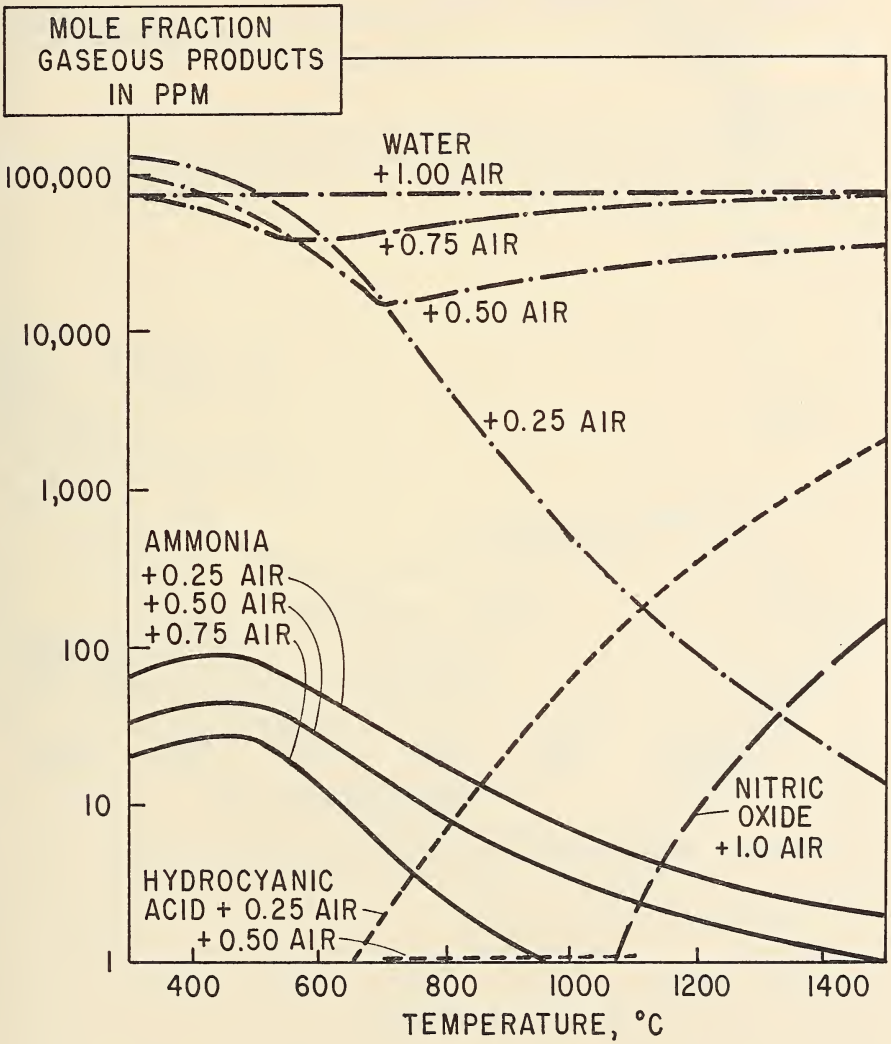


Fig. 10. Thermodynamically calculated vinyl chloride–air equilibria.

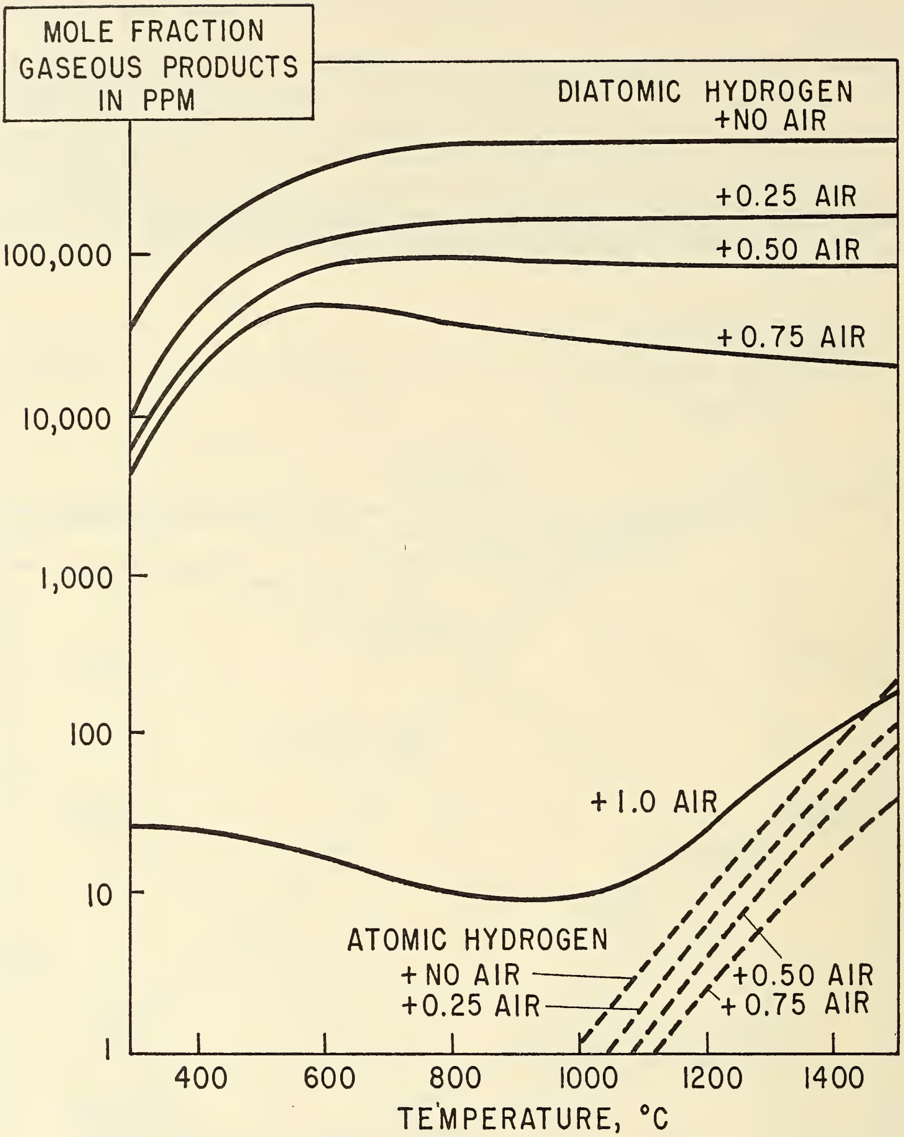


Fig. 11. Thermodynamically calculated vinyl chloride–air equilibria.

calculated equilibria between phosgene, carbon monoxide, and chlorine, according to the equation

$$COCl_2 \rightleftarrows CO + Cl_2.$$

The plot shows that phosgene is stable below about 200°C and, as the temperature is raised above 200°C, the phosgene begins to decompose to chlorine and carbon monoxide, and is all substantially decomposed by about 1000°C. Note that in order to form phosgene, the system must contain *both* chlorine and carbon monoxide.

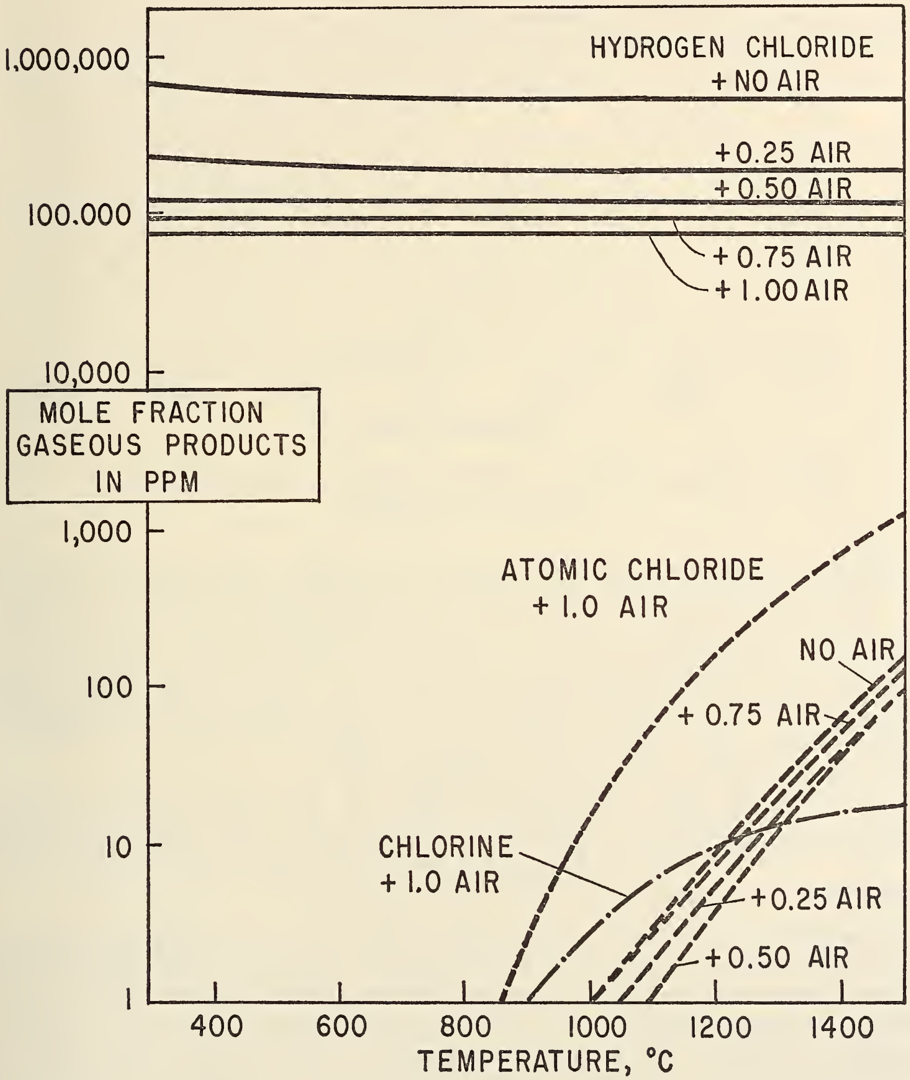


FIG. 12. Thermodynamically calculated vinyl chloride–air equilibria.

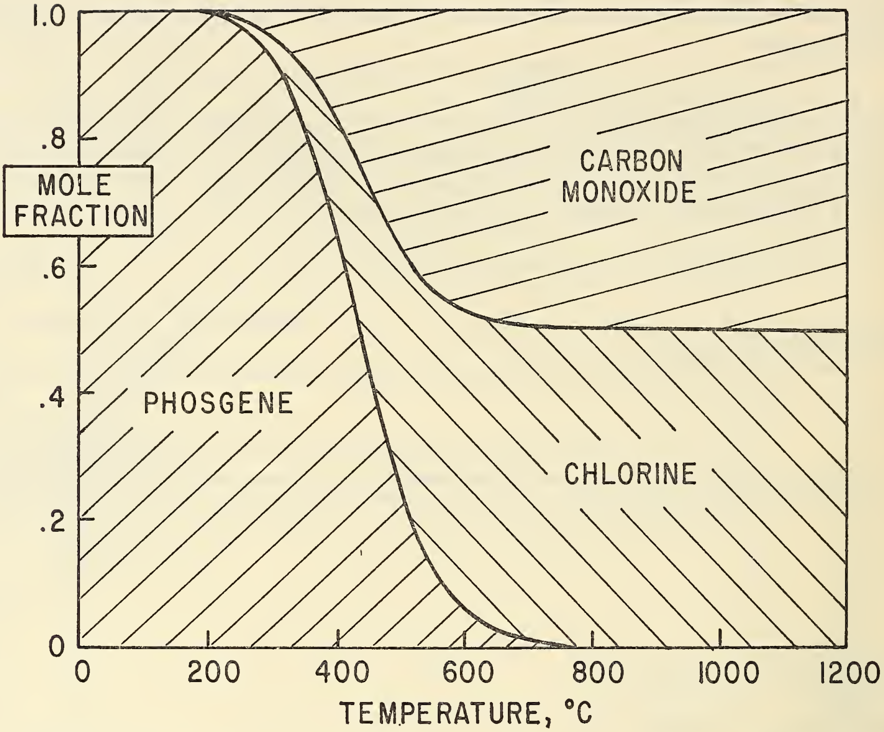


FIG. 13. Thermodynamically calculated equilibria between phosgene, carbon monoxide, and chlorine.

Reference to the above figures shows that, in the case of vinyl chloride, there are 3 hydrogens to every chlorine, and that hydrogen chloride is the most stable species that the chlorine can form. Note too that the highest carbon monoxide concentrations occur under oxygen deficient conditions, but these are the same conditions that also yield high hydrogen concentrations. Thus, under the lean oxygen conditions required to form carbon monoxide, there is no free chlorine to form phosgene. Likewise, under high oxygen concentrations where free chlorine is formed, the carbon monoxide has been oxidized to carbon dioxide.

On October 23, 1969, a meeting was called by the Manufacturing Chemists' Association to accumulate authoritative information on the combustion products of vinyl chloride monomer. After an intensive laboratory investigation by the manufacturers, on January 14, 1970, they reported:

"Phosgene is a very minor combustion product from vinyl chloride monomer. Very small quantities of phosgene (20–40 ppm) can be produced when vinyl chloride monomer is burning under very specific conditions which involves premixing vinyl chloride monomer with oxygen. Without premixing, no detectable amount of phosgene is produced. The detection of phosgene in the presence of gross quantities of hydrogen chloride produced from the burning of vinyl chloride monomer is an extremely difficult analytical test. When vinyl chloride monomer is burned in the presence of air, an almost quantitative yield of hydrogen chloride is obtained. The only other combustion products of any consequence are carbon monoxide, carbon dioxide, and water. Under diffusion conditions, the combustion of vinyl chloride monomer produces a very sooty flame. Approximately 10% of the available carbon is converted to carbon black." These findings were later published.[7]

Identifying Potential Chemical Reaction Hazards

The behavior of chemicals in fire problems is closely bound to the intrinsic energies of the molecules involved. Reactions that are capable of releasing energy are potentially hazardous, and the greater the energy release, the greater is the potential hazard. Therefore, a study of combustion or chemical reactions producing heat from a chemical thermodynamic viewpoint will prove rewarding, and has been my main interest for the past several years.

Once initiated, the energy generated may be derived from three sources. The first of these is the release of stored energy from a single compound. Acetylene is a good example of this case. Thermochemistry teaches that the elements graphite and hydrogen at 298°K can be synthesized into acetylene gas at 298°K by storing 54.19 kcal per mole in the acetylene molecule (see Figure 14). This acetylene molecule with its triple bond and its 54.19 kcal of stored energy can be thought of as similar to a tightly wound spring. Once released, the stored energy is added to the system, largely as heat. Thus, the decomposition of acetylene releases 48.2 kcal which heats the constituent elements, graphite and hydrogen adiabatically to 2898°K. This self decomposition of acetylene is the primary hazard. Now, if this graphite and hydrogen heated to 2898°K is released in oxygen, it would undergo complete oxidation, releasing 116.9 kcal, and produce a series of most stable oxidation products heated adiabatically to 3314°K. The expansion of these gaseous products to 3314°K would produce the maximum destruction acetylene can produce. The difference between this totally oxidized condition and the self decomposition is regarded as the secondary hazard of acetylene. These two quantities, primary and secondary hazards, are the basis of a method of potential hazard evaluation.

The second method of energy generation is the decomposition of a compound forming more stable products. Ammonium nitrate is an example of this case (see Figure 15). The synthesis of a mole of solid ammonium nitrate from its constituent elements at 298°K is accomplished by the release of 87.3 kcal. This, in itself, is quite a degradation in the absolute energy scale. Upon appropriate activation, solid ammonium nitrate may decompose into more stable products, gaseous nitrogen, oxygen, and water heated to 1246°K by the further release of 28.3 kcal. For ammonium nitrate, this decomposition is the primary hazard, and since the products contain excess oxygen, there is no secondary hazard.

The third method of energy generation is the energy-producing reaction of two or more chemical species. Octane and oxygen will be used as the example reaction. Thermochemically speaking, a mole of liquid octane can be synthesized from its elements at 298°K by the release of 60 kcal (see Figure 16). Self decomposition of liquid octane to form graphite and methane and hydrogen gases heated to 591°K by the further release of 17.2 kcal, is the primary hazard. Complete oxidation of liquid octane produces the most stable oxidation products heated to 3102°K by the release of 587.2 kcal, and will produce the maximum destruction this system can

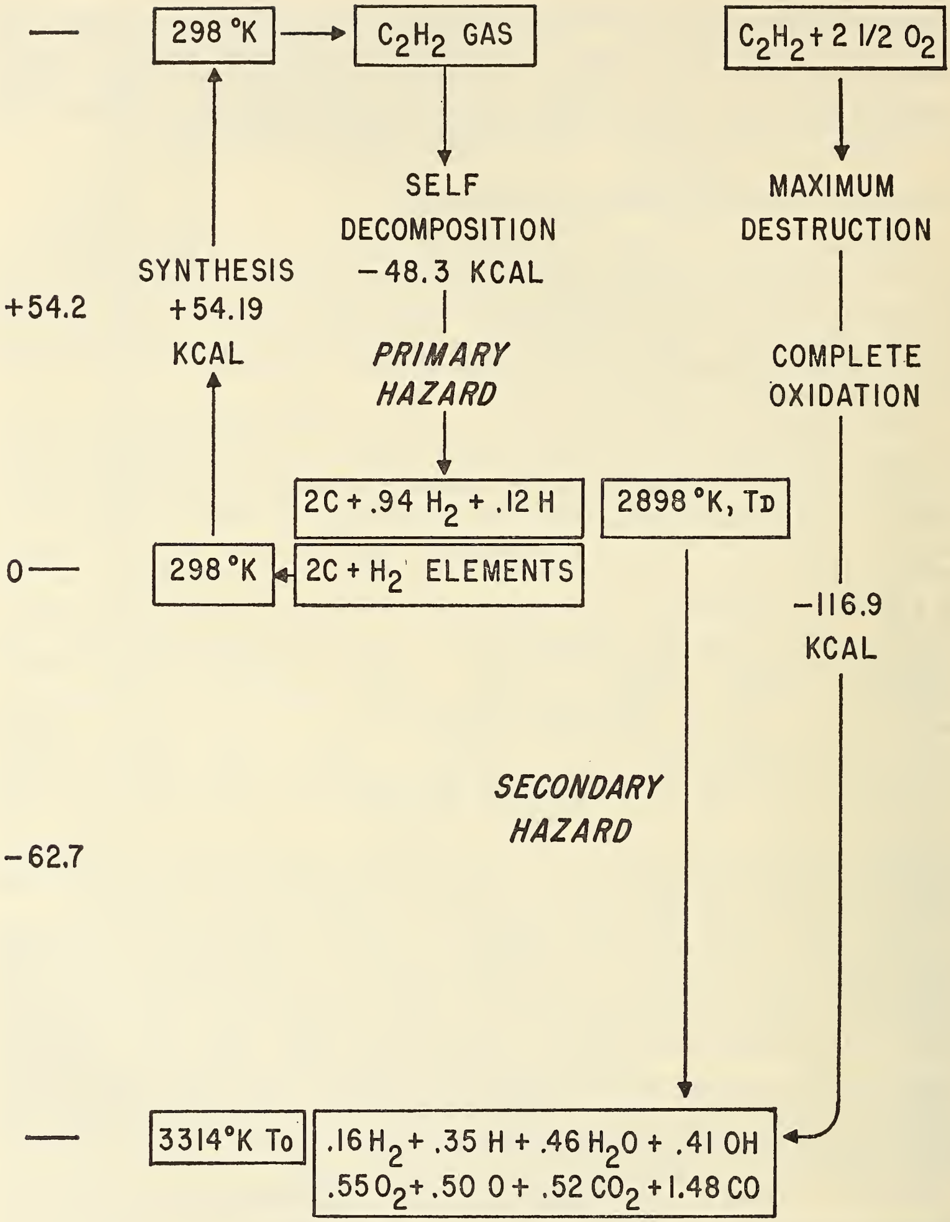


Fig. 14. Thermochemistry of acetylene.

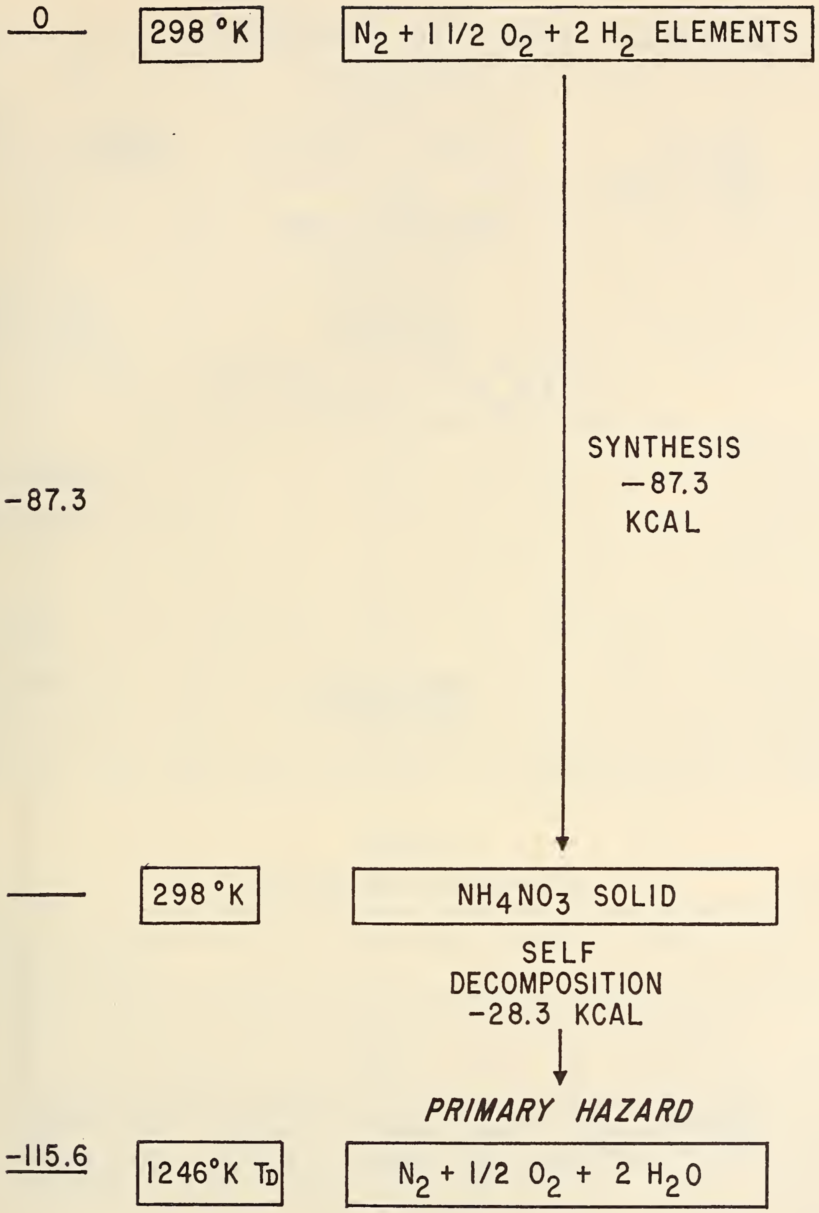


FIG. 15. Thermochemistry of ammonium nitrate.

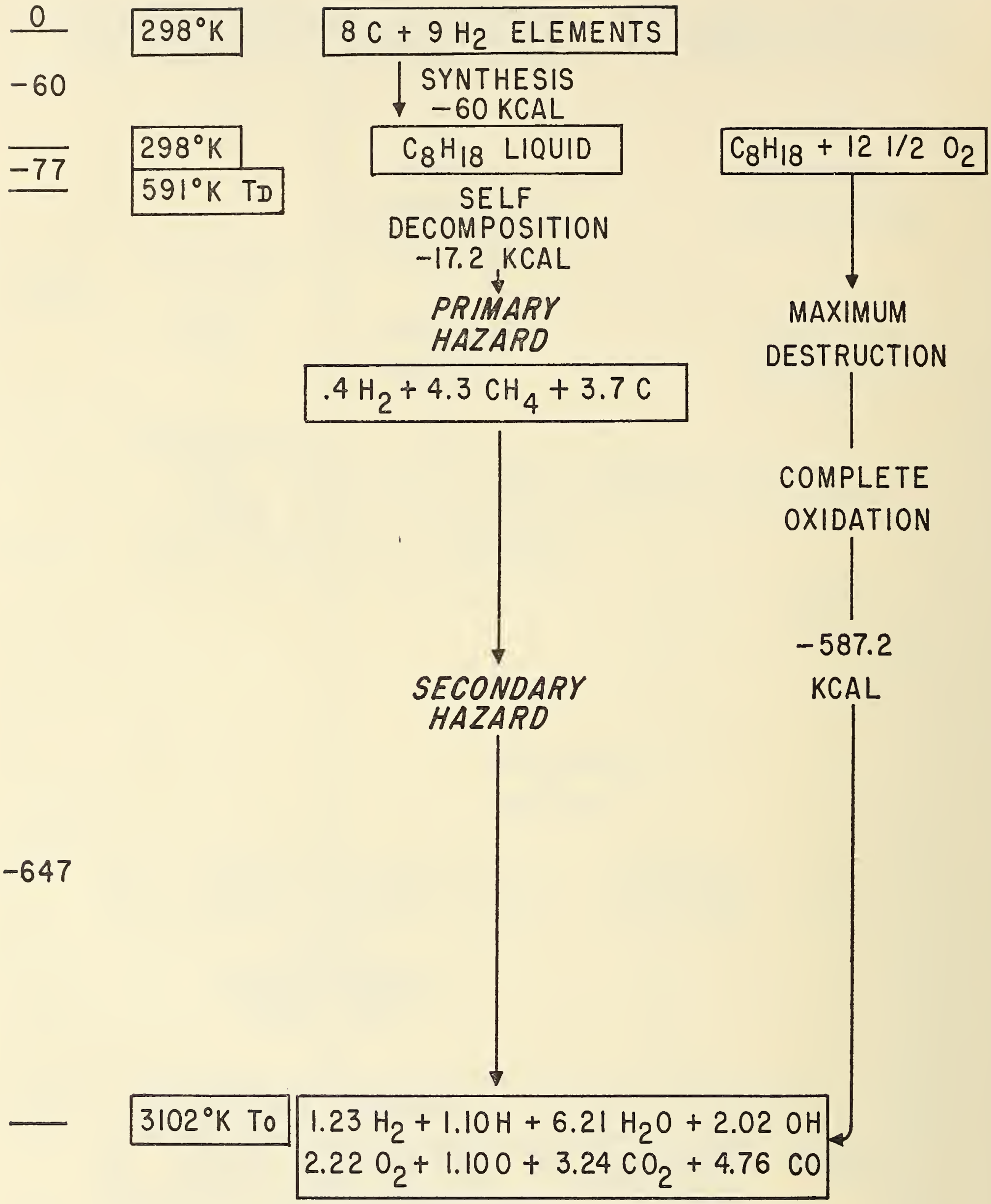


Fig. 16. Thermochemistry of octane.

produce. The secondary hazard is the difference between the self decomposition (denoted by subscript d) and the complete oxidation (denoted by subscript o). These energies and product gas temperatures are calculated from the thermodynamic properties of these systems, and are thus completely scientific and divorced from human emotions.

In an earlier study,[8] a correlation of the values of the primary and secondary hazards with the National Fire Protection Association Chemical Reactivity Rating,[9] as detailed in Table II, was presented. Continued work with this concept has shown that the correlation based on the self decomposition temperature T_d and the temperature of the fully oxidized products T_o is the most useful for potential hazard prediction. To introduce the concept here, twenty compounds plus acetylene and ammonium nitrate, whose NFPA Chemical Reactivity Ratings have been assigned, were selected, their T_d and T_o values calculated (see Table III), and the values of the primary and secondary hazards plotted in Fig. 17.

Observation of the data shows that the safest materials, NFPA Chemical Reactivity = 0, are to be found in the upper left-hand corner, while the most potentially hazardous materials, rated 4, are in the lower right-hand corner. Thus, a band from methane to nitroglycerine covers the range from safest to the most potentially hazardous materials. There is, however, considerable overlap in the ratings. Of this data, NFPA says "This material is not an official standard of the NFPA; it is only a compilation of data from various authoritative sources presented for information as a guide." Propyl alcohol falls between octane and acetone, and seems to be out of place for a 1 rating. The other three 1-rated materials, butyraldehyde, epichlorohydrin, and vinyl chloride, spread over quite a wide area. Acetaldehyde, ethylene, styrene, and vinyl acetate are clustered in the same area, and seem out of place since they carry a 2 rating. The 3-rated materials are all quite hazardous, and cover a wide range from 4-nitroaniline to ammonium nitrate to acetylene.

TABLE II

NFPA Chemical Reactivity rating

0	Materials which are normally stable even under fire-exposure conditions, and are not reactive with water.
1	Normally stable materials that may become unstable at elevated temperature and pressures, or which may react with water with some release of energy but not violently.
2	Materials which are normally unstable and readily undergo violent chemical change, but do not detonate. Includes materials which can undergo chemical change with rapid release of energy at normal temperatures and pressures or which can undergo violent chemical change at elevated temperatures and pressures. Also includes materials which may react violently with water, or which may form potentially explosive mixtures with water.
3	Materials which are capable of detonation or of explosive decomposition or of explosive reaction, but which require a strong initiating source or which must be heated under confinement before initiation. Includes materials which are sensitive to thermal or mechanical shock at elevated temperatures and pressures or which react explosively with water without requiring heat or confinement.
4	Materials which are readily capable of detonation or of explosive decomposition or explosive reaction at normal temperatures and pressure. Includes materials which are sensitive to mechanical or localized thermal shock.

TABLE III

Calculated decomposition and complete oxidation temperatures for NFPA Chemical Reactivity rated compounds

	State	NFPA	T_d(°K)	$T_o - T_d$
1. Acetone	(l)	0	704	2331
2. Methane	(g)	0	298	2756
3. Methyl alcohol	(l)	0	692	2189
4. Octane	(l)	0	591	2511
5. Butyraldehyde	(g)	1	1039	2104
6. Epichlorohydrin	(l)	1	975	2056
7. Propanol	(l)	1	615	2401
8. Vinyl chloride	(l)	1	1374	1714
9. Acetaldehyde	(l)	2	815	2201
10. Ethylene	(g)	2	1005	2170
11. Styrene	(l)	2	923	2268
12. Vinyl acetate	(l)	2	844	2179
13. Acetylene	(g)	3	2898	443
14. Ammonium nitrate	(s)	3	1242	0
15. Cellulose nitrate	(s)	3	2213	641
16. 2,4-Dinitroaniline	(g)	3	1904	1219
17. 4-Nitroaniline	(s)	3	1103	2013
18. Nitroethane	(l)	3	1064	1943
19. Nitroglycerine	(l)	4	2859	0
20. Nitromethane	(l)	4	2418	509
21. Propargyl bromide	(l)	4	1898	1266
22. 2,4,6-Trinitrotoluene	(s)	4	2025	1084

g = gas, l = liquid, s = solid.

Interspersed in this area are the 4-rated materials, potentially the most hazardous materials.

This type of calculation provides an objective method of segregating any material into its relative degree of potential hazard from the least hazardous materials to the potentially most hazardous materials. By such an ordering process, items having the same degree of potential hazard will be close to each other, permitting handling information on known materials to be extended and applied to materials where no handling information is available. Once the fire fighter is informed of the degree of potential hazard he is dealing with, he can operate more safely and effectively than before. It is, therefore, critically necessary for the chemicals and chemically derived materials of modern commerce to be studied from the energy point of view, and to calculate the degree of potential chemical reaction hazard appropriate for each material.

Real Chemical Reaction Hazards

It must not be forgotten that thermodynamics treats equilibrium systems and takes no cognizance of time. Thus, the calculated energy releases, and the product gas temperatures reached will represent the equilibrium case, and may require relatively long times to achieve. It is for this reason that these calculations are spoken of in the potential sense. We are living, however, in a real world and not a potential world. In a potential world, an energy release may cover years and cause no trouble whatever, but in a real world, the same energy may be released in 1 minute or in a fraction of a millisecond with altogether shattering results. The important factor that is also required *in addition* to the chemical thermodynamic information is the time-rate of energy release by the reacting system, or the overall kinetic parameters that govern the energy release. This is an area where chemical thermodynamics and chemical kinetics must be linked together to provide real answers for problems of the real world as we know it today. Joint studies between these two disciplines will prove to be very fruitful.

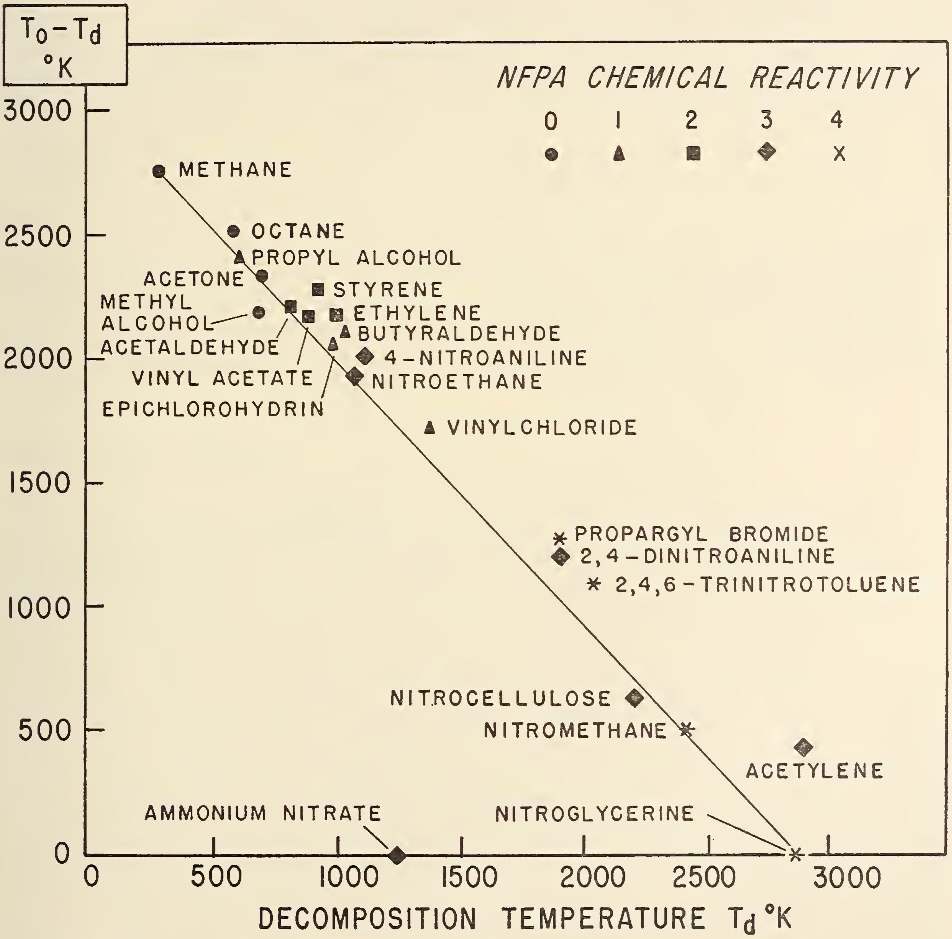


FIG. 17. Comparison of primary and secondary hazard ratings with the NFPA chemical reactivity rating.

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THE ROLE OF CHEMISTRY IN FIRE PROBLEMS: GAS-PHASE COMBUSTION KINETICS

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Introduction

The literature on combustion kinetics is extensive. A book entitled "Atomic and Free Radical Reactions,"[1] published in 1954, contains over 2000 references. A later, more selective book entitled "Chemical Kinetics of Gas Reactions,"[2] contains 1478 references. Another book, entitled "Chemistry of Combustion Reactions,"[3] contains 922 references. A fourth book, of limited scope, entitled "Chemistry in Premixed Flames,"[4] contains 283 references. A rough check shows that not very many of the same references appear in two or more of these books, suggesting that all four lists of references are only samples of what is available. I do not propose to provide a guide to this vast literature in this article, except to mention that the 16 volumes of the journal *Combustion and Flame*[5] and the published proceedings of the 13 international symposia of the Combustion Institute[6] certainly must be perused by anyone interested in the detailed progress in this area.

What I propose to do is to review a very few salient points and to provide commentary on how these may relate to fire problems. These are of course personal comments, based on my own limited experiences, and they must be recognized as such.

The Most Basic Approach

If a scientist with background in nuclear reactor physics or electromagnetic theory were assigned the problem of providing a scientific description of fire, his approach would surely be to formulate the relevant basic differential equations, based on Newtonian mechanics and classical thermodynamics, which he could do, and then to solve these equations, either analytically or numerically, which he could not do. He would encounter two major difficulties. First, real life fires on a scale larger than a few inches generally involve turbulent flow, with transport rates of species and energy up to an order of magnitude greater than for laminar flow under corresponding conditions. We know no way to describe turbulence from the basic equations, except with *ad hoc* assumptions of limited utility. However he might sidestep this difficulty by arguing that the turbulent behavior *might* be describable at least approximately (and highly precise description of fire is not really needed) by assuming a proportionality of some sort between the laminar and the corresponding turbulent behavior, perhaps with an empirically determined proportionality factor. This could give him the courage to tackle the laminar problem, which not only can be formulated and solved theoretically, at least with modern computers, but also can be studied experimentally on a small scale in the laboratory. This leads him to the second major difficulty. For those fire problems in which chemical kinetics plays a role (ignition, flammability limits, extinguishment, flame spread through premixed gas, transition to detonation, etc.), it is necessary to know the sequence of chemical reactions occurring which transform reactants to products (the mechanism) and the temperature-dependent rate of each step. In general, these are not known except for the very simplest fuels, such as hydrogen.

If we could calculate the rate of each *possible* reaction, we could then decide what actual reactions will occur, since we know from chemical thermodynamics the final state (the most stable state) which the system seeks and we know that it will go there by the easiest available route. The most basic approach would be to calculate the rates of all possible elementary reactions for all combinations of carbon-hydrogen-oxygen, say, once and for all, by the methods of quantum mechanics. The pioneering work of Schrödinger, de Broglie, Heisenberg, and Pauli (1925–1927) laid the foundations of quantum mechanics, and very soon thereafter (1927–1931), Heitler and London, Slater, Pauling, *et al.*, formulated ways of describing molecular structure in terms of the nuclei and electrons and the quantum mechanical relationships between them. The next step was to calculate the rates of chemical reactions in this way; in 1931 Eyring and Polanyi made the first pioneering treatment of the reaction

$$\mathrm{H} + \text{para-}\mathrm{H}_2 \rightarrow \text{ortho-}\mathrm{H}_2 + \mathrm{H}$$

by quantum mechanical methods. However the treatment was semi-empirical in that it was necessary to assume an arbitrary constant ratio between coulombic binding energy and exchange (resonance) binding energy for the diatomic molecules concerned, for all significant interatomic distances. Nonetheless, this was very exciting, in that it suggested that some day all chemical kinetics could be revealed by appropriate solutions of the Schrödinger equation. A tremendous effort, for that time, was initiated to tackle this project and by 1942, the book "Theory of Rate Processes," by Glasstone, Laidler, and Eyring,[7] was published, containing over 500 references. Even though the initial decade of effort did not yield a final quantitative solution to the problem, the work led to fantastically improved insights into the factors actually controlling the rates of reactions. The increasing availability of faster and faster computers throughout the 1950's and 1960's, as well as the general growth in scientific activity in this period, led to continuing onslaughts on this problem. *The Journal of Chemical Physics* over this period contains literally hundreds of publications attempting to quantify chemical reactivity in terms of quantum mechanics. Success has not yet occurred.

When will it occur? I have confidence that, sooner or later, if support continues to be available for basic science, this problem will be unraveled, with benefits not only to fire research but to numerous other applied fields. I have no idea if the time required is a decade or a century. However to significantly increase the probability of obtaining useful information from quantum mechanics on, say, fires of wood pyrolysis gases in the next decade, it would appear to be necessary to increase significantly the number of scientists now working on this problem. I would judge that there are at least several hundred competent scientists in the world today working in this area, with free exchange of results, so an effort perhaps beyond the capability of the fire research community is needed to influence probability of a breakthrough by this basic approach.

Experiments to Produce a Compilation of Reaction Rates

As an alternate to a general theory yielding reaction rates, one might systematically measure thousands of reaction rates for unimolecular, bimolecular, and termolecular reactions of possible interest in fire problems, over an appropriate range of temperatures, and tabulate these. Mechanisms could then be worked out. The difficulty is that virtually all reactions of interest involve free radicals and unstable species, and do not occur in isolation; i.e. at least one of the products of the reaction to be studied may react with one of the reactants, for example, to give other products, etc. Thus the measurement of gaseous reaction rates is very difficult and subject to uncertainties.

Nevertheless, a variety of ingenious techniques have been devised to measure individual reaction rates. These include:

(a) electrical discharge plus flow system[8]
(b) shock tube[9,10]
(c) explosion limit measurements[11]
(d) flash photolysis[12]
(e) measurements in flat premixed flames[4,13]
(f) interacting molecular beams.[14]

In all cases, the goal is to make the measurement in a very short time (microseconds), before secondary reactions interfere, which requires either high flow velocities or sudden initiating events (shock or flash). The ultimate experiment—two monoenergetic intersecting molecular beams with a single collision per reactant molecule—has not proven to have much utility because of the great experimental difficulties of producing the velocities and intensities required.

The other techniques have yielded quantitative information for quite a number of reactions. The present situation is that we have information good to perhaps a factor of 2 for several dozen reactions occurring in fires, other information good only to a somewhat lower accuracy, a factor of 4 to 10, for several hundred reactions, and there are hundreds, or perhaps thousands, of other gas reactions of probable importance in real fires of hydrocarbons, cellulosic fuels, plastics, and fabrics, with and without flame-retardants, on which we do not even know the reaction rate within a factor of 10.

Several compendia of measurements of rate constants exist. Perhaps the most carefully evaluated rate data is that issued in five bulletins by the High Temperature Reaction Rate Data Centre, Leeds University, England.[15] There are also compilations by Trotman-Dickinson *et al.*[16] on bimolecular reactions, and by Benson and O'Neal[17] on unimolecular reactions, and a new "Handbook of Kinetic Constants of Gaseous Reactions" by Kondratiev.[18]

As an illustration of the present state of kinetic data, a recent Combustion Institute symposium contains a tabulation by Browne, White, and Smookler[19] of kinetic parameters of 56 bimolecular and termolecular reactions involving 14 species:

monatomic	H, O, N
diatomic	H_2, O_2, N_2, OH, CO, NO
triatomic	H_2O, HO_2, HCO, O_3, CO_2

Also, in the same book, Newhall[20] provides a tabulation of 33 reactions involving the same species, with the exception of HCO, HO_2, and O_3, and the addition of N_2O and NO_2. In comparing the two lists, one sees that values differ moderately on almost every reaction. To compare ratios, one must note that most of the reactions are temperature-dependent, so that when different temperature dependencies are chosen for a given reaction by the two groups of authors, the plots of rate vs. temperature would in general cross at some temperature, yielding perfect agreement, while at other temperatures the values would diverge. (Combustion in air involves reactions over the range from about 600°K to 2400°K.) To illustrate the state of knowledge, one of the most important reaction is

$$CO+OH \rightarrow CO_2+H.$$

In this case, the two tabulations give rates with different temperature dependences (activation energies of 700 and 7700 calories), the values agreeing at around 1200°K, differing by a factor of 1.8 at 1500°K and a factor of 3.3 at 2000°K.

As another illustration, for the recombination reaction

$$H+OH+M \rightarrow H_2O+M,$$

one tabulation treats the rate as independent of temperature while the other treats it as varying inversely with the square root of absolute temperature. The values differ by a factor of 3.2 at 1000°K and a factor of 4.5 at 2000°K.

(I selected these illustrations at random, rather than in a search for best or worst cases.)

When one considers reactions of hydrocarbons, hydrocarbon fragments, and partially oxidized hydrocarbons, the available data are far more incomplete and inconsistent. To represent one extreme of opinion, I quote from a survey paper on reaction rates by G. von Elbe[21]: "With respect to complex systems, such as hydrocarbons and oxygen, we may never attain a state of quantitative kinetic knowledge." Another survey on "fundamental and broadly applicable combustion research" by Battelle Memorial Institute specialists[22] refers to hydrocarbon oxidation as "enormously complex," and concludes that the approach of rigorous chemical kinetics to practical problems involving hydrocarbon combustion such as air pollution "does not appear to be currently feasible." The alternative of empirical and phenomenological descriptions, such as "global" reaction rate models, is suggested.

Continued efforts to improve our compilation of rate constants could be aimed in any or all of the following directions:

(1) Tabulation, evaluation, and assignment of limits of uncertainty to data already published.

(2) Use of presently known techniques to check and refine values already measured.

(3) Use of presently known techniques to measure previously unstudied reactions.

(4) Development of new or improved techniques that might yield better measurements.

(5) Analysis of what rate information, to what precision, is most urgently needed for fire problems.

To estimate the progress to be expected in the next decade, it may be helpful to consider the time scale leading to the present state of capability of dealing experimentally with fast gas reactions. The original pioneering work demonstrating the critical importance of radicals and chain reactions was done in the 1920's and early 1930's by Semenov, F. O. Rice, Hinshelwood, Bonhoeffer, A. Farkas, L. Farkas, Harteck, Lewis and von Elbe, M. Polanyi, and many others. Positive direct identification and semiquantitative measurement of radicals in flames was not accomplished to any degree until the 1940's and 1950's, because of the need to refine detecting techniques such as mass spectroscopy and absorption spectroscopy. The shock tube, a powerful new tool for fast reaction kinetics, was first used by Carrington and Davidson in 1953 to study N_2O_4 decomposition. The beginning of modern flame-derived kinetics coincides more or less with development of flat-flame burners around 1950 by Powling and Egerton, and by Spalding. Fristrom and Westenberg made important refinements in techniques of flame structure measurement by mass spectrometry in the 1950's. Kinetic studies of atoms produced by electric discharges were vigorously pursued in the 1950's and 1960's by Kaufman and others. In 1967, Westenberg and de Haas successfully used electron spin resonance detection to study kinetics in a flow system. Thus, there has been an impressive continuous increase in capability to measure fast reactions such as occur in fire, over the past 50 years. We are not yet at the point where we can accurately measure any desired reaction, but we appear to be converging on this capability. Another decade of progress might bring us to that point.

In order to consider what good this would do in fire problems, let us consider specific problems. Obviously, the number of different fire problems which might be of practical importance and might involve chemical kinetics is enormous. However we will restrict our remarks to four rather broad areas, namely ignition, propagation, suppression, and toxic or smoky products.

Ignition and Flammability

The minimum energy which will just be able to ignite a gas mixture is in principle calculable if the chemical kinetics are known. For common combustibles (other than hydrogen) the kinetics are not sufficiently known and such calculations have not been successful, as far as I know. However, a well developed experimental technique exists for measuring the critical value of capacitance spark energy for ignition,[11] and we know that the energy needed is less than a millijoule for most combustible gas mixtures. From a practical viewpoint, we know that a malfunctioning household electric circuit, or a common match, is capable of supplying many orders of magnitude more energy than this, so more understanding of the critical energy requirement for ignition would appear to be of little value in reducing fire loss.

Another aspect of ignition is the ability of a substance undergoing slow oxidation to self-heat and spontaneously ignite. Familiar examples are oily rags, stored edible grains, sawdust, powdered coal, etc. Carbon disulfide vapor in air can ignite by contact with metallic surfaces no hotter than 125°C (steam pipes at moderately elevated pressures). This type of phenomenon is well understood in principle, as long as the chemical kinetics are known and the geometry is simple. A thorough recent review of the principles of "thermal ignition" (chain reactions, diffusion, and hydrodynamic factors ignored) is available,[23] with 70 references. The theory cannot of course be applied to any of the real cases of spontaneous ignition just mentioned, because the kinetics are not known. It may even be mentioned that in many of these cases of slow oxidation of organic solids at low temperature, biological oxidations are known to be involved, and sterilization will prevent ignition. In spite of the inability to treat real cases quantitatively, the availability of the theory certainly broadens our conceptual understanding of the phenomenon.

The really important practical aspect of ignition is that some solids or liquids are much harder to ignite with a pilot flame than others, and some are essentially nonignitable. Understanding of the reasons for these differences would be of great value in achieving wider use of fire-safe materials. For liquids, the concept of flash point temperature and its relation to vapor pressure and lower flammability limit is enormously useful, even though lower flammability limit has to be experimentally measured and is not theoretically predictable (not even for hydrogen, because of flame cell formation with very lean mixtures). Of course, even liquids below their flash points can burn if sufficiently preheated or if dispersed as a foam or mist. For solids, there is no concept like flash point, and ignition temperatures of solids, which can be measured by various empirical tests, give results which are highly test-dependent; i.e., *relative* rankings of two materials may reverse from one test to another. It must be presumed that gas phase kinetics as well as condensed-phase and interface kinetics play roles in solid ignition, but practically nothing is known about this. Either accidental impurities or deliberately introduced fire-retarding chemicals can have a large effect on ease of ignition of solids, which clearly involves chemical kinetics, but to what degree in the gas phase and in the condensed phase is usually not known. In some few cases, indirect evidence strongly suggests that the flame retardant gasifies and inhibits the gas reactions.[24]

A "flammability" test of a solid may measure its ability to ignite or its ability to continue burning after the ignition source is withdrawn. If it measures the latter, we may have a semantic problem as to whether we are studying ignition, but we are certainly studying something of great practical importance. Fenimore and Martin[25] devised a test for a solid in which it is ignited in atmospheres with varying O_2/N_2 ratio and the critical oxygen index (O_2/O_2+N_2) is determined for which combustion can continue. This test, permitting quantitative comparison of a wide range of materials, is now widely used, and clearly is strongly influenced by chemical kinetic parameters, since the effect of the nitrogen must be to lower the flame temperature and hence the gaseous reaction rate. No quantitative interpretation in chemical kinetic terms has been made of such test results as yet, to my knowledge.

I believe that the most useful thing that chemical kineticists could do at this time in regard to ignition and flammability is to devise exploratory experiments to reveal the role of gas kinetics in ignition and burning of cellulosic and plastic solids, including man-made fibers. For example, we could devise an apparatus for heating solids so as to generate pyrolysis gases at a controlled rate, determine the composition, and then feed these gases into a laboratory flame, introducing additives either as vapors or with the heated solid. The resulting flame structure and stability could be studied. Once we have an idea what reactions might be important, separate detailed study of the rates of these reactions could be justified. The other thing that is needed is further development of theory capable of accounting for the heat and mass transfer process occurring along with gas-phase and condensed-phase chemistry. Here we might note that, for a related problem, the burning of a solid propellant, elaborate theories for both ignition and steady burning have been developed over the past two decades, but controversy in regard to mechanisms still exists because sufficiently accurate experimental measurements of conditions at the igniting surface have not been achieved, and separate decomposition studies of the individual ingredients (e.g., ammonium perchlorate) have revealed tremendous complexity of behavior. Since fires are characterized by lower temperatures, less steep gradients, and slower rates than solid propellants, we may hope that experimental probing of igniting or burning wood or plastics will be more readily handled. The problem is not easy. Any help that can be gotten from kinetic understanding in developing better test procedures for evaluating ignitability or flammability of solids would be enormously valuable.

Propagation

Combustion may be divided into premixed flames and diffusion flames. While fires are usually diffusion flames, the great majority of combustion kinetics research has dealt with premixed flames because these are simpler to deal with both experimentally and theoretically (a one-dimensional model is possible). Inasmuch as peak temperatures are similar for the two types of flames, it is likely that many of the same reactions occur, so that one can hope that knowledge obtained from premixed flames may have some relevance to fires.

The theory of laminar propagation of flame through a premixed gas was apparently first formulated in terms of reaction kinetics in 1915 by Nusselt (cf. Ref. 26), who derived a simple formula showing the flame speed to be proportional to the square root of the product of the thermal conductivity of the gas mixture and the mean rate of heat release (or overall exothermic chemical reaction) per unit volume of flame. Thus, even in 1915, if we knew the kinetics of a gaseous flame we could have made an *a priori* prediction of flame speed. This theory has been highly refined and elaborated to include diffusional effects, multiple reactions, temperature-dependent rate constants, etc., principally in the period 1948–1958, most thoroughly by Hirschfelder and co-workers, and may be found in standard texts.[27,28] The application of this theory to actual flames has been very limited because of the lack of sufficient chemical kinetic knowledge for any real flame with oxygen as oxidant except the hydrogen flame. Another limitation has been the difficulty of application of theory, which requires a high-speed electronic computer, to complex reaction mechanisms involving branching chain reactions. Some of the best work on this problem has been done recently by Dixon-Lewis,[29] who has solved the time-dependent equations for a rich H_2–O_2–N_2 flame to give the steady-state concentration profiles and burning velocity.

Much has been learned about premixed flame propagation by refined experiments to measure flame structure, especially of expanded low pressure flames, by fine thermocouples, sampling with microprobes, and emission and absorption spectroscopy.[13,30] We presently have a reasonably good concept of the kinds of chemical processes occurring in a premixed hydrocarbon flame, and their probable effects on the propagation rate, even though we lack a quantitative theory.

Let us consider now how, if at all, this limited understanding of premixed flame chemistry relates to fire propagation problems.

First, consider flame spread through a cloud of flammable vapor, mist, or dust which has partially mixed with air prior to combustion. If this occurs indoors, we are primarily interested in the venting area necessary to relieve the pressure build-up before the building fails. This depends of course on the flame propagation rate, which depends on the fundamental laminar burning velocity of the mixture existing at any point (which is relevant to the foregoing research), but also on the turbulence present, and particularly on the additional turbulence generated by the event itself as it occurs, influenced strongly by any turbulence-generating objects in the path of the flame. Fortunately, there is evidence showing a relationship between speed of turbulent flame propagation for a given aerodynamic environment and fundamental laminar burning velocity of the combustible mixture which is present. Thus, the fundamental burning velocity is relevant, although far from the whole answer. Of course, laminar burning velocities can be measured directly relatively simply, if 10% uncertainty is acceptable, and such measurements have been made for hundreds of fuels over a range of fuel–air ratios, pressures and initial temperatures. Kinetic knowledge of why flames propagate at the velocities they do, while interesting, is apparently not needed for explosion venting research.

If the flammable vapor release occurs outdoors, and is substantial in size, as from a petrochemical plant or a liquefied natural gas reservoir, we are concerned with questions such as the possibility of a blast wave being generated, and the destructive radius of such a wave, which probably depends on turbulence and on laminar burning velocity somewhat as discussed above, and we are also concerned with questions such as how far downwind of the release point we will still be above the lower flammable limit. The latter question is purely aerodynamic. If we consider active control of such releases, perhaps by mixing devices such as water sprays or air jets which reduce the mixture below the flammable limit earlier than would occur naturally, again aerodynamics rather than chemistry is what is important. Of course the percentage of fuel corresponding to the lower flammable limit is chemically controlled, but flammability limits can readily be measured directly, so the lack of our ability to explain them in fundamental terms is apparently not holding up progress in dealing with vapor, mist, or dust explosions. Of course, basic chemical kinetic understanding of limits might give us some valuable new insight permitting better prediction or control of explosions, but it is not obvious that this is so.

Turning now to flame propagation over continuous liquid or solid fuels, we seek aspects that might be kinetically controlled. For flame spread over a liquid surface above its flash point, the rate of flame spread is known to be essentially governed by the rate of laminar burning velocity in the fuel vapor–air mixture existing just over the surface, as modified by any turbulence which may be present, and the previous statements about burning velocity apply. If the liquid is below the flash point, the flame will spread quite slowly, at a rate controlled by heat transfer which brings adjacent fluid to the flash point. The heat transfer depends dramatically on circulating currents within the liquid, near the surface, induced by temperature gradients from the flame.[31] This process is not completely understood, but does not appear to be dependent on chemical kinetics, except in the sense that the flash point itself, which is independently measurable, is chemical-kinetic controlled.

Various theories exist for flame spread rate over a *solid* surface which vaporizes by irreversible thermal decomposition rather than simple vaporization. Experimental data have been reviewed by Friedman.[32] The most successful theory to date is that of de Ris,[33,34] in that his theory successfully predicts the magnitude of the flame spread rate over solids without adjustable parameters, and also correctly predicts experimental variations with sample thickness and with pressure.

The theory assumes that each successive element of the surface must be brought up to a critical pyrolysis temperature characteristic of the material before it can ignite. This is obviously a chemical kinetic parameter, but it can in principle be measured in separate experiments and the results are not highly sensitive to the exact value used for the parameter. No gas phase kinetic parameters appear in the theory; i.e., the gas phase reactions are assumed to be infinitely fast, once fuel vapors and oxygen have diffusively mixed. Reaction is assumed to occur all the way to the surface; in other words, no flame stand-off distance (which would be kinetically controlled) is assumed. In reality of course there is an observable dead space between flame and surface, and previous theoreticians had assumed that this was of governing importance in flame propagation, since the heat transfer from flame to surface might be thought to vary in an inverse manner with the width of this dead space, possibly going to infinity if the dead space approached zero. de Ris treats the heat transfer as occurring in a two-dimensional flow field, and obtains a finite heat flux to the surface, since only an infinitesimal portion of the flame touches the surface, in the model. The crucial heat transfer is from the flame through the gas in front of the flame to the not yet ignited portion of the surface. In view of the success of this theory, there is good reason to believe that, at least to a first approximation, chemical kinetics affects flame spread over horizontal surfaces only insofar as pyrolysis is concerned, and to treat this de Ris's theory only requires knowledge of the surface temperature which must be reached for sufficient vapor production to give ignition, and the endothermic energy requirement of the solid. Chemical kinetic studies relevant to pyrolysis of solids would thus have a bearing on such flame propagation.

It should be mentioned that it has been well established by McAlevy and coworkers[32] that flame spread over thick horizontal plastic slabs increases with about the 2/3 power of pressure. Since gas-phase thermal conductivity as well as solid properties are essentially independent of pressure, it seemed logical to assume that a pressure-dependent chemical kinetic process in the gas phase exerted a controlling influence. However, de Ris's theory provides the needed 2/3-power pressure dependence aerodynamically, by showing that the gravitationally-induced gas phase flow above the fuel bed and toward the flame, expressed as mass flow per unit area, increases with the 2/3-power of gas density, and the propagation speed for a thermally thick fuel is proportional to this induced oxygen-supplying flow velocity. (For a thermally thin fuel, the same induced velocity effect is present, but the term representing it cancels out of the final equation for propagation rate, which therefore becomes independent of pressure.)

Let us consider one final case, flame propagation with several fuel elements separated by a gap. In this case, a fire burning at one location generates radiative and/or convective heat fluxes which ignite a nearby fuel element. Examples could be a forest fire, a fire in a room containing discrete flammable furnishings, a fire in a corridor with carpeting on the floor and a combustible ceiling or side walls, a row of houses, each 10 ft apart, a warehouse with 10-ft-wide aisles, etc. While the net effect is a propagation of the fire, it appears that what is really happening is ignition at a distance from the fire, by heat transfer. Thus the chemical kinetic factors which enter into the ignition process, as discussed in an earlier section, are highly relevant to this type of propagation. Of course, we already know empirically that a heat flux of a few tenths of a calorie per square cm per sec is sufficient to ignite many common combustibles, and the precise value, when measured for any material, is found to depend considerably on sample size and orientation. A large area of ignorance in regard to the kind of propagation under discussion is the ability to predict the magnitude of heat flux produced by a fire of given size at a given location near the fire. Of course, the emissivity of a flame depends in part on the soot content, which may be kinetically controlled. (Propagation by firebrands is also a possibility.)

To summarize these examples of fire propagation, factors other than chemical kinetics require the major research effort if better scientific understanding is to be achieved. Chemical kinetics however is involved in separately measurable parameters important in fire propagation, such as critical ignition heat flux, pyrolysis temperature and energetics of solids, flash points of liquids, and flammability limits and burning velocities of vapors, mists, or dusts.

Suppression

Let us consider agents which either are applied to an existing fire or are incorporated as additives (fire retardants) in otherwise flammable materials. In the former case, the common agents are

water (spray, fog, foam, film, gel, etc.)
dry powders ($NaHCO_3$, $KHCO_3$, $NH_4H_2PO_4$, etc.)
carbon dioxide
halogenated liquids (CCl_4, CF_3Br, CH_2BrCl, CF_2BrCF_2Br).

These may act in basically three ways to suppress the fire. The same agent often acts simultaneously in several ways.

A. The agent modifies the gas composition so as to render it nonflammable.
B. The agent reduces the rate of pyrolysis of the condensed-phase fuel, either by cooling or by chemical effect.
C. The agent acts as a physical barrier to heat or mass transfer.

Gas-phase chemical kinetics is directly involved in mode of action A and indirectly in mode of action B, since the degree to which the pyrolysis rate must be reduced by cooling in order to extinguish the gas flame is a function of gas-phase kinetics.

In the incorporation of fire-retardants into materials, enormous empirical information has been collected, as reviewed by Lyons[35] with about 1400 references, chiefly based on patents. Compounds of phosphorus, antimony, boron, chlorine, and bromine are prominent. The modes of action are generally unknown. In many cases, the primary effect appears to be to modify the pyrolysis products—for example, giving more char and less flammable volatiles. In other cases, the additive or reaction products thereof vaporize and perhaps inhibit the gas flame, and in yet other cases the additive forms a surface coating or barrier which may suppress glowing after the gas flame is extinguished.

In this discussion, we are concerned only with the gas phase chemical processes. The present state of ignorance prevents any quantitative statement in regard to how much the overall problem of improving fire suppression can be helped by better knowledge of the gas phase part. Clearly, we need coordinated studies of both condensed phase and gas phase processes as influenced by both physical and chemical effects of additives.

Let us consider some simple examples of gas-phase combustion inhibition. First, we know that an inert additive such as nitrogen or a nearby cold surface (quenching) will reduce burning velocity and ultimately render a mixture nonflammable. We believe that the primary effect is a reduction of flame temperature and a corresponding reduction in chemical reaction rates. Roughly speaking, when enough nitrogen is added to hydrocarbon–air mixtures to reduce maximum temperature below about 1500°K, the flammability limit is reached. The propagation reactions must have a finite activation energy, since it is known that very little reaction occurs in the cooler (or preheat) portion of a laminar flame. If

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

is the critical chain-branching reaction, with its activation energy of 17 kcal, then probably the nitrogen reduces the temperature so that the branching rate is no longer adequate, in view of prevailing heat losses (probably by transverse conduction), or possibly radical recombination reactions, and the flame limit is explained, at least to this qualitative extent. Now, when we add some substance other than nitrogen, we can predict the proportion needed to reach the flammability limit by producing the same degree of cooling, strictly on the basis of well known thermodynamic properties. When a substance proves to be much more effective than what would be calculated in this general manner, we say that it is a chemical inhibitor, and it must be in some way interfering with the chemical kinetics of the flame, and probably competing with the chain-branching process by reacting with chain carriers (H, OH, O). The best known example of such an inhibitor is bromine, incorporated into almost any volatile molecule that can decompose readily in the flame. Bromine is roughly an order of magnitude more effective than nitrogen, on a molecular or volume basis, and hence it is believed that some specific chemical reaction such as

$$H+HBr \rightarrow H_2+Br$$

or

$$OH+HBr \rightarrow H_2O+Br$$

must be responsible for the effect.

A number of researches have been done on this subject, as reviewed in 1967 by Fristrom,[36] in 1969 by McHale,[37] and again, most thoroughly, in 1971 by Fristrom and Sawyer.[38] No conclusive demonstration of the reaction mechanism has emerged. An unanswered question is whether the inhibiting species, perhaps HBr, can only act once during its passage through the flame, or whether it can be regenerated to act a number of times. If the latter, the kinetics of the regeneration process becomes very important.

While most such studies have been done in premixed flames, because they are relatively simple, it has been found that these bromine compounds also inhibit diffusion flames, which are more like fires. For example, Milne *et al.*[39] showed that with a counterflow methane–air diffusion flame, addition of either 0.8% CF_3Br to the air or 20% CF_3Br to the methane would produce an equal and large effect on the velocity at which blow-off occurred. This large difference in effectiveness of addition on the fuel and on the air side of the flame is related to the fact that methane and air combine in stoichiometric proportions of 9.5 to 1, so that the flame will be located well on the air side of the stagnation point where the two countercurrent flows meet. Thus, for this geometry, additive introduced into the air has a better chance to pass through the flame than additive in the fuel. Real fires would not burn in quite this type of geometrical arrangement, and further study is needed to understand this aspect of inhibitor effectiveness. However, testing inhibitors on real fires is not a very quantitative way of comparing effectiveness, as well as being completely useless in determining mechanisms.

It must be said that the first practical bromine-containing agents for suppression of gaseous flames, CH_2BrCl and then CF_3Br, were introduced two or more decades ago, a time when combustion scientists had not studied chemical flame inhibition at all, and in fact there was a widespread belief that it was not possible to inhibit or accelerate a flame with low concentrations of additives, because of the tremendous concentration of highly reactive radicals believed to be already present in the flame front. The data collected in the past two decades show conclusively that this view was wrong. Both practical fire-extinguishing tests and laboratory flame studies amply demonstrate that chemical perturbation of the flame is possible.

The most spectacular cases of chemical inhibition reported are by Lask and Wagner,[40] who found that roughly 2 parts in 10,000 (mole basis) of any of the following: chromium oxychloride CrO_2Cl_2, lead tetraethyl $Pb(C_2H_5)_4$, and iron pentacarbonyl $Fe(CO)_5$, could reduce the burning velocity of stoichiometric hexane–air to about 30% of its initial value. The mechanisms are quite unknown, and may well involve formation of fine metal or oxide particles in the flame. These effects deserve further investigation, even though the anti-knock mechanism of tetraethyl lead in internal combustion engines has never been completely unraveled, in spite of enormous research effort.

Sodium bicarbonate has been widely used for many years as a dry powder extinguishant. Comparisons of effectiveness with other salts strongly suggest a chemical kinetic effect above and beyond the obvious cooling and diluting effect of the endothermic decomposition. In the past decade, empirical comparisons of sodium bicarbonate with potassium bicarbonate have shown that the latter is more effective per unit mass, and even more effective per mole, than the former, so potassium bicarbonate is now in widespread commercial use. Assuming a chemical mechanism of inhibition, it has never been established conclusively whether homogeneous or heterogeneous reactions are of critical importance. Inasmuch as: (I) a variety of alkali metal compounds are effective; (II) there is a correlation between effectiveness and ease of decomposition or vaporization; and (III) homogeneous reactions can proceed more rapidly in a flame than surface processes requiring diffusion to and from the surface, it can be argued that any alkali metal salt may vaporize in a flame to form a common species with inhibiting power. Friedman and Levy[41] have proposed this, and have suggested that the inhibiting species is the alkali metal hydroxide vapor, undergoing reactions such as

$$KOH+H \rightarrow H_2O+K$$

or

$$KOH+OH \rightarrow H_2O+KO.$$

However, no proof of such a mechanism has appeared, and there are very few if any current research programs to investigate such mechanisms, to the writer's knowledge.

Let us consider the inhibition of the gas flame over a burning solid, by an additive to the solid. As previously noted, there is little available but speculation in this area. In one case, Fenimore and Jones[24] have done some careful work to demonstrate an example of this type of inhibition. Antimony oxide is a known inhibitor of certain plastics. They showed that it had no effect on polyethylene's limiting oxygen index, but a pronounced effect on partially chlorinated polyethylene, the effect increasing with increasing chlorination. This suggests formation of a volatile antimony halide which inhibits the gas flame. (It is already known that antimony pentachloride vapor is a good inhibitor of hydrogen flames.) They measured the antimony remaining in a partially burned piece of plastic and found a preferential loss of antimony, proving vaporization. The antimony did not vaporize preferentially when no chlorine was present. They replaced the oxygen in the atmosphere by nitrous oxide, thereby altering the gaseous chain reactions in the flame ($H+O_2 \rightarrow OH+O$, to give branching, no longer occurs) and found that there was no inhibition in this atmosphere. This seems to be very conclusive circumstantial evidence for gaseous inhibition by a volatile antimony halide when Sb_2O_3 is added to a chlorinated hydrocarbon.

To summarize this section, chemical kinetics is critically involved, and poorly understood, even for a suppressant acting by a physical mechanism, such as heat abstraction. Further, it is well established that certain suppressants in practical use, having been proven effective empirically, owe their effectiveness to chemical kinetic perturbations of the gas flame, the mechanisms being unknown. Further research could lead not only to new suppressants but also to new insights on how to use more effectively the suppressants we have. We need to learn not only the chemical gas-phase inhibition mechanisms but also the role of the gaseous reactions in the overall burning and extinguishment of real, solid fuels.

Toxic Products and Smoke

Fires burning in buildings under poorly ventilated conditions produce carbon monoxide at concentrations more than an order of magnitude greater than the lethal level. Furthermore, the products of incomplete combustion of organic materials generally contain smoke and eye-irritants which interfere with vision and hence escape.

In addition to these major problems, various secondary problems exist, which under some conditions could become very serious:

(A) Smoke may cause lung damage;
(B) If chlorinated combustibles are involved (as from polyvinyl chloride), then very probably hydrogen chloride and possibly phosgene may be produced;
(C) If nitrogen-containing organic combustibles are involved (polyurethane, wool), then hydrogen cyanide may be found;
(D) Partially oxidized hydrocarbons (acrolein, formaldehyde) may form;
(E) Fire-retardant additives (e.g., phosphorus compounds, antimony compounds, bromine compounds) may generate toxic products or stimulate smoke generation;
(F) Oxygen depletion and carbon dioxide have well known physiological effects;
(G) The toxic nature of a mixture of dangerous gases (and smoke) cannot

easily be established because of synergistic interactions between components.

To put the various toxic hazards in perspective, relative to carbon monoxide, we list the threshold limits for an eight-hour workday (Federal Safety and Health Standards, 1960):

Substance	*ppm (by vol.)*
CH_2CHCHO	0.5
$COCl_2$	1
HCl	5
HBr	5
HCHO	5
HCN	10
CO	100
CO_2	5000

This ordering must be balanced against the known ability of an underventilated fire to produce up to 10% CO (moisture-free basis), while concentrations of the more lethal gases, on the basis of measurements to date, are far lower than this.

Since smoke, carbon monoxide, and all other substances listed above, except HCl and HBr, are products of incomplete combustion, clearly chemical kinetics plays a key role in determining relative quantities of these substances. Both homogeneous and heterogeneous reactions would be expected to be involved. Results are known to depend not only on the chemical materials present, but also on the degree of ventilation of the enclosure (relative to the quantity of fuel therein), and the temperature level therein (both gas temperature and radiant flux impinging on surfaces).

In view of the tremendous difficulty of using a scientific approach to predict toxic concentrations or smoke levels for various combustibles burning under various conditions, research into the underlying kinetics must, in my opinion, be justified primarily on the basis of guidance which may be obtained in developing empirical material test methods.

There is practically no literature on this problem in the scientific journals. Empirical methods for measuring smoke generation capabilities of materials, by light obscuration, has been reviewed by the ASTM Committee E–5 on Fire Tests of Materials and Construction.[42] Smoke can consist either of tar vapors which condense (white smoke from a just-extinguished match) or soot (from a burning pool of benzene) or acid mist (if HCl is present) or various combinations thereof. There is of course a great difference in smoke generation by smouldering combustion as contrasted with flaming combustion, for many materials. For smoke forming by condensation, the cooling effect of ambient air mixing into the combustion products produces more smoke, but at the same time this mixing dilutes the smoke already present. Hence, at what point in the vicinity of the fire should smoke be measured?

Rasbash and Stark[43] have burned cellulosic fuels in compartments with variable ventilation, to study effects on gaseous products. Carbon monoxide concentrations up to 14% and methane concentrations up to 1.5% were found. The results were very roughly correlated on a plot of log(% CO) vs $\log(AH^{1/2}/W)$, where A and H are area and height of window opening, in meters, and W is weight of fuel in kilograms:

$AH^{1/2}/W$	% CO
10^{-4}	13
10^{-3}	7
10^{-2}	2
10^{-1}	0.2

The size of the chamber, the size of the fuel elements, and the degree of insulation of the chamber influenced the results. More recently, Tewarson[44] made similar experiments and found trends in his data which disagreed sharply with the trend shown above. For example, in many of Tewarson's tests the percent CO increased with increasing ventilation in certain regions, for a given fuel content in a given chamber. He also showed complex dependence of burning rate and maximum concentration of other species on test parameters (window opening, chamber volume, fuel content). He found different characteristic behavior patterns for fuel loadings above and below 12 kg/m^3. For wood-burning experiments, he reported CH_4 up to 4%, and C_2H_4 up to 2%, while CO ranged from 0.6% to 10.9%, with 8% CO being frequently found. No such experiments have been done as yet with fuels consisting of common plastics, and no satisfying explanations are available for the trends in the cellulose data.

It seems very clear that much more research along these lines is required. We need to be able to distinguish between these alternate mechanisms:

1. The undesirable product of incomplete combustion was produced by pyrolysis of a solid, and never passed through a flame front.
2. The undesirable product, produced by pyrolysis, survived in part its passage through a flame front.
3. The undesirable product was formed in a flame front.
4. The undesirable product was formed in a nonflame gas-phase process, associated perhaps with mixing of ambient gases of different composition and temperature with the original combustion or pyrolysis products.
5. The undesirable product was formed by interaction of products of a gas reaction with an element of solid fuel (e.g., $CO_2 + C \rightarrow 2\ CO$).

It seems unrealistic to me that choices between alternatives such as these will be possible solely on the basis of better knowledge of the chemical kinetics of individual reaction steps. The complexity of the problem is such that experiments with at least semi-realistic systems are probably required, perhaps involving highly localized sampling, and then the results of such experiments could lead to proposed generalized reaction mechanisms which might subsequently be quantified by use of specific reaction rates, determined separately.

Summary

The rates and mechanisms of chemical reactions important in fire are generally unknown. A half-century of chemical kinetic research has shown much progress, but the goal of quantitatively describing practical processes in basic terms will take some time to achieve.

While fires are basically diffusion flames, with different chemistry and perhaps different response to inhibitors than premixed flames, nevertheless certain premixed combustion parameters, such as flammability limit, minimum spark ignition energy, burning velocity, and quenching distance, have a degree of relevance to fires. The aforementioned parameters are each dependent in part on chemical kinetic mechanisms. Inasmuch as these parameters are easily measurable independently, it is not certain to what degree their further elucidation in chemical kinetic terms will help in solving fire problems. It appears desirable to have a better understanding of flammability limits.

There is an urgent need for exploratory experiments to define the role of gas-phase kinetics in ignition, flammability, fire retardancy, and toxic gas and smoke formation of common solid combustibles burning as diffusion flames. The ignorance in these areas is enormous and very few chemical kineticists have been willing to tackle these problems.

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CONDENSED PHASE COMBUSTION CHEMISTRY

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In this article we shall endeavor to survey the pyrolytic processes occurring in polymeric melts on the assumption that our comprehension of these processes are highly important if not critical for control of ignition and burning of materials.

PYROLYSIS OF POLYMERS UNDER HIGH VACUUM

A comprehensive review of the pyrolytic degradation of polymers has been made by Madorsky.[1] Other reviews covering pyrolytic and many other types of polymer degradation are also available.[2–6]

For vinyl and related polymers, a large variation in the number of pyrolysis products[1] from a given polymer occur (see Table 1). A few decompose to yield 100% pure monomer. The results in Table 1 are for certain experimental conditions, high vacuum, thin samples and low residence time in the furnace, and are essentially the primary products produced in the melt phase. In Table 2, overall activation energies are listed. It is seen that these cover a large range and that the larger values are close to 80 kcal/mole, which is an approximate upper limit for the carbon–carbon single bond. One may suspect then that these decompositions have been initiated by homolytic bond rupture of the typical bonds in the polymer chain.

In general it is now quite evident that the Rice-Herzfield mechanism modified for application to condensed phase polymeric systems can be applied to many polymeric decompositions. The energetics of decomposition can thus be discussed in terms of the elementary steps:

Initiation:

Random $$Q_i \xrightarrow{k_1} R_{i-j}+R_j$$

End $$Q_i \xrightarrow{k_{1e}} R_{i-1}+R_1$$

Propagation: $$R_i \xrightarrow{k_2} R_{i-1}+M$$

Transfer: $$R_i+Q_j \xrightarrow{k^3} Q_i+R_j$$

$$R_j \xrightarrow{\gg k_3} Q_{j-k}+R_k$$

Termination:

Combination $$R_i+R_j \xrightarrow{k_{4c}} Q_{i+j}$$

Disproportionation $$R_i+R_j \xrightarrow{k_4} Q_i+Q_j$$

TABLE 1

Yield of monomer in the pyrolysis of some organic polymers in a vacuum
(In per cent of total volatilized) (Ref. 1)

Polymer	Temperature range, °C	Yield of monomer, %
Polymethylene	335–450	0.03
Polyethylene	393–444	0.03
Polypropylene	328–410	0.17
Polymethylacrylate	292–399	0.7
Hydrogenated polystyrene	335–391	1
Poly(propylene oxide), atactic	270–550	2.8
Poly(propylene oxide), isotactic	295–355	3.55
Poly(ethylene oxide)	324–363	3.9
Polyisobutylene	288–425	18.1
Polychlorotrifluoroethylene	347–415	25.8
Poly-β-deuterostyrene	345–384	39.7
Polystyrene	366–375	40.6
Poly-*m*-methylstyrene	309–399	44.4
Poly-α-deuterostyrene	334–387	68.4
Poly-α,β,β-trifluorostyrene	333–382	72.0
Polymethylmethacrylate	246–354	91.4
Polytetrafluoroethylene	504–517	96.6
Poly-α-methylstyrene	259–349	100
Polyoxymethylene	Below 200	100

Here, Q_i is the number of polymer molecules composed of i monomer M units, and R_i is the number of radicals having i monomer units.

The rate of volatilization of the polymer would in general be given by:

$$d\text{``}M\text{''}/dt=k_2\sum_{L}^{\infty} R_i+\left(d\sum_{2}^{L-1} iQ_i/dt\right), \tag{1}$$

where "M" symbolizes total volatiles in terms of monomer segments, and L is the smallest degree of polymerization that must chemically decompose in order to vaporize.

If k_3 were zero, and only monomer of molecular weight m volatilizes, then

$$dM/dt=k_2R, \tag{2}$$

where $R=\sum R_i$. The fractional rate of weight loss C, based on initial weight of sample w_0, is:

$$dC/dt=(m/w_0)k_2R. \tag{3}$$

For the purpose of discussing the key characteristics of these reactions, we shall present a treatment of a simple case. One of the simplest mechanisms is composed of propagation, random initiation, and disproportionation. The steady-state condition then follows:

$$k_1[\rho V(t)/m]=k_4R^2/V(t). \tag{4}$$

TABLE 2

Activation energies of thermal degradation of some organic polymers in a vacuum (Ref. 1)

Polymer	Molecular weight	Temperature range, °C	Activation energy, kcal/mole
Phenolic resin	—	331.5–355	18
Atactic poly(propylene oxide)	16,000	265–285	20
Polymethylmethacrylate	150,000	226–256	30
Polymethylacrylate	—	271–286	34
Poly(ethylene terephthalate)	—	336–356	38
Isotactic poly(propylene oxide)	215,000	285–300	45
Cellulose triacetate	—	283–306	45
Poly(ethylene oxide)	9,000–10,000	320–335	46
Polyisobutylene	1,500,000	306–326	49
Hydrogenated polystyrene	82,000	321–336	49
Cellulose	—	261–291	50
Polybenzyl	4,300	386–416	50
Polymethylmethacrylate	5,100,000	296–311	52
Polystyrene	230,000	318–348	55
Poly-α-methylstyrene	350,000	228.8–275.5	55
Poly-α-deuterostyrene	High	321–341	55
Poly-β-deuterostyrene	High	326–346	56
Poly-*m*-methylstyrene	450,000	318.5–338.5	56
Polyisoprene	—	291–306	58
Polychlorotrifluoroethylene	100,000	331.8–371	57
Polypropylene	—	336–366	58
Polyethylene	20,000	360–392	63
Poly-α-β-β-trifluorostyrene	300,000	333–382	64
Poly-2,3,4,5,6-pentafluorostyrene	—	395–410	65
Polymethylene	High	345–396	72
Poly-*p*-xylylene	—	401–411	73
Polytetrafluoroethylene	—	423/5–513	80.5

In the units used $R/V(t)$ is the steady-state concentration of radicals. Thus, we have the number of radicals given by

$$R=[(k_1/k_4)(\rho/m)]^{1/2}V(t). \tag{5}$$

It is seen to be proportional to the volume or weight of the sample (ρ is the density of the polymer).

The final rate equation is

$$dC/dt=k_2[(k_1/k_4)(m/\rho)]^{1/2}(1-C). \tag{6}$$

Next, we define the zip length Z, which in this special case is identical with the kinetic chain length

$$Z=k_2R/[(2k_4R^2)/V(t)]=k_2V(t)/2k_4R=\tfrac{1}{2}k_2(m/k_1k_4\rho)^{1/2}. \tag{7}$$

In more complicated cases, the zip length is the ratio of the rate of propagation to termination plus transfer.

In this rare case, it is seen that Z is a constant. Also, since we have restricted termination to disproportionation, we have already assumed that $Z \ll \bar{P}_n$, where $\bar{P}_n$ is the number average degree of polymerization. By taking the weight loss to be entirely the result of monomer production by propagation we have assumed also that $Z > 1$.

We next determine the variation of $\bar{P}_n$ with the extent of reaction. For the purpose of finding the molecular weight dependence on conversion, we write a differential equation for the variation in the total number of polymer molecules

$$Q = \sum_{2}^{\infty} Q_i$$

with the extent of reaction

$$dQ/dt = k_4 R^2 / V(t). \tag{8}$$

Dividing by Eq. (3),

$$dQ/dC = [k_4 R^2 / V(t) k_2 R](w_0/m)$$
$$= (w_0/m)(k_4/k_2)\ [R/V(t)].$$

Replacing $R/V(t)$ from Eq. (7) and integrating, we find that

$$Q_t - Q_0 = (w_0/m)(C/2Z) \tag{9}$$

or

$$[w(t)/mP_n(t)] - [w_0/mP_n(o)] = (w_0/m)(C/2Z),$$

and then

$$(1-C)/P_n(t) - [P_n(o)]^{-1} = C/2Z. \tag{10}$$

Here, $P_n(0)$ and $P_n(t)$ are the number average degrees of polymerization initially and at time t, respectively. Transforming Eq. (10) to

$$P_n(c) = \frac{P_n(0)[1-C]}{\{1+[P_n(0)/2Z]C\}}. \tag{11}$$

It is seen that in the limit of $[P_n(0)/Z] \to 0$, $P_n(C)$ decreases linearly with $(1-C)$. On the other hand, as the ratio takes on larger positive values, $P_n(C)$ decreases more rapidly.

Variations of the above treatment are, on the whole, quite satisfactory for interpreting the mechanism of polymer decomposition of the type that produce mainly monomer.

Catalytic effects resulting from small concentrations of impurities or abnormal structures in the chain which lead to rapid initiation, change the behavior for some polymers drastically as one studies different samples, prepared and processed by different methods. Sensitivity of the decomposition to impurities, peroxides, ultraviolet light, gamma rays, and other agents is proportional, of course, to the kinetic chain length.

By incorporating transfer in the mechanism, the treatment can be applied successfully to most all vinyl-type polymers such as those in Table 1, with some exceptions—for example, polyvinyl chloride and polyvinyl acetate.

Table 3 lists zip lengths deduced from measurements of the decomposition behavior of four polymers. The two with the large zip length, $\sim 10^3$, have relatively

TABLE 3

Zip lengths for polymer depolymerization at 1%/min rates

Polymer	Zip lengths
Methyl methacrylate	$\sim 10^3$
α-methyl styrene	$\sim 10^3$
Styrene	~ 5
Tetrafluoroethylene	~ 3

low thermal stability. For the polymethyl methacrylate a variety of rates and activation energies (30–52 kcal/mole) have been reported.

ENERGETICS OF POLYMER DECOMPOSITION

From the rate equation for polymer decomposition, Eq. (6), it is seen that measurement of the temperature dependence of the rate yields an overall activation energy E_0 which is related to the activation energies of the elementary processes by

$$E_0 = \tfrac{1}{2}(E_1 - E_4) + E_2. \tag{12}$$

By definition, the bond-dissociation energy is $D(R-R) = E_1 - E_4$. Also, $E_2 = H_p + E_{-2}$, where H_p is the heat of polymerization and E_{-2} is the activation energy for the addition of monomer to a polymer radical. Table 4 presents values for E_{-2} taken from a recent review[7] of the thermochemical measurements pertinent to polymerization processes and Table 5 presents values for the heat of polymerization. Also in Table 4 are values of E_4, the activation for termination of large radicals in polymerization systems. Thus, these E_4 values are for radicals in low-viscosity liquid systems at or near 25°C. The fact that the E_4 values are positive finite quantities is assumed to be due to diffusion control, since activation energies for radical termination in the gas phase are effectively zero. In the degradation processes, the systems are high-viscosity polymer melts at 200°–400°C and E_4 values run 20–40 kcal/mole (1 cal = 4,184 joules).[4] Equation (12) now can be formulated as

$$E_0 = \tfrac{1}{2}[D(R-R)] + H_p + E_{-2},$$

or

$$D(R-R) = 2[E_0 - H_p - E_{-2}]. \tag{13}$$

Since E_{-2} values are small and not readily available, we may approximate values of $D(R-R)$ from

$$D(R-R) = 2[E_0 - H_p - 5]. \tag{14}$$

Assuming E_0 is independent of temperature the estimated values of $D(R-R)$ would be for 25°C. The results are not accurate enough for this factor to concern us. Application of Eq. (14) to several polymers which appear to initiate at random give the results in Table 6. The $D(R-R)$ values are quite large and support the view that in the cases listed carbon–carbon bond rupture is the initiating process for depolymerization. The high value of 90 kcal/mole for poly-α-methyl styrene may indicate an abnormally high E_{-2}, while that for polyethylene most likely

TABLE 4

Absolute rate constants (at 25°C), activation energies, and *PZ* factors for propagation and termination in radical polymerization (Ref. 7)

Monomer	Propagation			Termination		
	k_p, liter mole^{-1} sec^{-1}	E_2, kcal mole^{-1}	$PZ \times 10^{-7}$ liter mole^{-1} sec^{-1}	$k_t \times 10^{-7}$ liter mole^{-1} sec^{-1}	E_4, kcal mole^{-1}	$PZ \times 10^{-9}$ liter mole^{-1} sec^{-1}
Ethylene	470 (83°C)			100 (83°C)		
	50	6				
Styrene	20	6.4	0.45	0.23	1.9	0.06
Methyl methacrylate	269	4.7	0.09	1.5	1.2	0.11
Vinyl acetate	980	5.0	3.2	2.0	3.2	3.7
Vinyl chloride	6200	3.7	0.33	1200	4.2	
Methyl acrylate	720	7.1	10			
Vinylidene chloride	8.6			0.02		
tert-Butyl methacrylate	350	4.4		1.4	1.1	
Acrylonitrile	1450	4.1	3	200	5.4	3300
	52			0.5		
Acrylamide	18,000			1.45		
Butadiene	20	9	12			
Isoprene	10	10	12			
2-Vinyl pyridine	96	8		0.89	5	
4-Vinyl pyridine	12					
Nitroethylene	14,000	≈5				

TABLE 5

Standard enthalpies of polymerization (liquid-crystal) (Ref. 9)

Monomer	$-\Delta H°lc$, kcal/mole
Tetrafluoroethylene	41.5
	37
Ethylene	25.88, gc
	21.2
3,3-Dichloromethyl 1-oxacyclobutane	20.2
Vinyl acetate	21.2
Butadiene	17.6
Propylene	24.89
	19.5
Butene-1	19.0
Isoprene	17.9
Styrene	16.7
Methyl methacrylate	13.2
Ethyl methacrylate	13.8
Isobutylene	12.9
Formaldehyde	13.2
	7.4
α-methyl styrene	8.4
Tetrahydrofuran	5.3
Sulfur	−3.17
Selenium	−2.27
Cyclopropane	27.0
Cyclobutane	25.1
Cyclopentane	5.2
Cyclohexane	−0.7
Cyclooctane	8.3

results from the fact that it does not depolymerize to monomer and, hence, Eq. (14) does not strictly apply.

Polyethylene volatilizes at 410°C by a random scission process having an overall rate constant $k_0 = 10^{17} \exp(-72{,}000/RT)$ sec^{-1}. Stress–relaxation measurements[9] of a crosslinked polyethylene in the region of 300°C indicate that the chains rupture with a rate constant $k = 10^{20} \exp(-73{,}300/RT)$.

The similarity in the two results indicates that an identical process determines the results of both experiments.

Instead of calculating the value of $D(R-R)$ for polyethylene from its activation energy for random degradation, it is more informative to assume that the random decomposition of polyethylene occurs by a chain reaction process with transfer as the propagating process. Taking this process to initiate by a random carbon bond rupture with $D(R-R) = 80$, then we calculate an activation energy of 34 kcal/mole for the transfer process in the melt.

OTHER TYPES OF POLYMER DECOMPOSITION

Table 7 lists some other polymers which decompose by mechanisms quite different from those so far discussed. These produce to a greater or lesser degree char and certain volatile products. There are in main two types of decompositions. In one, side groups split from the chain leaving a charred residue, for example, polyvinyl chloride which dehydrochlorinates, and cellulose which can with the aid of catalysts be made to dehydrate leaving a carbon residue. The second type is those containing mostly aromatic group links in the polymer chain. These have been shown to cross-link and, hence, ultimately form carbon and various small volatile species. The polymers in Tables 1 and 2 decompose endothermically. Those in Table 7 tend to decompose exothermically. There are polymers which are exothermic in polymerization and exothermic in decomposition.[10] The dehydration of pure cellulose is exothermic by 29.4 kcal per mole of water produced, yet it decomposes mainly to levoglucosan and flammable tars, a process that is probably endothermic at 25°C. Table 8 lists thermodynamic quantities for various conceivable decomposition processes for polyethylene and polytetrafluoroethylene. Thus, thermodynamic considerations alone are insufficient for predicting the thermal decomposition behavior of polymers, since as is also likely for cellulose, the actual observed decomposition mechanisms (*d* and *f* in Table 8) have positive free energies at 25°C while decomposition processes with large negative free energies are not observed. Heats of polymerization, Table 5, are very useful for choosing conditions of polymerization, but are of less value in predicting thermal stability.[7]

INDUCED AND OXIDATIVE DEGRADATION

Some polymers particularly those with long zip lengths are sensitive to electromagnetic radiation and decompose at temperatures 100 or more degrees lower when irradiated.[4,6,11] Such polymers when irradiated at room temperature or lower can also develop concentrations of free radicals and will give off a small burst of volatile monomer on subsequent heating to a modest temperature.

The most stable samples of polymethylmethacrylate decompose to monomer with an activation energy of 52 kcal/mole. If the initiation process is by a radiation mechanism, the activation energy for decomposition would be given by Eq. (12), with E_1 set equal to zero,

$$E(\text{photo}) = E_2 - \tfrac{1}{2}E_4. \tag{15}$$

For polymethylmethacrylate, this gives $E(\text{photo}) = 9$ kcal/mole, and would occur readily at or near room temperature. For poly-α-methyl styrene and polytrifluoroethylene, $E(\text{photo})$ values of 25 and 13, respectively, have been estimated.[8] Fortunately, few polymers appear to have very long kinetic chain lengths.

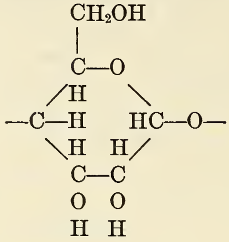
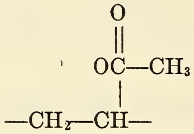
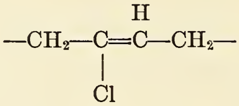
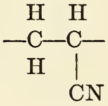
TABLE 6

Estimated dissociation energies, $D(R\text{–}R)$, for polymer bonds and initiation rates for depolymerization (8)

Polymer	$D(R\text{–}R)$, kcal/mole	k_1, sec^{-1}
Tetrafluoroethylene	80	$10^{30} \exp(-120{,}000/RT)$
α-Methyl styrene	90	$10^{19} \exp(-65{,}000/RT)$
Methyl methacrylate	68	—
Ethylene	(90)	$[k_0 = 10^{17} \exp(-72{,}000/RT)]$

TABLE 7

Principal products from pyrolysis of polymers (Ref. 2)

Polymer	Structural unit	Principal volatile products
Cellulose		Levoglucosan; CO; CO_2; H_2O
Vinylidene chloride	$-CH_2CCl_2-$	HCl
Vinyl chloride	$-CH_2-CHCl-$	HCl; C_6H_6
Vinyl acetate	 $-CH_2-\overset{\overset{\overset{\overset{O}{\|}}{OC-CH_3}}{|}}{CH}-$	CH_3COOH
Chloroprene	 $-CH_2-\underset{\underset{Cl}{|}}{C}=\overset{H}{C}-CH_2-$	HCl
Acrylonitrile	 $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\underset{CN}{|}}{C}}-$	Small amounts of HCN; acrylonitrile
p-Xylene		4% of xylene; toluene, benzene, methylstyrene, methylethylbenzene
Benzyl		7% of toluene; benzene, xylene
Phenyl		H_2

Polymer decomposition may also be catalyzed or inhibited by gases.[4] Small catalytic quantities of oxidant gases will act essentially as electromagnetic radiation and initiate depolymerization with near-zero activation energy. In a burning process, then, one might anticipate a lower activation for polymer decomposition because of the presence of the oxidant.

Recently, we have studied[12] the thermal decomposition of an aromatic polymer (poly[*N*,*N*-(*p*,*p*′-oxydiphenylene) pyromellitimide]) under 1 to 150 mm pressure of oxygen, and over the temperature range of 480° to 520°C. We found the much faster oxygen-induced rate of initial weight loss to depend upon the 0.4 power of the oxygen pressure. One would, by postulating a chain reaction and oxidative initiation, anticipate an 0.5-power dependence. The oxidation of hydrocarbons at low pressure when measured by oxygen consumption normally has a first-power dependence upon oxygen pressure.

The physical deterioration of polymers by oxidative aging processes[13,14] has long been of concern to the polymer field. Depending on the polymer and conditions, most polymers oxidize slowly at ambient temperatures and antioxidants are incorporated in polymeric articles.

Oxidative aging will, in general, be expected to enhance the ignition probability and combustibility of polymers. Studies of pyrolytic decomposition are normally carried out on highly purified materials and, thus, data such as listed in Tables 1 and 2 are not likely to be always characteristic of aged materials.

TABLE 8

Thermodynamic quantities* for decomposition of polyethylene and polytetrafluoroethylene (Ref. 8)

		ΔH, kcal/mole	ΔS, cal/mole/°K	ΔF, kcal/mole
a	$\sim CH_2CH_2\sim \rightarrow CH_2{=}CH_2$	22.35	34.07	12.19
b	$\rightarrow 1/3\ C_6H_6 + H_2$	16.46	34.28	6.23
c	$\rightarrow 2\ C$ (Graphite) $+ 2\ H_2$	9.85	46.76	−4.10
d	$\rightarrow n$-Alkenes $[(1/18)CH_3(CH_2)_{33}CH{=}CH_2]$	1.09	2.03	0.49
e	$\rightarrow C$ (Graphite) $+ CH_4$	−8.04	27.49	−16.23
f	$\sim CF_2CF_2\sim \rightarrow CF_2CF_2$	46	45	33
g	$\rightarrow 2\ C$ (Graphite) $+ 2\ F_2$	194	71	172
h	$\rightarrow C$ (Graphite) $+ CF_4$	−27	35	−38

* With the exception of graphite all the substances are taken to be in the "ideal" gas state at 298.2°K. For the high polymers, this "ideal" gas state is evidently for the polymer in its most extended conformation (Ref. 18).

Burning of Polymers

Friedman[15] has pointed out that plastics burn with several times the intensity of cellulose and that the heat of combustion per gram (or cc) for polyethylene is greater than that for cellulose by over a factor of 2. Also, cellulose absorbs water and tends to char while polyethylene is lyophobic and burns without char production. These variations in behavior and properties suggest that a comparison of enthalpies of combustion and approximate reaction temperatures may be helpful.

In Table 9 the enthalpies for the burning of polyethylene with three different oxidants are compared along with data for cellulose. All the species are taken in the gas phase, except for carbon. The values obtained with carbon as graphite and carbon as vapor are both listed. The well known observation that oxidative attack on the hydrogen in hydrocarbon occurs more easily than attack on carbon suggests the separation of the burning process into two separate processes, one for the burning off of the hydrogen and one for a hypothetically sequential combustion of the carbon. The reactions are compared on the basis of one polymer carbon. Hence, the factor 1/6 for the cellulose. We would have preferred to have compared the heats of combustion with activation energies for the same process. Since such data was lacking in most instances, we used general information and experience to deduce comparative reaction temperature. The approximate reaction temperature for the hydrogen oxidation is hundreds of degrees below that for graphite oxidation. It is evident from the table that the usefulness of chlorine-containing substances as flame retardants is related to the relative ease with which chlorine will attack hydrogen and the relative difficulty it has in reacting with carbon. This serves to emphasize again considerations of importance to flammability long known from studies on the decomposition of cellulose,[16] where the presence of small amounts of slightly acidic or ionic substances will catalyze the dehydration of cellulose. The size of the exothermicity of the dehydration process suggests that this process should occur more readily than it has been observed.[16]

Heats of Vaporization and Decomposition

It has been indicated that heats of gasification,[15] presumably the sum of the heats for vaporization and decomposition, of plastics are important in the mathematical analyses of burning systems. In these treatments, a parameter called the B-number is defined as

$$B=\frac{r\cdot H-C_g(T_s-T_a)}{L+C_c(T_s-T_i)}, \tag{16}$$

where r is the stoichiometric mass fuel–air ratio, H and L the respective heats of combustion and "vaporization" per unit mass, C_g and C_c heat capacities of gas and liquid, and T_s, T_a, and T_i are, respectively, the temperatures of surface of the burning material, the ambient air, and the interior of the material. Thus the B-number is the ratio of energy released by the burning to the energy required to vaporize the fuel. Values of L for polymers are, in general, untabulated as such. For polymers, we may take L to be the sum of the heats of molecular decomposition H_d, and molecular vaporization H_v

$$L=H_d+H_v. \tag{17}$$

TABLE 9

Comparison of enthalpies (kcals) of combustion-type reactions

Reaction	ΔH_c, kcal Carbon as:		~Reaction *T*, °C (carbon as graphite)
	Graphite	Gas	
$-CH_2-+1/2\ O_2 \rightarrow C+H_2O$	−52.9	118.8	100
$C+O_2 \rightarrow CO_2$	−94.1	−265.8	500
	−147.0		
$-CH_2-+F_2 \rightarrow C+2HF$	−123.5	48.2	low, <0
$C+2\ F_2 \rightarrow CF_4$	−220.0	−391.7	300
	−343.5		
$-CH_2-+Cl_2 \rightarrow C+2\ HCl$	−39.2	132.5	200
$C+2\ Cl_2 \rightarrow CCl_4$	−25.5	−197.2	high, >1000
	−64.7		
$1/6\ C_6H_{10}O_5 \rightarrow C+5/6\ H_2O$	−14.0	157.7	300 (cat. <250)
$C+O_2 \rightarrow CO_2$	−94.1	−265.8	500
	−108.1		
$H_2+1/2\ O_2 \rightarrow H_2O$	−57.8		

If the material decomposes into small molecules, then it is likely that $H_d \gg H_v$. Conversely, if it decomposes into large molecules then $H_v \gg H_d$. However, since L here is units of heat per gram, this effect will not be pronounced.

For the relatively few polymers which decompose (depolymerize) back to the original monomer we have values for H_d since, for these systems, H_d is equal to the enthalpy of polymerization, Table 5. Since the values in Table 5 are for the process at 25°C, we calculated L values at 25°C. Heats of vaporization at 25°C were estimated except where values were in the literature. These L values are listed in Table 10 along with values for polystyrene and polyethylene. For these polymers, which decompose to products other than monomer, we deduced heat of decomposition in several ways. For polyethylene, we had previously calculated a value of the enthalpy of decomposition; see Table 8, Reaction (d). This was based on the concept that this decomposition can be approximated by the indicated Reaction (d). Here, we assume that the products predominantly a variety of *n*-alkanes and *n*-alkenes can be represented by a n-$C_{36}H_{72}$ alkene (molecular weight, 504). A second calculation was made assuming the products were representable by a n-$C_{18}H_{36}$ alkene (MW, 252). In Table 10 we list the molecular weight (or average) of the decomposition products. For the alkenes the heats of vaporization would be comparable to those for the corresponding alkanes. We have been investigating the

TABLE 10

Estimated heats of gasification for some polymers at ~25°C

Polymer	m, (g/mole)	L (cal/g) Calc.	L (cal/g) Exptl., Ref. (17)
Methyl methacrylate	100	232	380 at 460°C
Formaldehyde	30	630	440 at 160°C
α-Methyl styrene	118	158	
Tetrafluoroethylene	100	415	
Styrene	(198)	241	
Ethylene (d)	(504)	102	
Ethylene (d′)	(252)	141	
Ethylene (b)	(21)	683	
Ethylene (a)	28	924	

vaporization of linear alkanes[18] and find that their heats of vaporization in kcal/mole can be approximated by

$$\Delta H_v = 3.21\ n^{2/3} - 0.0193\ T + 2.92, \tag{18}$$

when n is the number of carbon atoms in the alkane and T is in °K. The 2/3 power dependence is interpreted to indicate that these flexible molecules coil up and vaporize as spheres. Thus, the incremental heat of vaporization continually decreases with size of molecule.

In Table 5 we have data on various hypothetical decomposition processes for polyethylene; we also calculated L values shown in Table 10 for decompositions a and b. As the temperature increases, one anticipates that the decomposition mechanism will shift from d to d′, b and a (see Table 10).

For polystyrene, which decomposes to give 42% monomer, the heat of polymerization and the heat of vaporization of styrene, weighted by the actual number of bond ruptures, were used for the calculations.

The measured L values of Dmitriev *et al.*[17] are listed in Table 10 for comparison. Their value of 440 cal/gm polyformaldehyde is exactly the molecular heat of polymerization divided by 30, the molecular weight of the monomer.

At the decomposition temperature of 160°C, formaldehyde would be above its critical temperature and there would be no heat of vaporization; on the other hand, one would expect the heat of polymerization to increase. The higher experimental value for methyl methacrylate suggests that other decomposition processes are becoming important rather than the decomposition to monomer. The temperature (460°C) is several hundred degrees above that used in earlier degradation studies.[1]

We have for some time considered it desirable to measure heats of decomposition. However, available instruments, such as the differential scanning calorimeter, were not completely suitable, partly because the temperature range did not extend as high as we wished to go and partly because of problems in handling and measuring the volatile products. Several polymers (for example, polyvinylidene fluoride) which decompose to hydrogen fluoride and char probably have exothermic heats of decomposition. For polyvinylidene fluoride, one estimates an exothermic heat of approximately 20–30 kcal/64 g.

ACTIVATION ENERGIES FROM REGRESSION RATES

An extensive study of the burning of polymers has been carried out by Blazowski, Cole, and McAlevy.[19] An experimental arrangement was used which permitted measurements to be made of the length of polymer rod consumed per time interval and the surface temperature of the burning polymer. From such measurements, determination of activation energy for polymer consumption under burning conditions were made. Results were reported for six polymers. Their results are listed in the last column of Table 11 for direct comparison with the activation energies reported[1–3] for polymer pyrolysis based on weight loss of polymer heated under vacuum. From the point of view of this writer, the results show good agreement. An experimental value for the activation energy of Delrin is not available. However, from its heat of polymerization (13.2 kcal/mole) and low decomposition temperature, one anticipates an activation energy between 20–30 kcal/mole.

The pyrolytic activation energy for nylon is low; but, in pyrolytic studies, nylons behaved very erratically, having activation energies and rates that depended upon the method of sample treatment. On the other hand, the pyrolytic E_a for polypropylene is high. In view of the many experimental effects possible in both pyrolytic and regression rate studies, the agreement is very good.

In studies of polymer pyrolysis, the weight loss is measured isothermally and the sample is uniformly held at a given temperature, i.e., there is no temperature gradient. The rate of weight loss is not often dependent upon the conversion to the first power but may, as in polyethylene and polystyrene, have a continually varying dependence upon conversion and hence upon the weight of sample remaining. However, the rate of weight loss initially $(-dw/dt)_0$ is always observed to be proportional to the initial weight w_0. At any other point of conversion during a given experiment, we also find that

$$(-dw/dt)_c = Kw_c.$$

Now, what one expects to find in regression rate studies is that the rate of regression $(-dl/dt)$ would be related simply to rate of weight loss by

$$-dl/dt = -dw/\rho A dt = Kw_a/\rho A_a = Kl_a,$$

TABLE 11

Comparison of activation energies from pyrolysis of polymers (Ref. 1) and regression rates (Ref. 19)

Polymer	E_a Pyrolysis	E_a Regression rate
Methyl methacrylate	32–52	42–48
Ethylene	72	73
Propylene	58	40
Formaldehyde (Delrin)	($\gtrsim$20)	24
Nylon 6,6	42	65
ICRPG Urethane	—	30

where ρ and A are density and burning area, respectively. By assuming a constant active weight w_a at the measured surface temperature as the source of volatile fuel, we can equate $dl/dt=Kl_a$, where l_a is the active thickness for the pyrolyzing skin. It is interesting to note that, with available data,[19,1–3] one finds that l_a values of $1\text{–}2\times10^{-2}$ mm for polymethylmethacrylate, and $1\text{–}2\times10^{-3}$ for polyethylene, and are relatively constant with regression rate.

A final comment is that while polymers volatilize at a rate proportional to the weight of material, liquids (and also crystals) vaporize at a rate proportional to surface area. This difference should perhaps be kept in mind, since in many other aspects amorphous polymers are considered analogous to liquids.

CONCLUDING DISCUSSION

There is a considerable amount of pertinent thermochemical and kinetic data on reactions in the condensed phase of polymer melts that is applicable to problems of flammability and combustibility. It appears, however, that no extensive effort has been made to apply available data and also it is not clearly evident what information is important and required. It seems evident that the main problem is the lack of experimental procedures and theory for characterizing, measuring, investigating, and standardizing fire phenomena. Fire damage is often the result of unforeseen factors or unanticipated situations.

The areas of polymer degradation which are most pertinent to the fire area would include:

1. Volatile products at temperatures and rates near those occurring during burning.
2. Heats of decomposition measurements, particularly in the higher temperature region.
3. Studies of oxidant induced weight loss and oxidation or combustion under oxygen-deficient conditions.
4. The variation in combustibility and volatile products with aging of materials.

One can calculate that the rugs and padding in a house have enough combustible fuel to consume fifty times the oxygen in the house. Also, if only half the oxygen is consumed and some asphyxiative[20] gases are produced, not to mention carbon monoxide, the condition is lethal.[20] The important factor is obviously the speed of burning and ignitibility of the materials. Such properties are likely to be enhanced with deteriorated or aged materials.

5. Study of pyrolysis, combustibility, and ignitibility of mixtures of materials, blends, and bulk samples simply placed in the same furnace, for instance.

The volatile species from one substance may react vigorously with another substance or its volatiles. Another not unlikely possibility is that volatiles from one polymer will initiate or catalyze the decomposition of another polymer, producing fuel of low flash point, while a third polymer provides ignition by rapid exothermic decomposition.

Our basic knowledge is quite limited in the area of materials compatibility for fire safety. This is becoming an extremely pertinent item because modern technology is introducing an extreme variety of materials into the field; consider, for example, the variety of substances in textiles, garments, composite structures, and building materials.

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CONTRIBUTIONS OF ANALYTICAL CHEMISTRY TO FIRE PROBLEMS

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INTRODUCTION

One can readily picture early cave man, having "caught" a fire, staring at the flame and wondering what it was. With time, more civilized man would come to consider fire as one of the four basic elements from which all matter was composed. His lack of understanding of fire would eventually lead him to invent a special property, phlogiston, in order to explain the visible flame. It was not until the latter part of the 18th century, however, that, with the beginnings of modern chemistry and the beginnings of *quantitative chemical analysis*, man began to acquire understanding of the chemical nature of fire. Since then, man has come a long way in developing his understanding of fire, but the complexities of the chemical processes involved, their speed and their dependence on composition and environment leave not-so-primitive man still staring at a flame and wondering what it really is.

Fire is exceedingly important to man in two ways, first, because he has learned (and seems to be doomed to have to continually relearn) that it can be so very destructive, and, second, because he has partially learned to harness it to do his bidding, and with it is now literally moving mountains. For these reasons he has applied a great effort to learn more about it, and still is.

In order to understand what fire is, and how it behaves and propagates, a great number of scientific disciplines must be invoked, not the least of which is analytical chemistry. Again, however, because fire is so complex, it is exceedingly difficult to separate these disciplines discretely, and in looking at the various approaches to the study of fire it is readily apparent that analytical chemistry is not only the handmaiden of other disciplines but is intimately interwoven with them. The determination of products, intermediates, unstable species, highly reactive species, excited states, etc., during the combustion process must continue to remain one of the critical keys to greater understanding of the mysteries of fire, understanding which, hopefully, will lead to greater control of fire. Though analytical chemistry has already contributed a great deal towards our understanding to date, one can readily see that the challenges to the analyst and analytical chemistry in the future are even more demanding and exciting.

WANTED AND UNWANTED FIRE

Fires come in two great classes—wanted and unwanted. In the former category fall man's comforts and joys, fires for cooking and warmth, fires for power and locomotion, fires to go to the moon and back, but in this category also fall man's hates, fires for battle, to kill, to burn property and maim humans. In the second category fall man's fears, the uncontrolled burning of his home, his forests, his goods, his loved ones. And though much of the chemistry of a fire may remain the same, the approach in studying it—or controlling it—may take a different tack, depending on whether the fire is useful or destructive, and depending on what the individual researcher wants to learn. Because of the complexity of fires, the researcher often chooses, and may limit himself to, a certain aspect of combustion to suit his own curiosity or purpose. For example, he may want to study the chemical reactions occurring in the preflame stages of combustion so that he may learn how to control succeeding stages, or he may want to study the flame itself with all its "hot" species such as free radicals, ions, etc., in order to get at the kinetics and mechanisms of combustion, or he may want to study products formed in fires, particularly those that might be highly toxic, in order to evolve techniques for protecting life, or he may be interested in determining the best way to suppress a fire, or he may want to learn why some materials ignite spontaneously under one set of conditions but not under others which on the surface appear to be more severe. The complexity of fire is well illustrated by this apparent anomaly as shown in Table 1 in which it is seen that with increasing temperature a fuel may exhibit alternating zones of ignition and apparent non-ignition. Such behavior is hardly in keeping with the classical concept that the rates of chemical reactions increase with increasing temperature. The ultimate goal in all of these studies however, is to achieve better means of enhancing wanted fires or controlling or preventing unwanted fires.

The study of fire is further complicated by the fact that there are so many different kinds of fires, based not only on different fuels and oxidizers, e.g., rockets,

TABLE 1

Zones of spontaneous ignition (pos.) and nonignition (neg.) (in air)

Navy special fuel oil (Sample NRL-71-7)*		*n*-Hexadecene**	
Temperature range (°F)	Result	Temperature range (°F)	Result
Below 473	Neg.	Below 493	Neg.
473–479	Pos.	493–505	Pos.
480–486	Neg.	506–518	Neg.
487–542	Pos.	519–613	Pos.
543–548	Neg.	614–691	Neg.
549–571	Pos.	Above 692	Pos.
572–580	Neg.		
581–585	Pos.		
586–632	Neg.		
633–659	Pos.		
660–666	Neg.		
Above 667	Pos.		

* ASTM Method D 286–66T.

** 21 ml. reaction chamber.

metals, metal–halocarbon, etc., but also based on environment (with the same fuel and oxidizer), e.g., an exploding oil tanker and an automobile engine. Thus, the demands on analytical chemistry to evolve appropriate techniques applicable to study of the particular fire in question become very acute. In this regard, researchers have been inventive indeed, and all sorts of approaches have been tried, many very successfully.

The literature is replete with discussions of these, but to a large extent the approaches used are described in articles and books devoted to what is learned from the analytical results rather than to the analyses themselves.*

TECHNIQUES

It is impossible to cover all the techniques used and their many variations. A few are mentioned below.**

Wet Methods

Although in the past few decades analytical chemistry has tended to become more and more highly instrumented, wet methods are still used, for example for following the concentrations of peroxides.

Orsat

Both wet and dry. Tedious but useful when only a few species are involved. Old wet method for O_2, CO_2, etc., still carried on some ships for flue gas analysis.

Mass Spectrometry

An exceedingly useful tool for the analysis of both stable and unstable species. Particularly useful when coupled to a small computer. Unstable species, such as ions, can be measured by having the inlet to the spectrometer be the direct probe into the flame (Knudson probe).

Gas Chromatography

A tool developed in the past decade and a half which has proven to be exceedingly useful for analysis of stable species. It is unusually versatile, accurate and sensitive and can analyze very small samples. Coupled to a small computer it can yield a great deal of information relatively quickly. An example is shown in Figs. 1 and 2, Fig. 1 being the chromatogram of a sample taken from a butane cool flame and Fig. 2 the computer print-out, which includes retention times and concentrations.

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* For this reason, no attempt has been made to cite references or to give a bibliography. The extent of the literature on the subject is shown by the many well known books on fire, combustion, etc., by the biennial publication of the Symposia (International) on Combustion, by the various journals on the subject, by the extensive abstracts in Fire Research Abstracts and Reviews, etc.

** The author is highly indebted to the excellent treatise "Flame Structure" by Fristrom and Westenberg for much of this part of the paper, and the reader is referred to this work for more details.

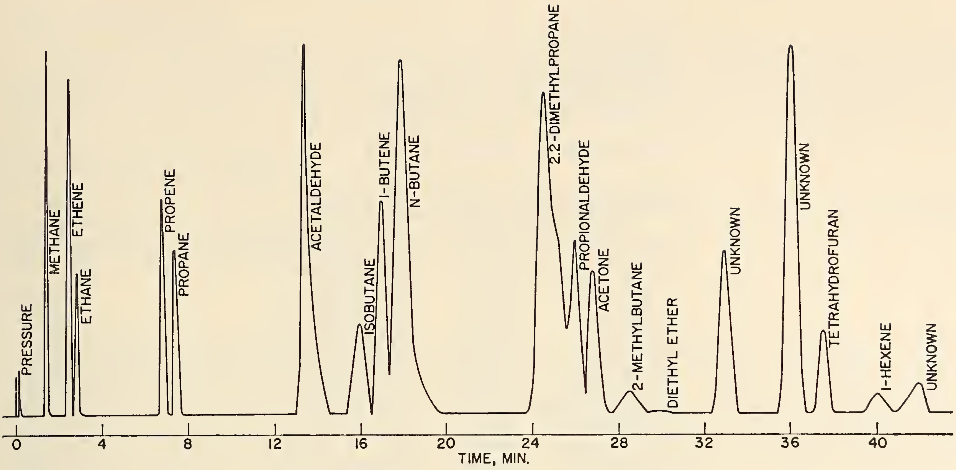


FIG. 1. Chromatogram of a sample taken immediately downstream of a butane cool flame.

Gas Chromatography–Mass Spectrometry

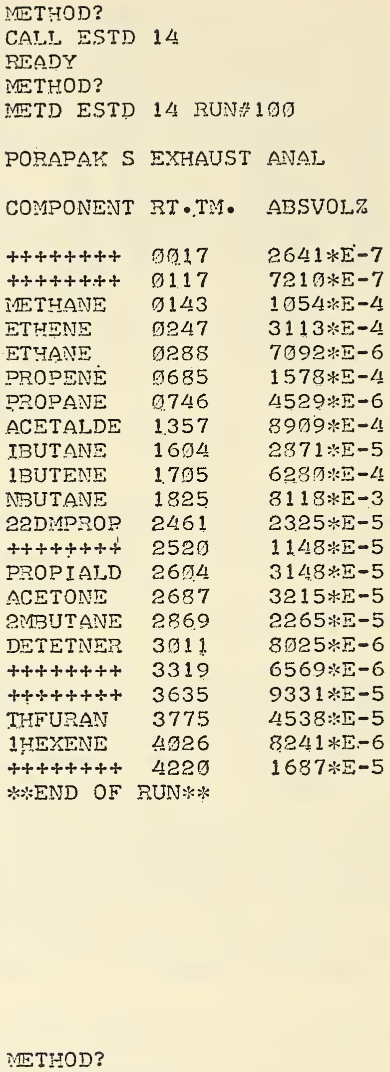
The combination of a gas chromatograph and a mass spectrometer in tandem gives the analyst an exceptionally powerful tool for stable species, especially for complex mixtures. Normally in a very complex mixture, such as that occurring in early stages of a flame or from pyrolysis or incomplete combustion, data from a mass spectrometer alone is difficult to analyze. But, if the mixture is first passed through a chromatograph, the sizes of the eluted peaks tell how much of a given component is present, the retention time gives an index of what it might be, but if a mass spectrometer is coupled to the chromatograph essentially as though it were a detector, identification is usually unequivocal. Even in mixtures where separation is incomplete on the chromatographic column, the few components that may be present in a single peak can still be identified by the spectrometer.

Absorption Spectroscopy

This is a particularly useful tool to look into the flame itself because unlike many sampling probes it does not disturb or distort the flame. It has proven particularly useful for study of free radicals, especially OH. Absorption spectroscopy, both *ir* and *uv* (very little in the visible) has also proven useful for condensed samples taken from flames by probes, etc.

Flame Photometry

Particularly useful for identification of species that emit light in the flame as a result of the reactions taking place, e.g., excited HCHO in cool flames. It gives considerable insight into these reactions and where they occur, but data are difficult to interpret quantitatively.



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METHOD?
CALL ESTD 14
READY
METHOD?
METD ESTD 14 RUN#100

PORAPAK S EXHAUST ANAL

COMPONENT RT.TM.  ABSVOLZ

++++++++  0017    2641*E-7
++++++++  0117    7210*E-7
METHANE   0143    1054*E-4
ETHENE    0247    3113*E-4
ETHANE    0288    7092*E-6
PROPENE   0685    1578*E-4
PROPANE   0746    4529*E-6
ACETALDE  1357    8909*E-4
IBUTANE   1604    2871*E-5
1BUTENE   1705    6280*E-4
NBUTANE   1825    8118*E-3
22DMPROP  2461    2325*E-5
++++++++  2520    1148*E-5
PROPIALD  2604    3148*E-5
ACETONE   2687    3215*E-5
2MBUTANE  2869    2265*E-5
DETETNER  3011    8025*E-6
++++++++  3319    6569*E-6
++++++++  3635    9331*E-5
THFURAN   3775    4538*E-5
1HEXENE   4026    8241*E-6
++++++++  4220    1687*E-5
**END OF RUN**



METHOD?
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Fig. 2. Computer print-out of data obtained in Fig. 1.

Tracers and Scavengers

A variety of tracers can be used very successfully for studying reactions in fires and combustion. These include the use of stable isotopes (e.g., deuterated compounds, compounds containing O^{18}, etc.) or radioactive isotopes, or compounds added to a flame, such as N_2O which reacts with both H and O atoms (to give N_2 and NO) and hence can be used to measure their concentrations. Scavengers can also be used, especially in microprobes, in which the scavenger is added in excess immediately after sampling at the orifice to quench radicals or other unstable species.

ESR Spectroscopy

Electron spin resonance can be used to measure free radicals and atoms in flames due to their having an unpaired electron. Direct measurements (flames in the resonant cavity) are hard to interpret but probing has been successful.

Photography and Schlieren

These can be very useful for recording positioning of flames, showing gradients, fast reactions, intensities, etc., and are used extensively.

Ions

The electrical properties of flames and fires are particularly intriguing and the determination of charged species is a subject all its own. Many different kinds of measuring devices have been used, mass spectrometry, collision cross sections, Langmuir probes, radio-frequency absorption, photography, etc. Special studies have been made of ions in rocket exhausts and their effect on communications black-outs.

TGA

Thermal gravimetric analysis—coupled with gas analysis—is a useful tool for measuring pyrolysis, particularly of solids, and can be used to give indices of flammability potential and behavior.

Reactors and Burners

The *Vertical Tube Reactor*: Many, many different reactors, burners and other devices have been used for studying fires and flames. Of special interest (at least to the author, since it was developed in his laboratory) is the Vertical Tube Reactor in which flames can be separated into three distinct luminous stages separated in space by non-luminous regions. This is illustrated in Fig. 3. The beauty of such a reactor is that it makes studying and probing the flame much easier, and also allows for the insertion of scavengers or reactive species into the different stages of the flame processes.

Probing

Probing to obtain valid samples is exceedingly difficult. In sampling flames by use of probes, one must not disturb the flame, and must also assure himself that reactions do not take place in the probe itself. Probes can be designed and used to collect meaningful samples, such as the microprobe described by Fristrom and Westenberg (loc. cit.), but the researcher must be forewarned that it is not easy.

APPLICATIONS AND STUDIES

The applications and contributions of analytical chemistry to fire problems and research are legion. It must be emphasized that analytical chemistry *per se* may not be the end objective but without it the end objective could not be achieved. Only a few examples can be given and in only one or two of these will we permit ourselves the luxury of an excursion into detail.

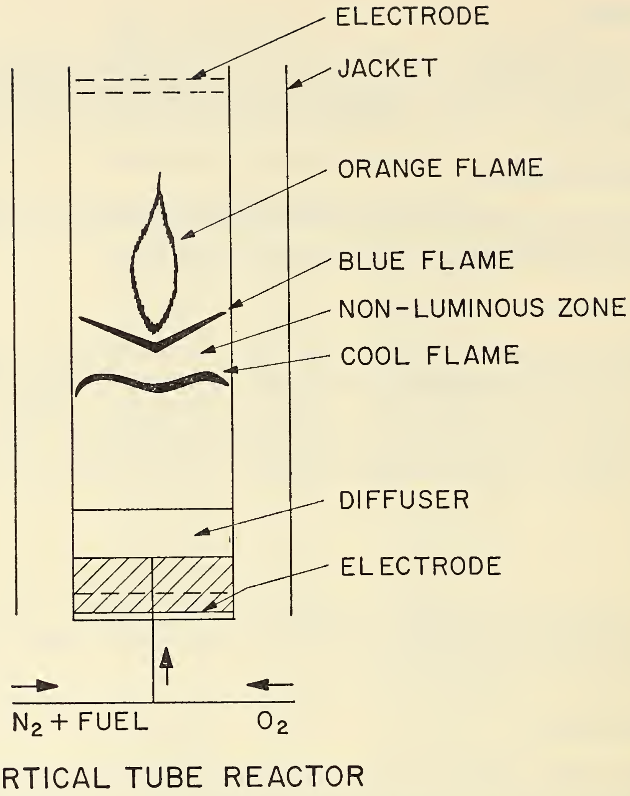

FIG. 3. Schematic of the vertical tube reactor showing relative positions of flame stages.

Safety

Safety is an area where analysis has had a very important impact. For example, as man has acquired a better understanding between flammability characteristics of liquid petroleum fuels and their composition he has been able to insist that new designs in refinery techniques be put into practice so that the fuels would be safer. One need only remember the rashes of fires that used to occur many years ago with kerosene, and even with gasoline, until by virtue of greater control of composition, as measured by different analytical techniques, the properties of such products have been modified so as to make them much safer. The story keeps repeating itself as new fuels and oxidizers are developed, especially high energy ones, which for that very reason are often unstable and hence dangerous. The various analytical techniques used to measure properties of fuels and oxidizers often end up as requirements in the specifications used for the purchase and sale of the products, and in order that there shall be no misunderstanding or disagreement between seller and purchaser, these techniques are very carefully worked out. Indeed, whole societies, such as the ASTM, devote a great deal of attention to this very point, and are continually developing new means for measuring not only composition or performance, but safety as well.

Fire Suppression

Again, analytical chemistry has played a large part in achieving better materials and techniques for suppressing fires. The development of commercial materials such as "Light Water" and "Purple-K-Powder" are greatly abetted by acquiring understanding of what is needed composition-wise. Even today, the composition of "Light Water" concentrate is being radically modified because analysis has shown that problems in corrosion require it. Analytical chemistry has also played a significant role in the development of vapor phase inhibitors that interfere or react with free radicals and other chain carriers in the combustion process.

Flammability

This is related to safety but will be treated separately because it is so critical in creating a potential for fires. For example, the characteristics of the vapor space above a liquid petroleum product must be known (hence measured) if one is to design safer fuels and fuel handling and storage systems. A petroleum fuel does not burn in the liquid phase, it must evaporate first. But petroleum fuels are complex mixtures of hundreds of components, so that neither the composition nor properties are the same from batch to batch of a given product. Yet, knowledge about the vapor space is critical if prevention of fires is to be achieved by control of that space, control which has not always been achieved as attested to by many disastrous explosions, especially in tankers.

The Navy is concerned about the properties of JP–5 jet fuel since an aircraft carrier may contain as much as 1.5 million gallons of it, and it is not carried in a protected part of the ship. For safety's sake, the specifications for JP–5 state that it shall have a minimum flash point of 140°F. But this is not a fixed property, and can vary depending on the ullage, as can be seen in Fig. 4. This shows the minimum temperature at which the vapor space is flammable for two JP–5's and for a pure hydrocarbon, *n*-undecane. The vapor concentration above *n*-undecane is fixed, since it is a pure compound, and, hence, so are the flammability properties as shown in the figure. But the JP–5's, being indefinite mixtures, have varying flammability properties with ullage, and are not consistent as shown by the fact that one fuel has a small variation with ullage whereas the other one shows a very marked effect. Indeed, extrapolation of the curve for this latter fuel shows that as one approaches zero ullage, the vapor space above the fuel would be flammable at 120°F. This shows that this particular fuel, even though it more than meets the specification with a measured flash point of 144°F, can be flammable, and hence hazardous, at a much lower temperature.

Another important point from the standpoint of safety deals with the stratification of fuel vapors in large tanks. There is often a barrel or two (or more) of product left in a tank after discharge from a tanker. During discharge, air replaces the fuel. If the product is highly volatile, such as gasoline, JP–4, naphtha, or crude, right after discharge there will be a very thin layer of fuel vapors immediately above the liquid that is too fuel-rich to burn. Just above that there will be a small layer that is in the flammable range, and above that, the vapor is too lean to burn. With time, the two bottom layers expand until eventually (if enough liquid exists) the whole space is too rich to burn. A few measurements have been made in real-

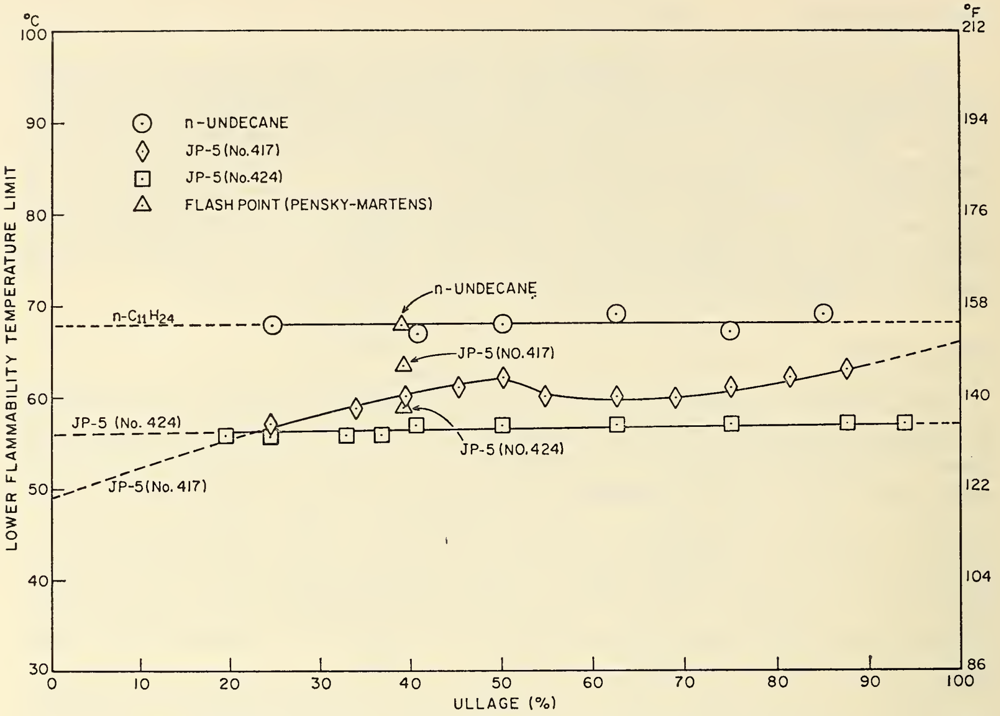

Fig. 4. Effect of ullage on the lower flammability temperature limit.

life situations in tankers, using simplified techniques, and these have indicated that it takes days for this process to occur, but details about how large the flammable layer is, where it is, and how long it lasts under the wide variety of fuels and practices that are used are mostly unknown. Indeed, the paucity of good solid information on this subject is amazing, yet it certainly is important, especially for ships running empty, as shown by the explosions of the three super-tankers off the coast of Africa.

There is a requirement in the specifications for several Naval fuels, called the "explosiveness" test. Essentially, the requirement states that, at 125°F, the concentration of fuel vapors above the liquid in a container should be less than 50% of the lower flammability limit. The present method for this test uses an explosion meter as the means of analyzing the vapor concentration, which is also the method commonly used in the field. But the response in an explosion meter is dependent on the structure of the hydrocarbon (meters are usually calibrated with *n*-hexane) and so a new and more accurate method was desirable. In our laboratory we have designed a new analytical tool for measuring vapor concentrations as a function of their flammability (the "flammability index") based on the hydrogen flame ionization detector, so popular in gas chromatography. A hydrogen–air flame does not generate ions, but if organic vapors are added, chemi-ions are formed. Most fortuitously, for hydrocarbons the amount of these ions is a function of the molecular weight and concentration present, so that effectively the ionization detector counts carbons present. But, as shown in Fig. 5, for most hydrocarbons (and their mixtures) these are also related to flammability. Hence, an analytical scheme has been developed, based on the hydrogen flame ionization detector which measures flammability index directly. Although still in the bread-board stage, we have already demonstrated the accuracy of the method, as shown in Tables 2 and 3.

It is easily seen that this new analytical tool will be applicable to the study of all the situations described above.

Detection

Devices for the early detection of fires and/or activation of alarms and extinguishers exist which are based on chemical characteristics of fires and which semi-quantitatively measure such properties as heat, ionization, light, etc. They are semi-quantitative in the sense that they must sense a given amount or rate of change of a fire property before triggering so as to not give false alarms, and yet do this early enough to allow for corrective action. Such devices are based on thermocouples, low-melting solids, photocells, ion probes, distortion of laser beams, etc., but there is still a real need for better and better detectors.

Efficiency and Power

Even though internal combustion and jet engines have been developed largely empirically,* extensive use of analytical chemistry has been made in the study and control of the "wanted" fires in such engines. There is always the desire to squeeze that extra erg of energy out of an engine and one must determine what is happening, and where, in order to do so. The location and efficiency of burning in boilers is very important if fuel is to be used economically and the design and operation of sprayer plates is controlled by this. Also, analytical chemistry has been very important to the study of the mechanisms by which tetraethyl lead reduces knocking, and very clever probing devices have had to be developed to obtain samples from high speed engines. There are many other examples.

TABLE 2

Flammability index of pure hydrocarbons in air

Hydrocarbon	Concentration C, % v/v	Lower Flammability L, % v/v	Flammability index (E) Expt.	Flammability index (E) Calc. ($E=C/L$)
Methane	1.66	5.0	0.26	0.33
i-Butane	0.45	1.8	0.25	0.25
i-Butane	0.90	1.8	0.50	0.50
i-Butane	1.35	1.8	0.75	0.75
n-Hexane	0.499	1.2	0.42	0.42
n-Octane	0.200	0.89	0.22	0.22

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* Indeed, had we waited until we really understood the full chemistry of combustion before we designed these engines, we would still all be walking, such is the complexity of the combustion process.

$$E = C/L \tag{1}$$

$$\rho = k_1 n C \tag{2}$$

Eliminating C between Equations (1) and (2):

$$E = \rho / k_1 n L \tag{3}$$

$$nL = k_2 = \text{constant} \tag{4}$$

$$E = \rho / k_1 k_2 \tag{5}$$

$$E = k\rho \tag{6}$$

Where

E = Flammability Index

C = Concentration of Hydrocarbon Vapor (%v/v)

L = Lower Flammability Limit (% v/v)

ρ = Response of Flame Ionization Detector

n = Carbon Number

k_1, k_2, and k are constants

FIG. 5. Equations showing relationship of flammability index with flame ionization detector response.

THE FUTURE

The analytical chemist now faces many demanding but interesting challenges in man's involvement with fires. One of his primary aims, obviously, is to obtain better control over both wanted and unwanted fires (and their products) by achieving better understanding of them. The following are some examples of areas of challenge.

Pollution

Now that the public has "discovered" pollution and is pressing Congress into doing something about it, techniques for measuring pollution from all sorts of fires will become in much greater demand. Most of these will have to be aimed at the "wanted" fire (including those designed to study and control unwanted fires or to train people in combatting them) since people are still conditioned to be somewhat philosophical about unwanted fires and to accept their consequences as still being part of the disaster. Therefore, we are talking largely of wanted fires for the generation of heat and power. The trends in demands for the future are already quite obvious. As the lid on pollution is clamped ever tighter, there will be a need to develop analytical techniques that will be more and more sensitive, accurate, simple, cheap and rugged. For example, we are becoming much more interested in simple devices for measuring not only the total oxides of nitrogen, but how much of which ones. It is also becoming important that we do this accurately down to the fractional ppm range as opposed to, say, determining CO_2 in percentage values. For some materials, such as ozone, we will be interested in the parts per billion range. The time is coming when public authorities with a minimum of technical training will want to have such devices available for enforcement purposes, for example at automobile inspection stations.

The problem of disposal of wastes is also becoming more acute and the possibility of incinerating them on a large scale will have to be considered. Instead of open burning, special incinerators will be required and a high efficiency of burning becomes mandatory. Considering the increasing complexity of materials and the increasing use of elements and molecular moieties not found in nature, analytical methods for more varieties of pollutants will be needed, in addition to the present CO_2, CO, NO_x, SO_2, HX, HCN, smoke, organics, etc. For example, there is an increasing use of fluorine in articles of commerce. What and how much do we look for if these find their way into incinerators?

If one looks at the trends in concentrations of pollutants that will be allowed, it becomes apparent that the only direction they will be going will be down. This results from increased knowledge of subtle nonlethal effects of low concentrations. The need for increased sensitivity in analytical methods is apparent. The need for continuous monitoring (as in stationary power plants) also becomes apparent. And as we continue to discover the need for control of additional materials (e.g., certain types of organics), the need for analytical techniques for these new substances will also constitute a challenge.

TABLE 3

Flammability index of hydrocarbon mixtures in air

n-Alkanes (% v/v)							Other hydrocarbons	Percent flammability index	
CH_4	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$		Expt.	Calc.
1.2	—	—	0.22	0.20	0.055	—	—	71	76
1.2	—	0.25	0.22	0.20	—	—	—	85	90
—	—	0.50	—	0.20	—	—	—	63	64
—	0.28	0.25	0.22	0.20	—	—	—	87	85
—	0.33	0.29	0.26	0.14	0.13	—	—	105	105
—	—	0.46	—	—	—	—	0.078% Decalin	49	49
—	0.28	0.25	0.22	—	—	—	0.063% *n*-Octene-2	70	71
—	0.28	0.25	0.22	—	—	—	0.062% 2,3,4-TMP	70	71
—	—	—	0.42	0.37	—	—	0.14% Benzene	94	94
—	—	0.25	0.22	0.20	—	—	0.14% Meth. cyclopent.	77	78
—	—	—	0.32	0.29	0.13	0.049	0.076% *n*-Hexene-1	94	95

Toxicity

Many people are killed by fires due to "suffocation," "asphyxiation," "smoke inhalation," etc., without the real cause of death being pin-pointed. Also, it has been observed in a number of fires, particularly in relatively confined spaces, that some men (without respiratory protection) will fight the fire, help clean up and, except for the usual symptoms of exposure, appear to be in good health only to die of pulmonary edema a few days later. Again the true culprit may not be known. Although the toxic compounds generated may be essentially the same as those that must be considered under pollution, we are now concerned with acute rather than chronic toxicity. The problems of analysis are different in that sensitivity is not as important, but the variety of materials may be greater due to incomplete combustion especially of materials that may not burn "clean" such as plastics, paints, polymers, etc., to yield HCl, HCN, added CO, HF, NO_x, unsaturated aldehydes, other organics, etc. Also the concentration of potentially lethal agents may change markedly and quickly as new and different materials are attacked by the fire, or as the oxygen gets used up. The challenge to the analytical chemist to give us the right answers is very real, answers that we can rely on to provide increased and quick protection to the people. For example, the Navy now issues chemical protective masks to all of its men on ships. Can these be used and under what conditions, and when should they not be used? Should additional stop-gap protection be provided? These are important issues.

Unusual Atmospheres

Man seems to be determined to encapsulate himself and to place such capsules in a very hostile environment, environments that would be lethal if man were to be dumped into them suddenly. Examples are space ships, submarines, sea-labs, and even commercial jet aircraft at 30,000-plus feet.* We are even semi-encapsulating ourselves in not-so-hostile environments but in such fashion that egress is difficult. Access to large amounts of fresh air are limited because of recirculation of air-conditioned air. Ships and high-rise buildings are examples of this class. A fire started in such systems could easily be feeding on highly vitiated air in a very short time, and the chemical course of the fire could easily deviate markedly as the fire progresses. In submarines, space ships, diving capsules, hyperbaric (O_2-enriched) medicine, etc., the actual composition of the atmosphere is controlled—it is no longer air. Nitrogen may be substituted by helium, oxygen concentrations might vary from 4% to 100% and pressures from 7 to 0.3 atm as shown for SeaLab II and Apollo in Table 4.** Yet, most of our fire experience

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* Most of us who ride these aircraft don't stop to realize how hostile the environment really is just across the thin skin of the aircraft should we suddenly be dumped into its really sub-zero temperatures, too little oxygen partial pressure to support most of us, a violent depressurization and a blast of what air is there going by at 600 mph.

** Many of us like to compare the combustion of foods in the body with combustion of organics in fires, in that a certain level of oxygen is needed for both. However, once we get into these unusual environments, a very important difference appears. In order to sustain life comfortably, we need a partial pressure of oxygen of about 0.2–0.3 atm., regardless of the total pressure. This means that the concentration of oxygen must be adjusted accordingly. But from the standpoint of fires, it is the concentration of oxygen that is important, much more so than the partial pressure. Thus, in the environment inside SeaLab II, the aquanauts tried to light matches but with no success—4% oxygen is much too low to sustain such a fire.

TABLE 4
Oxygen levels in various environments

Environment	Total pressure (atm)	Concentration of O_2 (%)	Partial pressure (atm)
Apollo	1/3	100	0.3
Normal	1	21	0.2
SEALAB II	7	4	0.3

has been in air. We have already learned much about fire behavior in such environments through studies by NASA, Air Force, Navy, FAA, and others. One of the outstanding features of such fires is that rates of burning are markedly increased even with relatively small oxygen enrichments, and that materials that appear to be flame resistant in air (e.g., fireproofed fabrics) will burn merrily at higher oxygen levels. In 100% oxygen, even Teflon will "burn," and common combustibles burn almost explosively as was demonstrated so disastrously in the Apollo fire in 1967. Fires in capsules are particularly bad because there is no place for the occupants to run. The composition of fire products and their potential toxicity are also going to depend on the particular atmosphere. Problems of detection, analysis and control of such fires (partly by studying fire properties as a function of composition of materials) again challenge the analytical chemist to provide new techniques and new knowledge.

Control

The challenge of control of fires, both wanted and unwanted, continues to exist. Means to achieve control can be reached either empirically or by developing understanding and knowledge. It is in the latter area that analytical chemistry can play a vital part. As man continues to try to improve the efficiency of his engines and power and heating plants, he must learn still more about what is happening and when and where. In studying suppression of unwanted fires, he aims to learn more of the mechanisms involved so that he can learn to modify the course of the oxidation (e.g., what free radicals are formed, how they propagate chain reactions, which ones are most amenable to reaction with inhibitors, etc.).

Detection

In the case of unwanted fires, the sooner these are discovered, the better the chance of minimizing their damage. Therefore, the challenge continues to exist to develop new and better detectors, and the analytical chemist must continue to improve, adapt and invent new techniques.

Probing, Sampling, Doping, Scavenging

It has already been mentioned that probing, sampling, "doping" (in the sense of adding selected reactive species into chosen parts of the flame structure) and scavenging (in the sense of removing reactive species from a flame by reaction to give identifiable products) are all very powerful analytical tools for study of flames. It has also been mentioned that these are not easy. But, if properly designed and applied, they can give a wealth of information not otherwise obtainable. Different forms of each are possible, for example, probing might include use of laser beams, ion probes, sound pulses, etc. Sampling implies more than the collection of stable species. It includes sampling directly into measuring devices such as the Knudson leak into a mass spectrometer. Doping can be by a very wide variety of agents and can be introduced into different parts of the flame (the Vertical Tube Reactor lends itself particularly well to this). Scavenging, being closely related to doping, can also be by a wide variety of agents (to essentially "freeze" a reaction or a species in place so that it can be sampled and identified). Because fires are so complex, and parts of it so transient, all of these techniques must be designed and applied with great judgment so that the true events are not masked by spurious second events caused by the technique itself. But, because the pay-off is great, elaboration of such techniques will not be denied, thus posing a real challenge to the imagination and inventiveness of the analytical chemist.*

The "Non-Fire"

A great deal of effort, regulations, monies, equipments, etc., are expended to minimize the ravages of unwanted fires. The ultimate solution to the problem of course, is total prevention, that is, use materials, practices, etc., that will not allow a fire to happen in the first place. Or, to put it in another way, to have "non-fires." One might define a "non-fire" as a fire that would normally have happened at a given time and place, just as fires do today, except that this particular event did *not* happen because we had developed enough knowledge (and had used it) to include into the system the proper materials, geometry, practices, behavior, etc. to prevent it. One trouble with "non-fires" is that it is exceedingly difficult to prove that we did indeed have a "non-fire," because life goes on as before, and "who notices?" For this reason, it is much more difficult to solicit research support from sponsors to study non-fires, than it is to get support for study of, say, extinguishment after a particularly disastrous conflagration. This, coupled with a certain amount of mental laziness or lack of imagination on the part of us researchers, tends to push us into expending our major efforts and dollars in researching the last big fire (fires of the past) rather than the next big fire and "non-fire" (fires and "non-fires" of the future). It is another way of saying that the stop sign at the crossing goes up after the accident.

In a broad sense one might also think of a "non-fire" as being a fire that had an incipient beginning but was quenched so quickly that no damage resulted. These, of course, would result because automatic detectors and extinguishers were present and worked. Obviously these would be and are installed in particularly hazardous areas where we anticipate trouble.

In order to have "non-fires" we certainly need a lot more knowledge, acquired through research and development in many, many disciplines, not just analytical chemistry, and in particular how to apply the knowledge thus gained into our everyday living and environment. The control in the composition of materials,

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* In this regard, the individual who pursues such endeavors may think of himself as some other kind of chemist or investigator and is really looking for answers that these techniques will yield, but in the process, whether he knows it or not, he is an analytical chemist.

how these are used, how they are juxtaposed, how they are handled, what the contribution of the human element is, the precautions and preventive measures taken, etc., etc., obviously all come into play in designing a "non-fire," and must be included in our attempts to reach the utopia of "non-fires," a utopia which is certainly worth striving for.

In conclusion, wouldn't it be great if we could say that next Tuesday afternoon we will have a non-fire at the Blank refinery and on Thursday morning Tanker X will not blow up and, perhaps that at this very moment, in this very building, we are having a "non-fire," because we were smart enough?

THE CHEMISTRY OF FIRE RESISTANT MATERIALS AND SUPPRESSION

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HISTORICAL BACKGROUND

During the past decade, we have witnessed a rapid and continued expansion of plastic products. In this period the flammability characteristics of the predominantly organic polymers have assumed great importance. In the 1950's and 1960's plastics were considered for many applications due to their ease of fabrication, novelty, and other favorable physical properties in spite of undesirable flammability characteristics. Nitrocellulose enjoyed a long era of extensive use in spite of its almost explosive character. The gradual maturity of the plastics industry with a corresponding increase in the variety and sophistication of its products resulted in a corresponding demand by the consumer and by regulatory agencies for improved flammability characteristics. At the present time, the lack of adequate fire retardance of most commercially available plastics appears to be one of the largest barriers to the opening of extensive new markets for these materials in the building and construction industry, in transportation applications, in household furnishings and furniture, in floor coverings, and in clothing.

The importance of fire-retardant chemicals and technology to the chemical and plastics industry has recently been the subject of several meetings whose proceedings add greatly to the technical literature.[1–7]

In addition to reviewing the current technology in fire retardation of polymeric materials, it was pointed out at these meetings that the consumption of fire-retardant chemicals has risen from approximately 65 million pounds in 1960 to greater than 200 million pounds in 1969. Figure 1 illustrates the growth in sales of fire retardants in the United States for the period 1960 through 1969.

The importance of fire retardance to the overall growth of the plastics industry has led to the introduction of many new fire-retardant compositions with increasing frequency during the past five years. Although this expanding research into the act of fire-retardant technology has uncovered many new facts about the mechanisms of fire retardation of polymeric materials, the technology of fire retardancy in polymer compositions still retains a high degree of empirical character.

Of the many empirical facts accumulated in the technology of fire-retardant plastics over the years, the following have been shown to be the most useful and commercially practical:

1. The incorporation of halogen atoms into a polymeric composition, either as an additive or by chemical reaction, decreases the flammability or increases the fire retardance of the composition.
2. A combination of antimony oxide and halogen is more efficient than either of the individual materials at the same total concentration. In other words,

the combination of antimony and halogen displays an efficient synergism as a fire-retardant combination.[8]

3. The addition of some phosphorous compounds of specific structures retard the burning of many plastics.[9]
4. A combination of phosphorous and halogen also exhibits considerable synergism as a fire retardant.
5. The most efficient combination of fire-retardant materials varies considerably, depending upon the chemical structure of the plastic to which it is applied.[10]

In the previous section, the general mechanisms of thermal and oxidative degradation of polymers were discussed. Some of those concepts are extended in this section to fire-retarded polymers.

MECHANISM OF FLAME RETARDATION IN POLYMERS

Many investigations[11–17] have suggested mechanisms of polymer flame retardancy, but the general theories based on the decomposition of the flame re-

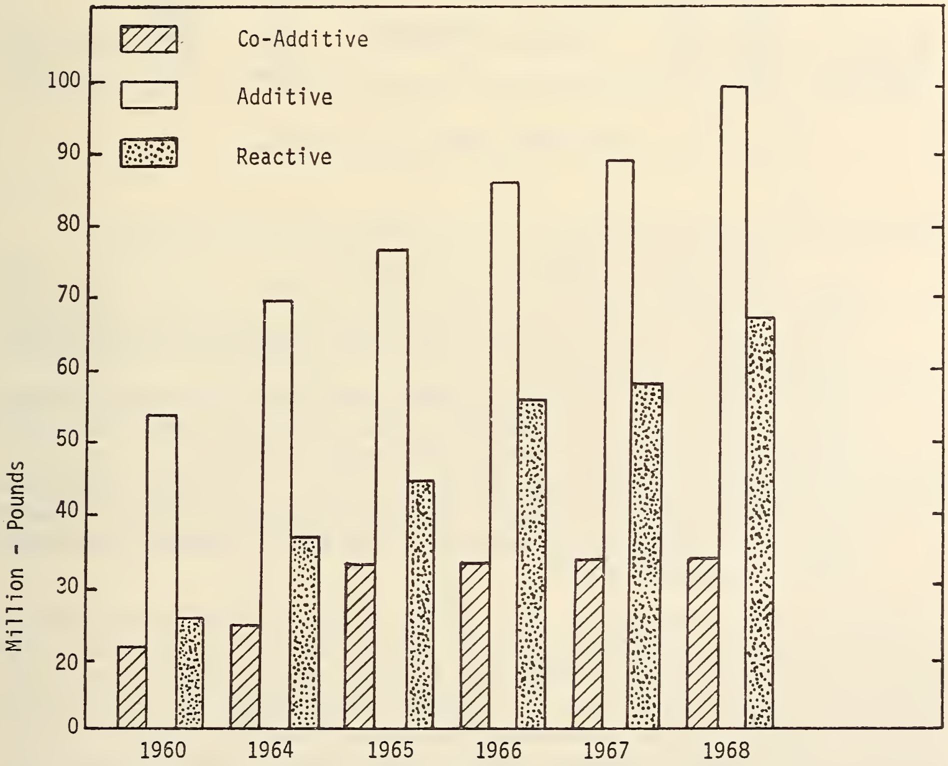


FIG. 1. Sales of flame retardants.

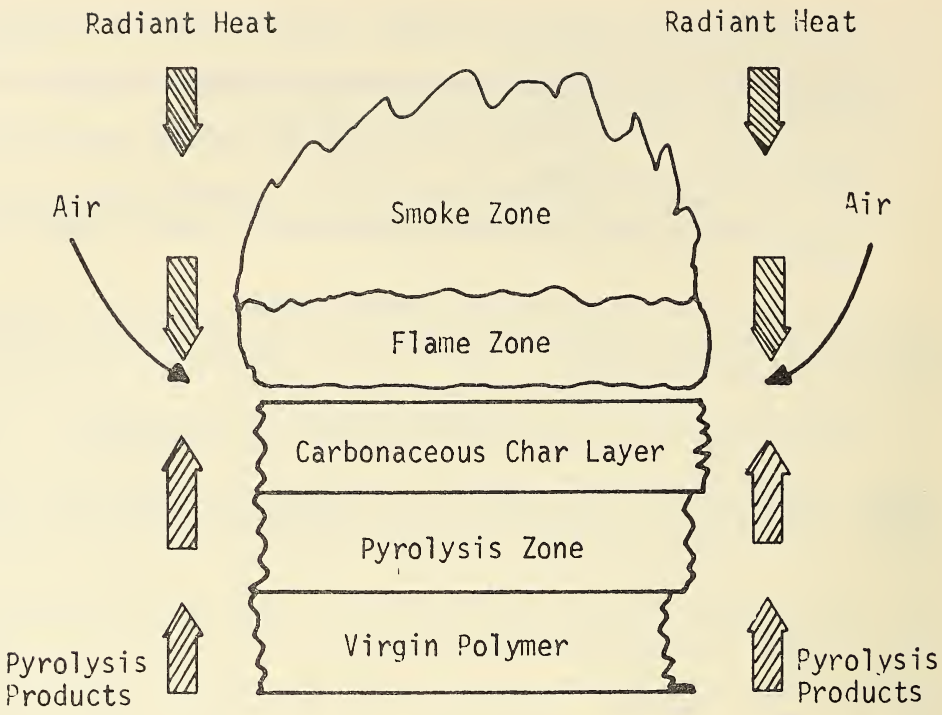
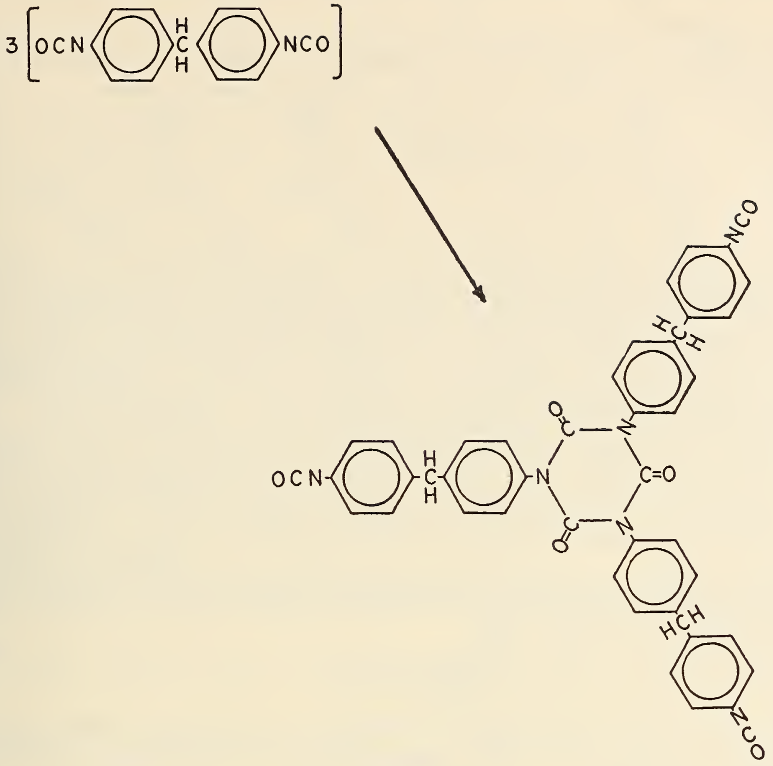


FIG. 2. Generalized model of burning polymer.

tardants under burning conditions were summarized by Bell[13] as follows:

1. Gas theory: large volumes of incombustible gases are produced, which dilute the oxygen supply.
2. Thermal theory: the fire retardant decomposes endothermically and lowers the temperature of the flame.
3. Chemical theory: decomposing polymers evolve smaller molecules or monomers and these in turn break down to give active high-energy free radicals dissipating their energy and thus extinguishing the flame.
4. Coating theory: the fire retardant fuses to form a protective layer which coats the combustible materials, thus preventing the further access of oxygen to the substrate; or intumesces to give a carbonaceous foam which acts as a thermal insulator.

A model of a burning polymer, shown in Fig. 2, can be useful in discussing the role of halogens in flame-retarding polymers. Einhorn *et al*,[18] and Riccitiello *et al*,[19] studied the flammability characteristics of modified polyisocyanurate foams. The isocyanurate ring structure, found in these polymers, was formed by the cyclization of three isocyanurate groups. Increased thermal stability and improved flammability characteristics were obtained by the incorporation of polyfunctional aromatic isocyanates such as 4,4′-diphenylmethanediisocyanate. The cyclization reaction is shown in Eq. (1).



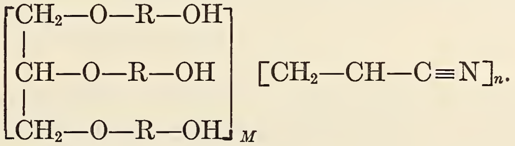
(1)

Isocyanurate Structure

The highly aromatic structure of the isocyanurate polymer restricts motion in the polymer chain and produces brittleness.

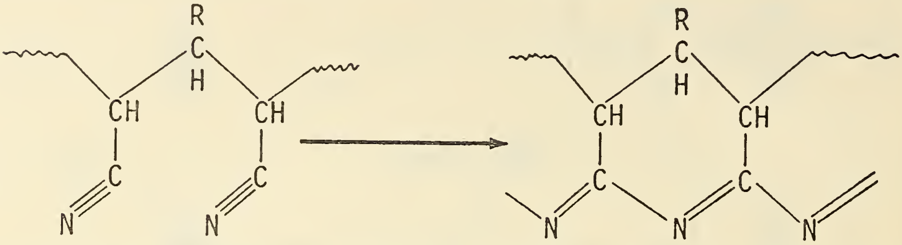
Riccitiello, *et al*,[19] introduced urethane linkages into the isocyanurate polymer to obtain the desired degree of flexibility. The urethane linkages decompose from 180° to 275°C, with a char yield of 0 to 35%.[20]

The isocyanurate ring structure decomposes between 300° and 325°C, with an approximate char yield of 50%. The polyol used to prepare these isocyanurate polymers was derived from glycerin and propylene oxide to which pendant nitrile groups were grafted. The polyol had the following structure:



$$\left[\begin{array}{l} CH_2\text{—}O\text{—}R\text{—}OH \\ | \\ CH\text{—}O\text{—}R\text{—}OH \\ | \\ CH_2\text{—}O\text{—}R\text{—}OH \end{array}\right]_M [CH_2\text{—}CH\text{—}C{\equiv}N]_n.$$

Acrylonitrile was selected as the grafting monomer because nitrile linkages cyclize to form a high-temperature-stable heterocyclic structure at temperatures below 200°C. The cyclization reaction of the nitrile groups is shown in Eq. (2):



(2)

Thus, referring back to the generalized model shown in Fig. 2, we see the formation of stable-char structure developing in the pyrolysis zone at approximately 180°–200°C. This precursor char structure, which forms in high yield serves as an effective diffusion barrier and thus retards the migration of volatile degradation species into the gaseous phase. The carbonaceous layer also provides an effective thermal insulation barrier to shield the underlying substrate from the burning region.

The volatile pyrolysis products were degraded into carbon and other products as they entered the combustion zone (700°–1000°C.). For flame propagation, energy feedback from the flame envelope to the polymer (shown in Fig. 2) must be sufficient to sustain volatile fuel production. This feedback of energy from the envelope to the polymer depends on a number of parameters which include the efficiency of combustion, the flame temperature, the carbon content and its radiation emissivity, and the geometry of the flame.

Volans[16] suggested the most effective approach to flammability control in a flame-retardant modified polymer might be:

1. Limitation of the fuel supply to the flame by reduction of the pyrolysis reaction or modification of the fuel products, e.g., production of more tars, coatings, and chars.
2. Reduction of the energy liberation in the flame by modification of the combustion reaction, e.g., allowing more carbon to escape the flame.
3. Reduction of energy feedback to the polymer surface by reducing the flame temperature or emissivity.[21]
4. Increasing the concentration of a flame inhibitor species above a concentration at which the combustion reaction fails to continue.

Fuel Supply Control

Design of the molecular structure of polymers will permit the synthesis of high-temperature resistant materials which give off little or no volatile fuel. Materials such as the polyimides, benzimidozoles, and certain polyamides are examples of polymers which contain few hydrogen atoms and which are precursors for carbon or graphite.

Einhorn[22] described several model urethane and isocyanurate polymers in which potassium fluoroborate was incorporated to give rise to the formation of a protective layer of "glass" on the surface of the char and thus hinder gaseous fuel production. Holmes and Shaw[23] and Grundfest[24] showed that phosphorous compounds would limit the burning of polymers only if nonvolatile phosporic acid derivatives were formed upon pyrolysis.

Role of Halogen in the Fire Retardation of Polymers

Rosser, Wise, and Miller,[25] and Wilson, O'Donovan, and Fristrom[26] showed that HBr, HCl, and Cl_2 premixed in hydrocarbon–air flames were active flame-inhibiting agents. It appears that the principle action is the modification of radical concentration and/or distribution in the reaction zone. Thus, interference to the propagating and branching steps is produced. Halogen compounds appear to act by substituting a radical of low reactivity for the propagating radicals. Corrosion or toxicological considerations limit practical extinguishments to halogenated hydrocarbons. The chemistry of halogenated hydrocarbons includes that of the halogens and halogen acids. The effectiveness of those inhibitors appears to be $F<Br<Cl<I$ and is proportional to the number of halogen atoms in the inhibitor molecule.

Differences in halogen compounds are likewise important, especially in regard to the nature of the attached hydrocarbon structure. First, this may be saturated primary, secondary, or tertiary. Second, this could be unsaturated allyl, benzyl, vinyl, or aryl structures. The presence of nearby nonpolar or polar groups may markedly affect the behavior of the carbon-halogen bonds. Knowing that these differences in chemical structure affect the thermal and hydrolytic stability of analogous single halogenated molecules, suggests that these structural differences very probably have an influence upon the effectiveness of halogens as fire retardants in polymers.

Fristrom[27] reported that all of the halogens, with the exception of iodine, can sustain hydrogen flames. The reactions for these systems are similar, as shown below:

$$H+X_2 \rightleftarrows HX+X \qquad (3)$$

$$X+H_2 \rightleftarrows HX+X \qquad (4)$$

$$X+X+M \rightleftarrows X_2+M^* \qquad (5)$$

$$H+H+M \rightleftarrows H_2+M^* \qquad (6)$$

$$H+X+M \rightleftarrows HX+M^*. \qquad (7)$$

Halogen molecules and the halogen acids (excepting fluorine) react rapidly with both O atoms and $\cdot OH$ radicals to form the corresponding halogen atoms.

In the case of Br and I, the atoms are unreactive with respect to hydrogen, molecular oxygen, and the common hydrocarbon fuels. The result is the substitution of a stable unreactive radical. The Cl atom reactivity is sufficient so that inhibition is less pronounced, and in some cases even a promotion of reaction can occur.

Reactions of halogen species with oxygen atoms and hydroxyl radicals are as follows:

$$O+X_2 \rightleftarrows OX+X^* \qquad (8)$$

$$OH+X_2 \rightleftarrows HX+X\ (OX+HX)^* \qquad (9)$$

$$O+HX \rightleftarrows OH+X\ (OH+H)^* \qquad (10)$$

$$OH+HX \rightleftarrows H_2O+X. \qquad (11)$$

Halogenated hydrocarbons are rapidly attacked under flame conditions to form halogen acids and halogen atoms. This allows secondary inhibition reaction, as shown below, to take place:

$$R\cdot X + H \rightarrow HX + R\cdot \qquad (12)$$

$$R\cdot X + OH \rightarrow H_2O + \cdot RX \qquad (13)$$

$$R\cdot X + O \rightarrow OX + R\cdot \qquad (14)$$

Fluorocarbon molecules show inhibition properties in excess of that which would be predicted on the basis of the halogen atom substitution. F_2 and HF do not inhibit flames. This is probably associated with the stability of the fluorocarbon radicals under flame conditions. A number of plausible reactions can be written down, but little reliable kinetic information is available at this time.

The principal reactions should be with hydrogen atoms. Reactions with oxygen atoms are thermodynamically favorable, but sterically improbable. The compound CF_2 has been reported by Modica and LaGraff[28] to react with molecular oxygen in a shock tube at 2000°K, but the elementary steps are not clear.

Possible reactions of CF_3 and CF_2 in flames are:

$$CF_3 + X + H \rightarrow HX + CF_3 \qquad (15)$$

$$CF_3 + H \rightarrow CF_2 + HF \qquad (16)$$

$$CF_2 + H \rightarrow CF + H \qquad (17)$$

$$CF_2 + O \rightarrow CO + 2\ F \qquad (18)$$

$$CF_2 + O_2 \rightarrow CO + F_2 + O \qquad (19)$$

The above mechanisms may not apply directly to diffusion flames, where combustion mechanisms are different, due to the extreme concentration gradients and poor stability. Halogen inhibitors were found to be more effective when added to air rather than to the fuel side of the diffusion flame. However, the amount of inhibitor, added to the air side, required to extinguish the diffusion flame was of the same magnitude as that required for a premixed flame.[19]

Role of Halogens in the Condensed Polymer

Many references are found in the literature which discuss the action of halogens on vapor flames such as hydrocarbon–air flames. But surprisingly little information has been published on the mechanism of flame suppression in solid polymers.

Fenimore and Martin adopted the limiting-oxygen index method to measure the flammability of solid polymers. The limiting oxygen index n of a material is defined as the percentage concentration of oxygen in a mixture of oxygen and nitrogen which will just sustain combustion of the material

$$n(\%) = 100[O_2/(O_2+N_2)]. \qquad (20)$$

For air, $n=21$. Figure 3[18] shows the effect of oxygen on the combustion of isocyanurate foam.

This method is simple and reproducible and has proven to be a useful tool for mechanistic studies of flame suppression in polymers. One important characteristic of this test is that the vertical sample burns downward, monitoring any convective heating of the burning material. An important limitation to this method is the fact that some materials melt too easily and abstract more heat from the surrounding diffusion flame than is required to pyrolyze the polymer. Recently, Stuetz[30] reported on further modifications to the limiting-oxygen index test by using an upward burning flame as well as the downward flame to study fire retardancy mechanisms.

Fenimore and Jones[31] established that HCl or Cl_2 added to an O_2–H_2 atmosphere exerted only a very slight inhibition, whereas equivalent chlorine substituted in polyethylene gave a strong inhibition effect. This suggested that chlorine works in

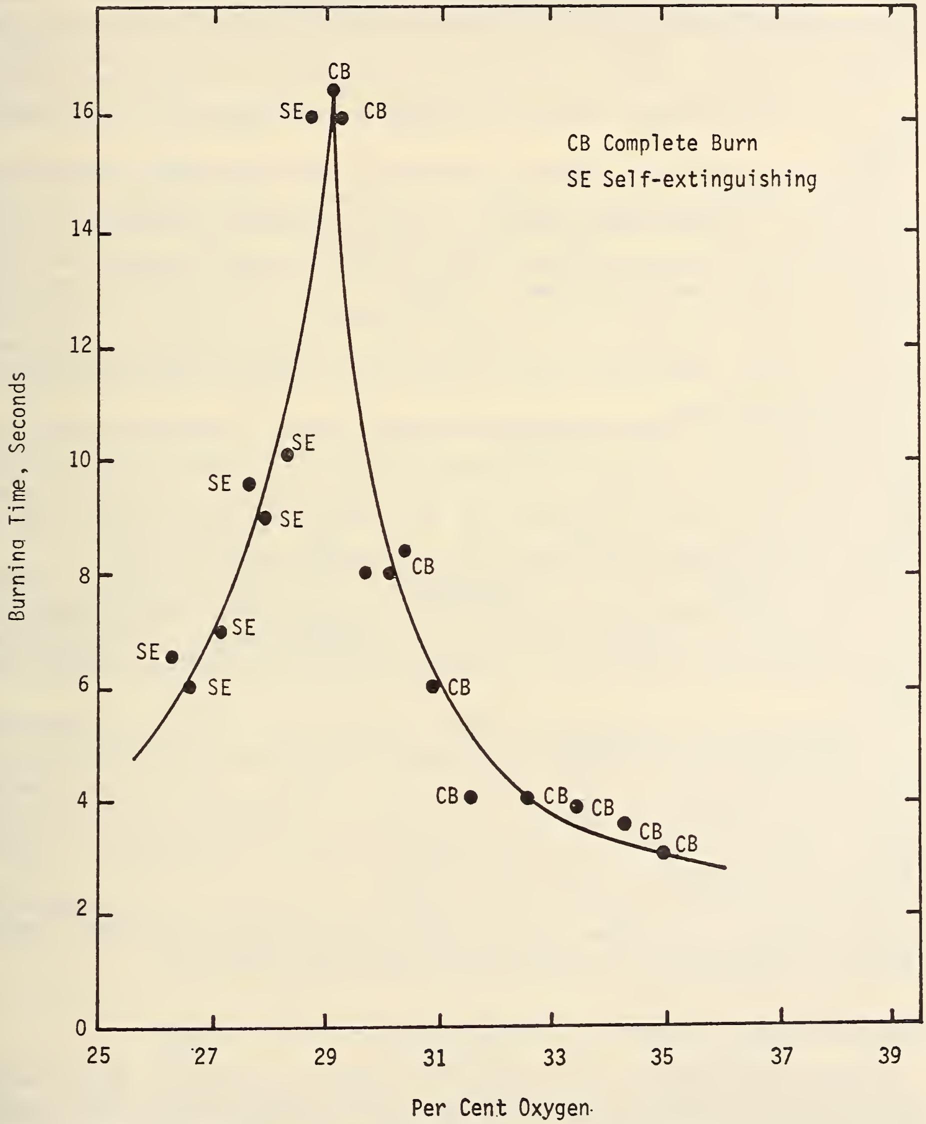


FIG. 3. Effect of oxygen on the combustion of isocyanurate foam.

the condensed phase of polyethylene. A fire retardant which is effective in the condensed phase should remain effective when the polymer burns in an oxidizer other than oxygen. Fenimore and Jones[31] proved this by showing the effective chlorine inhibition of polyethylene burning in N_2O–N_2 as well as in O_2–N_2. This mechanism suggests that fire retardants which work well in one polymer may not perform in the same manner in another material.

Fenimore and Jones[32] showed that tetrabromo bisphenol A in polyethylene is more effective than chlorine in O_2–N_2, but was less effective in a N_2O–N_2 atmosphere. Similarly, *tris*-(2,3-dibromopropyl) phosphate in polyethylene is more effective than its chlorine analog in O_2–N_2, but not in N_2O–N_2. The above reactions suggest that bromine inhibits or poisons the flame rather than the condensed phase.

During a transient ignition period, the pyrolysis gas may change its composition, hence it may be crucial to the flame retardancy of some halogenated fire-retardant polymers.

Eichhorn[14] reported that dicumyl peroxide and other free-radical generators increased the inhibiting action of bromine in polystyrene, and he further stated that this mechanism operates largely outside the flame front but in the condensed phase. It is believed that the peroxide and halogen radicals abstract hydrogen from the polymer, and the resultant polymer radicals then react with halogen compounds or radicals. Those species with a lower vapor pressure decompose in a higher temperature range to cause the release of HBr when it can be more effective. Ingram[33] proposed a similar mechanism when he used *N*-chloro and *N*-nitroso compounds as free-radical generators.

Gouinloch, Porter, and Hindersinn,[34] however, offered a different explanation. They stated that the added peroxide degraded the hot polymer and gave a more fluid melt, therefore, requiring more heat to sustain combustion of the fresh surface after the molten polymer dripped away. They showed that the peroxide was ineffective when dripping was prevented by incorporation of glass fibers.

Piechota[35] reported that the concentration of chlorine alone was not the decisive factor for the effectiveness of a product. This phenomenon could only be interpreted on a manifestation of the different trends toward intramolecular thermal hydrogen chloride elimination as governed by the composition of the flame retardant. See Table 1.

Chlorinated tall oil eliminated hydrogen chloride under relatively mild conditions, with 81% of the chlorine being released as hydrogen chloride. In this case, self-extinguishing urethane foams were prepared with only a 4% level of chlorine. In the case of chlorinated diphenyl, the release of hydrogen chloride was very difficult and self-extinguishing characteristics could not be obtained in similar urethane foams even at the 10% chlorine level.

Tilley[36] reported that neither sodium chloride nor sodium bromide contributed to the protection of urethane foams during fire exposure. Presumably, neither halogen or hydrohalide was available from salts during combustion.

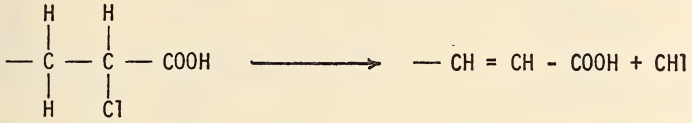
Flame Retardance Conferred by a Halogen in a Reactive Intermediate

Numerous investigators have reported on studies in which the flameproofing elements such as a halogen or phosphorous or both are incorporated into a reactive intermediate. Li[37] used pentaerythritol dichloride as the polyhydric alcohol moiety in preparing unsaturated polyester resins. A chlorine content of at least 25% was considered essential to obtain a desired level of flame retardancy.

Al'Shits[38] and coworkers used a mixture of pentaerythritol dichloride and trichloride to flame retard unsaturated polyester resins. The trichloride was used to form end groups in the linear chains thus raising the molecular weight of the polymer (as compared to previous studies using only the dichloride) while also

TABLE 1

Intramolecular elimination of HCl from different chlorine compounds

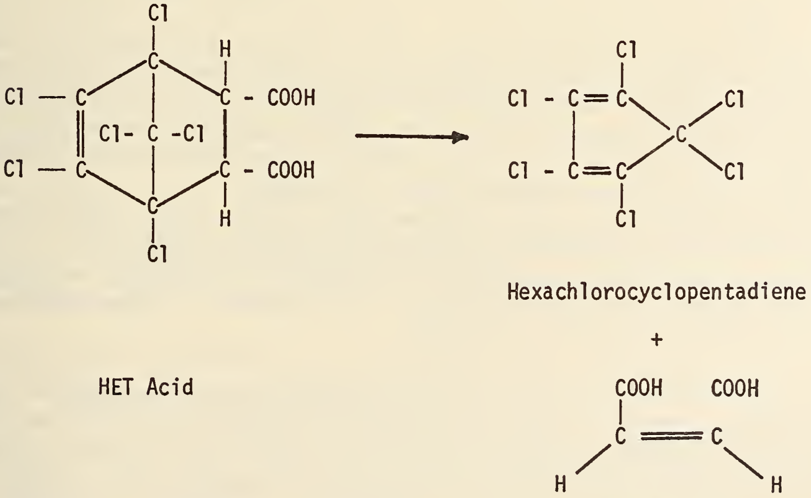


$$-CH_2-CHCl-COOH \longrightarrow -CH=CH-COOH + CHl$$

Chlorinated fatty acid — unsaturated acid

$3\,Cl-\theta-\theta-3\,Cl \xrightarrow[-HCl]{}$ nonaromatic compound

Chlorinated diphenyl

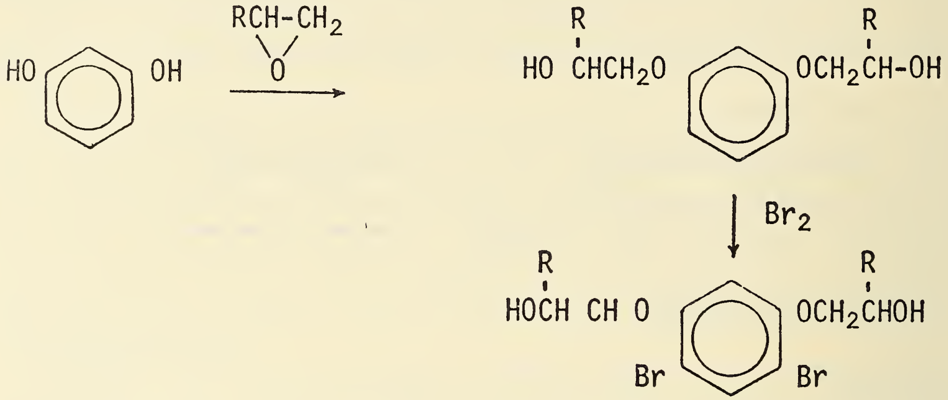


$NH_4Cl \longrightarrow NH_3 + HCl$

ammonium chloride

raising the halogen level in the polyester. These polyester resins were prepared using a two-stage condensation reaction. In the first stage, excess maleic and phthalic anhydride were reacted with pentaerythritol dichloride. Sufficient pentaerythritol trichloride was then added so that the total hydroxyl groups in the system would predominate and the condensation reaction would be completed.

Resorcinol has been used as the starting material to prepare halogen-containing diols.[39,40] The resorcinol was epoxylated with ethylene or propylene oxide to yield 1,3-*bis*-(betahydroxyalkoxy) benzenes. These were then brominated in a buffered solution to form *B*,*B*′-(4,6-dibromo-1,3-phenylenedioxy) dialkanols which were used to prepare self extinguishing polyesters according to the reactions:



Other interesting halogen-containing diol structures were synthesized via a Diels–Alder reaction of hexahalocylopentadienes with unsaturated diols (such as 1,4-butenediol) used as the dienophiles.[41,42] Replacement of some of the chlorine atoms by bromine in the diene increases the flame-retardance properties in polyesters, while replacement of some of the chlorine atoms with fluorine yields polyesters with enhanced aging and heat resistant properties.

Recently, considerable interest has been shown in polyester resins based on tetrachlorophthalic anhydride and tetrabromophthalic anhydride.[43–47]

Laboratory studies were conducted to evaluate the chemical and physical parameters which govern the flammability characteristics of these retardants in model unsaturated polyester resin systems.

The highest saturated-to-unsaturated molar ratio consistent with good resin properties was selected in order to permit synthesis of polyesters with the highest possible chlorine content. A ratio of saturated-to-unsaturated acid of 1.1 to 1.0 was selected since high ratios of tetrachlorophthalic anhydride to maleic anhydride would cause a rapid drop in heat-distortion temperature. This ratio was held constant in all model systems by adjusting the amount of phthalic anhydride used. Propylene glycol was selected as the glycol for this study and a 5% molar excess was used in all formulations. The resins were prepared by a conventional fusion esterification with the reaction temperature being maintained at 190°–195°C. The resins were processed to an acid number of 30, styrenated to a level of 25% or 30%, and inhibited with 125 ppm of hydroquinone. Table 2 presents the formulations used to prepare resins based on tetrabromophthalic anhydride. Table 3 shows the formulations used to prepare resins based on tetrachlorophthalic anhydride.

TABLE 2

Formulations for polyester resins based on tetrabromophthalic anhydride

Moles TBPA	Moles PA	Moles MA	Calculated % bromine on dilution with:	
			25% styrene	30% styrene
0.80	0.30	1.0	30.4	—
0.50	0.60	1.0	22.0	20.5
0.30	0.80	1.0	14.8	13.8
0.25	0.85	1.0	12.7	11.8
0.23	0.87	1.0	11.8	11.0
0.20	0.90	1.0	10.5	9.8
0.07	1.03	1.0	5.0	—

Figures 4 and 5 present the idealized structures of crosslinked polyester-based polymers containing the halogenated fire retardants.

The effect of fire retardants on the thermal characteristics of model polyester resin systems was determined using differential thermal analysis and thermogravimetric analysis. Figures 6 and 7 illustrate the effect of fire-retardant concentration on the decomposition temperature for specimens fire retarded with the two anhydrides.

Relatively little difference was observed in the decomposition temperatures for the series containing 25% styrene and the series containing 30% styrene. The control samples containing only the halogenated fire retardant showed a slight lowering of the decomposition temperature. The incorporation of triethylphosphate into these halogenated systems showed no marked synergistic effects. Incorporation of antimony trioxide (2% or 5% by weight) resulted in a substantial lowering of the decomposition temperature with an observed minimum occurring at approximately 11% bromine concentration or at approximately 21.7% chlorine content.

Two small-scale test methods were employed under controlled laboratory conditions to evaluate the relative effectiveness of the polyesters modified by the halogenated fire retardants. These tests were the ASTM D-757—Globar Test and the HLT-15—Intermittant Flame Test. In the ASTM D-757—Globar Test, at equal concentrations of halogen, the specimens based on tetrabromophthalic

TABLE 3

Formulations for polyester resins based on tetrachlorophthalic anhydride

Moles TCPA	Moles PA	Moles MA	Calculated % chlorine on dilution with:	
			25% styrene	30% styrene
1.0	0.0	1.0	21.7	20.3
1.0	0.1	1.0	10.2	18.9
0.9	0.2	1.0	18.7	17.4
0.8	0.3	1.0	17.0	15.8
0.5	0.6	1.0	11.5	—
0.2	0.9	1.0	5.0	—

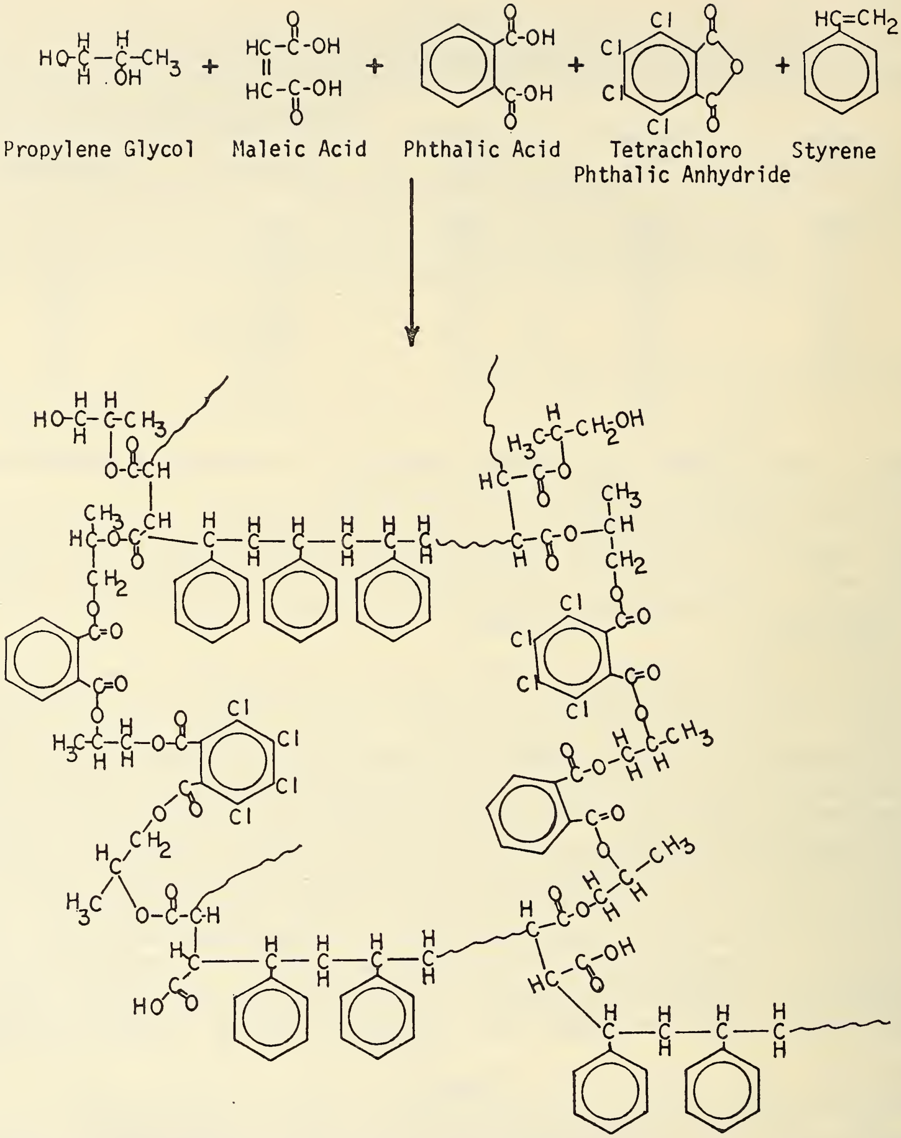


FIG. 4. Idealized structure of a crosslinked polyester-based polymer containing tetrachlorophthalic anhydride.

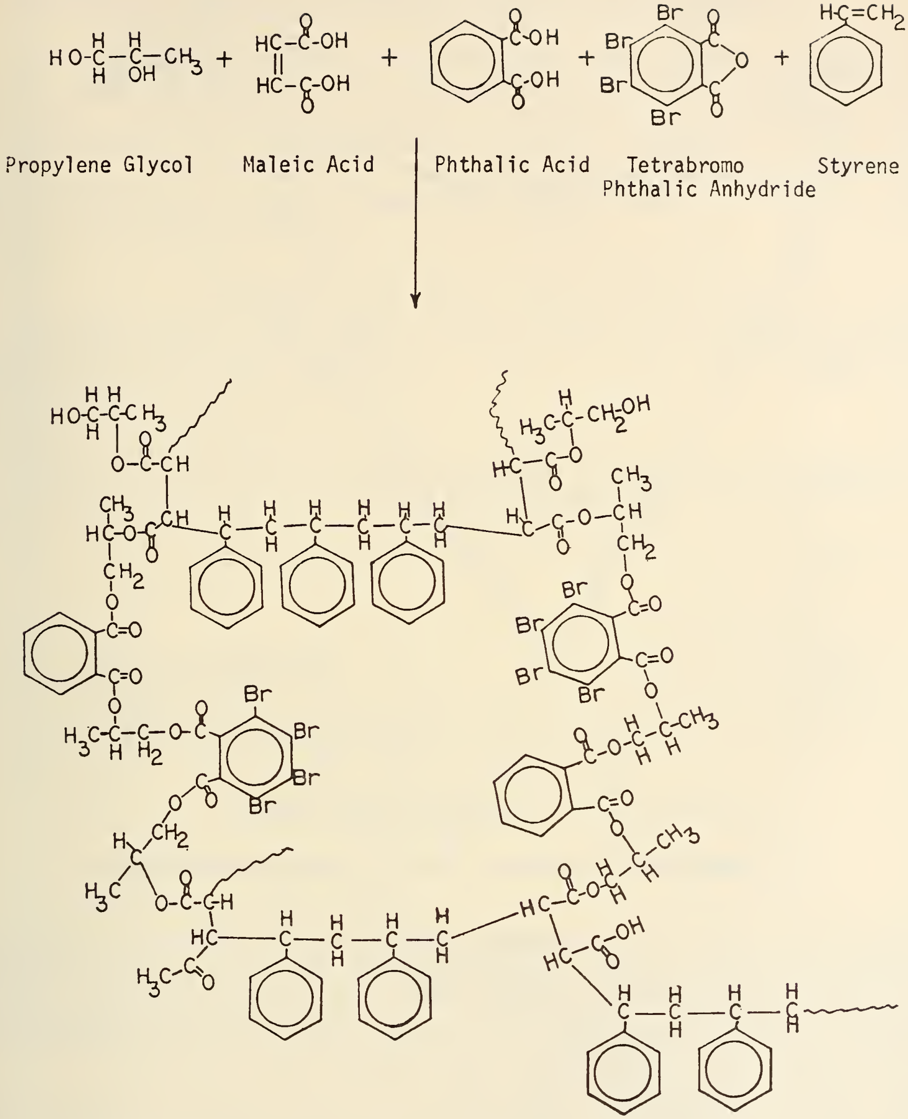


Fig. 5. Idealized structure of a crosslinked polyester-based polymer containing tetrabromophthalic anhydride.

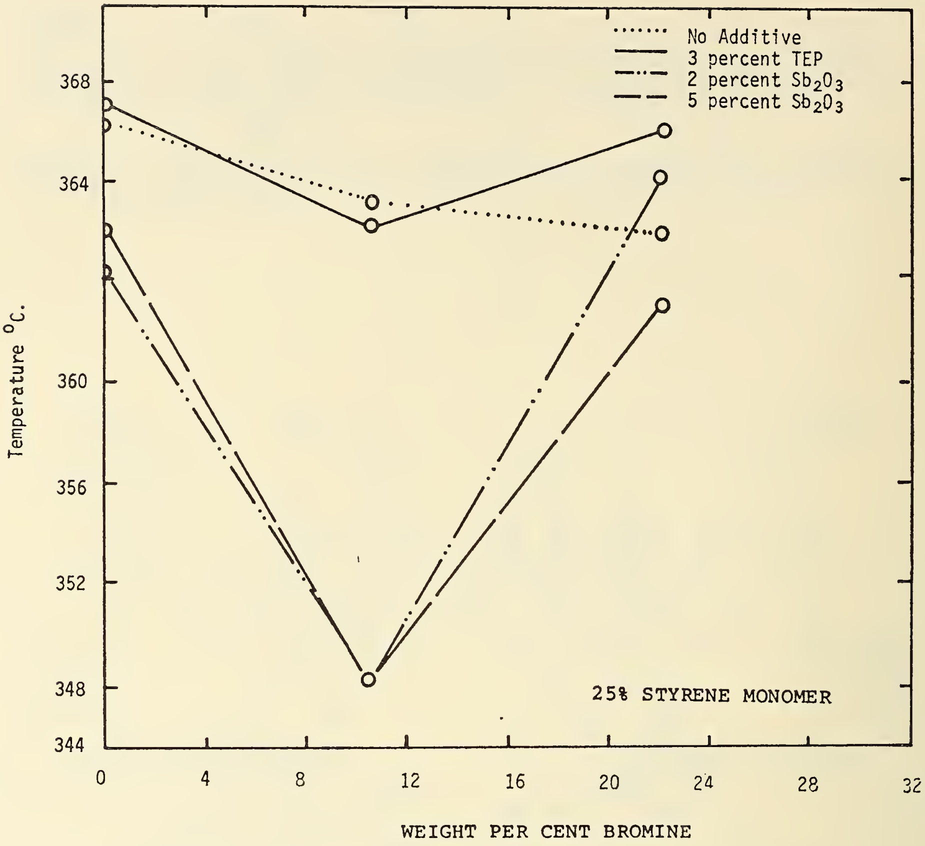


FIG. 6. Effect of tetrabromophthalic anhydride on polymer decomposition.

anhydride had lower flame-propagation values than were observed for similar specimens based on tetrachlorophthalic anhydride. The incorporation of triethyl phosphate reduced the burning slightly. The incorporation of antimony trioxide exhibited a strong synergistic effect and markedly improved the flame propagation characteristics of the test specimens. The synergistic type of reaction will be discussed in greater detail later in this section.

The HLT-15—Intermittant Flame Test is more severe than the ASTM D-757 test because the specimen is suspended in a vertical position and heat from the flame is carried upward by convection along the length of the specimen. In addition, the specimen is ignited five times using increasingly longer ignition periods. The brominated specimens obtained a maximum rating without additional co-retardants. Slight improvements were seen with the addition of triethyl phosphate. The chlorinated specimens were not able to exhibit burning characteristics to obtain greater than a 40 rating by this test method. Incorporation of antimony trioxide improved the ratings of both the brominated and chlorinated specimens, but the brominated specimens were more effectively fire retarded than the chlorinated specimens.

Fire Retardance Conferred by a Halogen in a Nonreactive Intermediate

Nonreactive fire retardants are generally used with thermoplastic polymeric systems where incorporation of a reactive material would affect crystallinity, heat-distortion temperature, and resistance to ultraviolet light or humidity. Low-molecular-weight fire retardants have a tendency to migrate or outgas during processing or while in actual use. Thus, consideration should be given to those compounds having a molecular weight high enough to prevent sublimation, migration, or volatilization.

SYNERGISM DURING FIRE EXPOSURE

Synergism is the term applied to the observed ability of two materials to influence the properties or response of a material to a greater degree than equal amounts of the two materials used separately.

Antimony–Halogen Synergism

Various antimony compounds have been used as flame retardants for material and synthetic polymers.[48–51] Antimony trioxide (Sb_2O_3) and antimony oxychloride

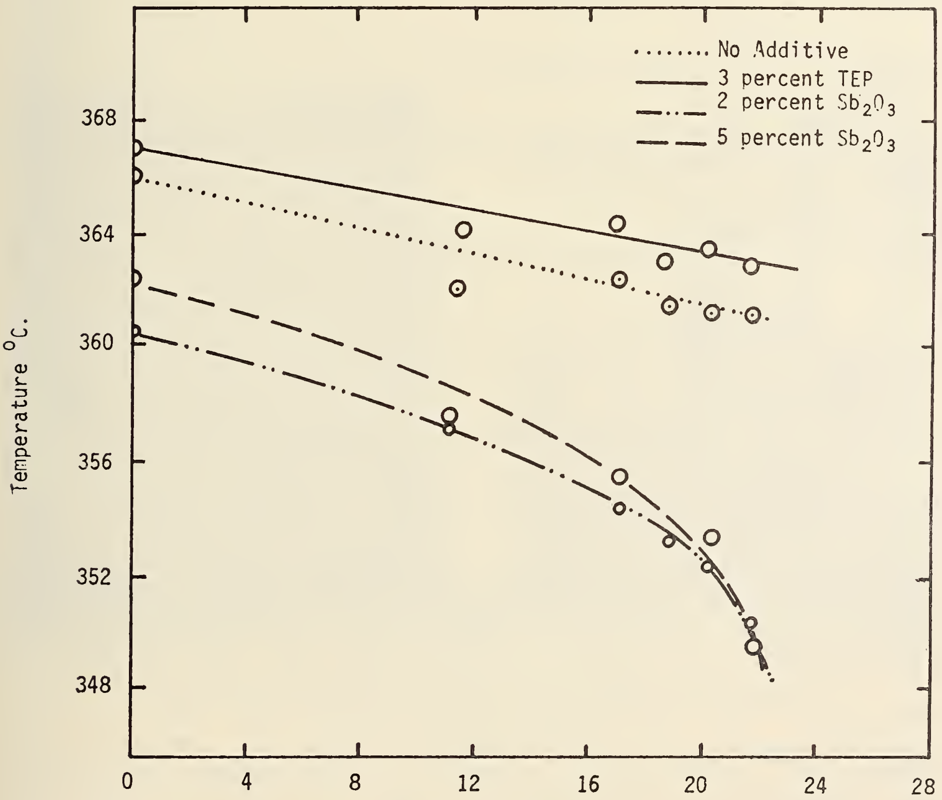


FIG. 7. Effect of tetrachlorophthalic anhydride on polymer decomposition.

(SbOCl) are the most commonly used antimony compounds for modifying the flammability characteristics of polymeric materials. Schmidt[52] and Drake[53] reported that antimony trioxide by itself was a very poor flame retardant. Little[49] observed that the optimum flame retardancy occurred when the mole ratio of antimony: chlorine is 1:1.

The HCl evolved from the decomposition of chlorinated organic compounds reacts with antimony oxide to produce the trichloride (B.P. 223°C) or the oxychloride, which in turn decomposes to the trichloride. The strongly acidic trichloride is thought to function as a dehydration catalyst for materials such as cellulose as well as a flame quencher for flammable gases. Equations (22)–(25) summarize the thermal reactions of antimony compounds.

$$Sb_2O_3 + 6\ HCl \rightarrow \underset{\text{(B.P. 223°C)}}{2\ SbCl_3} + 3\ H_2O \qquad (22)$$

$$Sb_2O_3 + 2\ HCl \rightarrow 2\ SbOCl + H_2O \qquad (23)$$

$$5\ SbOCl \xrightarrow{170°\text{–}280°C} SbCl_3 + Sb_4O_5Cl_2 \qquad (24)$$

$$3\ Sb_4O_5Cl_2 \xrightarrow{320°\text{–}700°C} 2\ SbCl_3 + 5\ Sb_2O_3 \qquad (25)$$

Pitts, et al,[54] found the thermal decomposition of SbOCl to proceed in four basic steps as illustrated in Eqs. (26)–(29).

$$5\ SbOCl(s) \xrightarrow{245°\text{–}280°C} Sb_4O_5Cl_2(s) + SbCl_3(g)\uparrow \qquad (26)$$

$$4\ Sb_4O_5Cl_2(s) \xrightarrow{410°\text{–}475°C} 5\ Sb_3O_4Cl(s) + SbCl_3(g)\uparrow \qquad (27)$$

$$3\ Sb_3O_4Cl \xrightarrow{475°\text{–}565°C} 4\ Sb_2O_3 + SbCl_3(g)\uparrow \qquad (28)$$

$$Sb_2O_3 \xrightarrow{658°C} Sb_2O_3(l) \qquad (29)$$

Einhorn *et al*[55] have shown the effectiveness of the antimony–halogen synergistic reaction in reducing the tendency for crack growth and enhancing the development of a homogeneous char structure in unsaturated polyester resins through the use of infrared photographic techniques. Figure 8 shows the degradation of a polyester resin casting fire retarded by the incorporation of 11.5% by weight of tetrabromophthalic anhydride. Figure 8a illustrates the melting region, the region of char formation, and also shows flame propagation by burning gases in the boundary region. Figure 8b shows the development of a crack which has started in the boundary region. Figure 8b shows the development of a crack which has started in the boundary region, char sintering, and after-flow (cooling). Figure 8c shows the

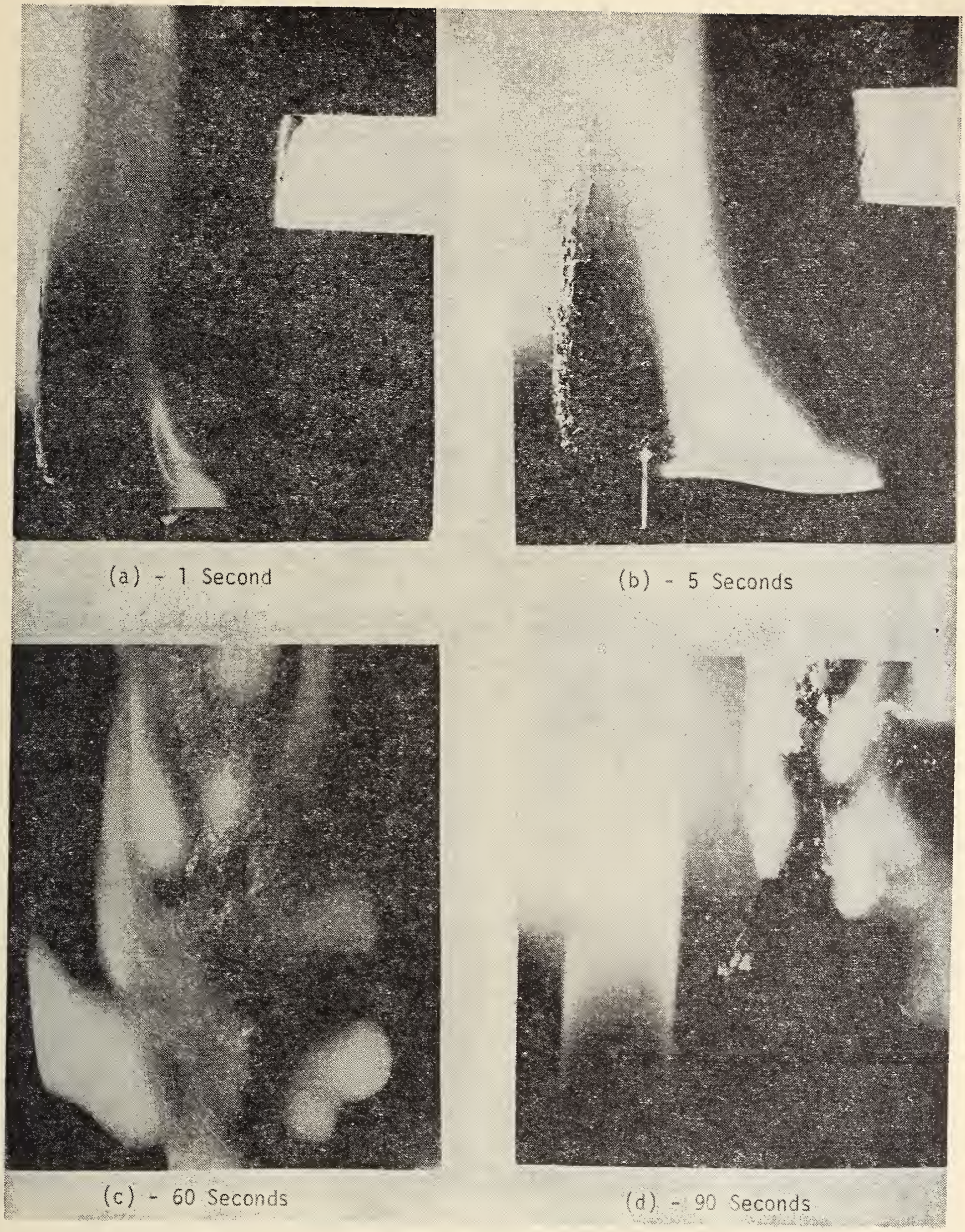
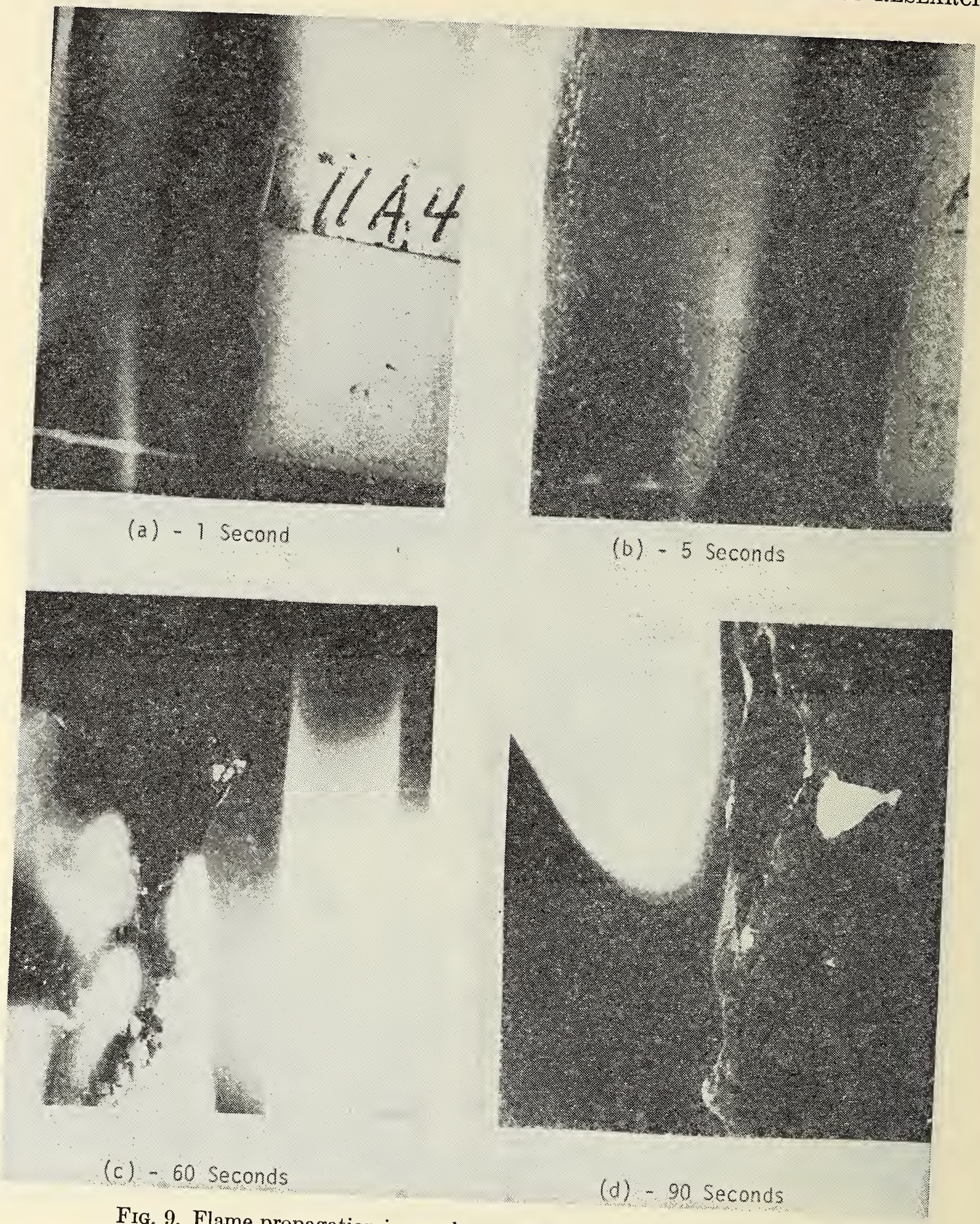


FIG. 8. Flame propagation in a polyester resin casting fire retarded by tetrabromophthalic anhydride.



(a) - 1 Second

(b) - 5 Seconds

(c) - 60 Seconds

(d) - 90 Seconds

Fig. 9. Flame propagation in a polyester resin casting fire retarded by tetrabromophthalic anhydride and antimony oxide.

extension of the melting zone and further crack growth. Figure 8d shows char sintering and flame propagation behind the weak nonhomogeneous char front.

A fire-retarded polyester resin casting with 5% antimony oxide and 11.5% tetrabromophthalic anhydride was subjected to burning as shown in Fig. 9. Figure 9a shows the development of a strong char structure in the flame front. In contrast to the plastic having only the halogen-containing retardant, there is no evidence of flame propagation beyond that area in direct contact with the flame source by burning gases in the boundary layer. Figure 9b shows the gradual erosion of the strong homogeneous char structure in the area of actual flame contact. Figure 9c shows rapid extinguishment of the flame front after travel beyond the initial flame source. Figure 9d illustrates the char structure after flameout.

Phosphorus–Halogen Synergism

Mitchell *et al.*[56] studied the effect on autoignition temperature and on char strength when urethane foams were fire retarded with phosphorous and halogen-containing fire retardants. The results are summarized in Table 4.

The foams retarded with halogen-containing compounds were totally consumed without the development of char structure, while those retarded with phosphorous and halogen-containing compounds showed both a quenching response to fire exposure and the development of a carbonaceous char structure.

Hilado[11] explained the mechanisms employed by phosphorous and bromine compounds as follows:

> "Without phosphorous, hydrogen bromide is believed to be the most active bromine compound. Since this compound boils in the combustion zone, when it participates in successive halogenation and dehydrohalogenation reactions. The presence of phosphorous promotes the formation of char, which further restricts movement in the gaseous phase, and results in the formation of phosphorous tribromide, phosphorous pentabromide, and phosphorous oxybromide, which are less readily gasified and are heavier gases (molecular weights of 270.70, 430.52, and 286.70, respectively). Since these bromides are continually regenerated in the halogenation-dehydrohalogenation process, their effectiveness increases with their residence time in the combustion regions, and keeping them in effect control twice as long would tend to make them twice as effective."

TABLE 4

Effect of phosphorous and chloride inhibitors on the autoignition temperature and char strength of a urethane foam

Inhibitor			
Phosphorous content, %	Chloride content, %	Autoignition temp., °F	Char strength
0	0	950	None
0	50	950	None
5	50	1000	Weak
10	0	1150	Strong

The fluxing action of phosphorous is probably limited to the interface of the combustion and pyrolysis regions so that any excess over the amount needed to stabilize the char is ineffective. Since phosphorous oxides can effect only so much dehydration while the continually regenerated bromides can repeat the dehydrohalogenation process phosphorous/bromine combinations would be more effective than phosphorous oxides in promoting char formation.

The mechanism of the phosphorous–chlorine synergism is similar to that of the phosphorous-bromine synergism. It is more widely utilized because of the greater availability of chlorine-containing compounds. The phosphorous–chlorine synergism is less effective than the phosphorous–bromine synergism to the same degree and for the same reasons that chlorine is not as effective, on an equal weight basis, as bromine. The chlorides of phosphorous are lower boiling and lighter gases than the corresponding phosphorous bromides, and can be expected to have a shorter residence time in the combustion zone.

PHOSPHOROUS-BASED FIRE RETARDANTS

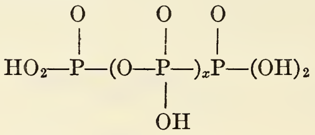
Phosphorous has an atomic number of 15, and an atomic weight, for the single natural-occurring isotope, of 30.98. The electronic structure is $1s^2 2s^2 2p^6 3s^2 3p^3$ for a total of 15. Bonding in phosphorous compounds can include simple sharing of the $3p$ orbitals or various $3s$–$3p$ orbitals. The $3d$ orbitals are readily available, thus allowing for *spd* hybrids. Most phosphorous–ligand single bonds are now thought to be hybrids. The PO single bonds in PO_4^{3-} are sp^3 hybrids, the Cl–p bonds in $POCl_3$ are a mixture of p^3 and sp^3 character. The pentavalent and hexavalent compounds are *spd* hybrids as in $PCl_5(sp^3d)$ and PCl_6–(ion–sp^3d^2). Many P–ligand bonds have considerable π bond character.

Table 5 lists typical phosphorous-containing compounds that are used as fire retardants. Lyons[57] points out that almost all of the fire retardants that contain phosphorous are in odd oxidation states.

The behavior of phosphorous-based fire retardants has been studied in detail in several cellulosic systems. Tang and Eichner[58] reported that ammonium phosphates reduced the thermal decomposition temperature during pyrolysis of cellulose.

TABLE 5

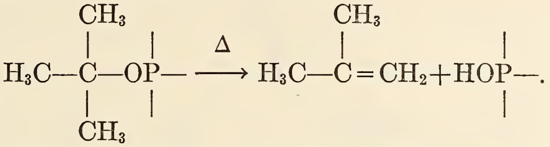
Fire retardants containing phosphorous

Oxidation number	Structure	Name
−5	$(HO)_3PO$	Phosphoric acid
+5	 $HO_2-\overset{O}{\overset{\vert}{P}}-(O-\underset{\underset{OH}{\vert}}{\overset{O}{\overset{\vert}{P}}}-)_x\overset{O}{\overset{\vert}{P}}-(OH)_2$	Polyphosphoric acid
+5	$POCl_3$	Phosphorous oxichloride
+3	PBr_3	Phosphorous tribromide
+1	$HP(O)(OH)$	Hypophosphorous acid
−1	H_2POH	Phosphinous acid
−3	H_3P	Phosphine

Similar findings were observed by Einhorn[59] in the formation of chars and the effect of reaction and additive-type phosphorous-based fire retardants on urethane polymers.

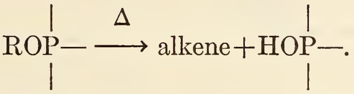
Phosphorous compounds that can decompose to acids are effective fire retardants. It is currently believed that phosphorous compounds are acid precursors and further that the acids perform the key role in char formation and in the inhibition of afterglow.

Equation (30) illustrates the formation of phosphorous acids during the thermal decomposition of a typical phosphorous compound:



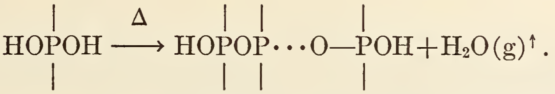
$$\mathrm{H_3C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O\underset{|}{\overset{|}{P}}{-}} \xrightarrow{\Delta} \mathrm{H_3C{-}\overset{CH_3}{C}{=}CH_2+HO\underset{|}{\overset{|}{P}}{-}}. \tag{30}$$

Equation (31) shows that the same reaction will occur in any alkyl ester when subjected to higher temperature:



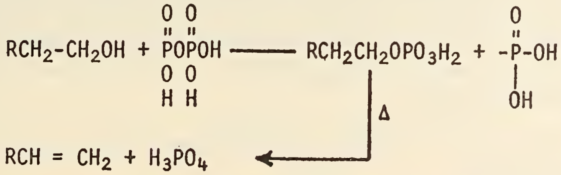
$$\mathrm{RO\underset{|}{\overset{|}{P}}{-}} \xrightarrow{\Delta} \text{alkene}+\mathrm{HO\underset{|}{\overset{|}{P}}{-}}. \tag{31}$$

Acid fragments will polymerize when subjected to heating to produce polyacids.



$$\mathrm{HO\underset{|}{\overset{|}{P}}OH} \xrightarrow{\Delta} \mathrm{HO\underset{|}{\overset{|}{P}}O\underset{|}{\overset{|}{P}}\cdots O{-}\underset{|}{\overset{|}{P}}OH+H_2O(g)\uparrow}. \tag{32}$$

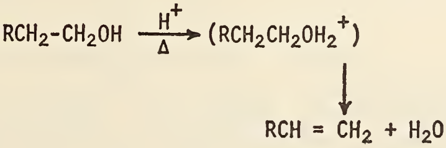
The polyacids are strong mineral acids, and also strong dehydrating agents, which are capable of protonating other species. The polyacids greatly enhance char formations in polymers containing multihydroxyl grouped urethane, polyesters, and cellulose. The formation of a strong carbonaceous char is thought to proceed via ester formation or through an intermediate carbonium ion:



$$\mathrm{RCH_2{-}CH_2OH + \underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}O\underset{\underset{H}{O}}{\overset{O}{\overset{\|}{P}}}OH} \longrightarrow \mathrm{RCH_2CH_2OPO_3H_2 + {-}\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}{-}OH} \tag{33}$$

$$\mathrm{RCH_2CH_2OPO_3H_2} \xrightarrow{\Delta} \mathrm{RCH = CH_2 + H_3PO_4}$$

ESTERIFICATION AND DEHYDRATION



$$\mathrm{RCH_2{-}CH_2OH} \xrightarrow[\Delta]{H^+} \mathrm{(RCH_2CH_2OH_2{}^+)} \longrightarrow \mathrm{RCH = CH_2 + H_2O} \tag{34}$$

SIMPLE CARBONIUM-ION MECHANISM

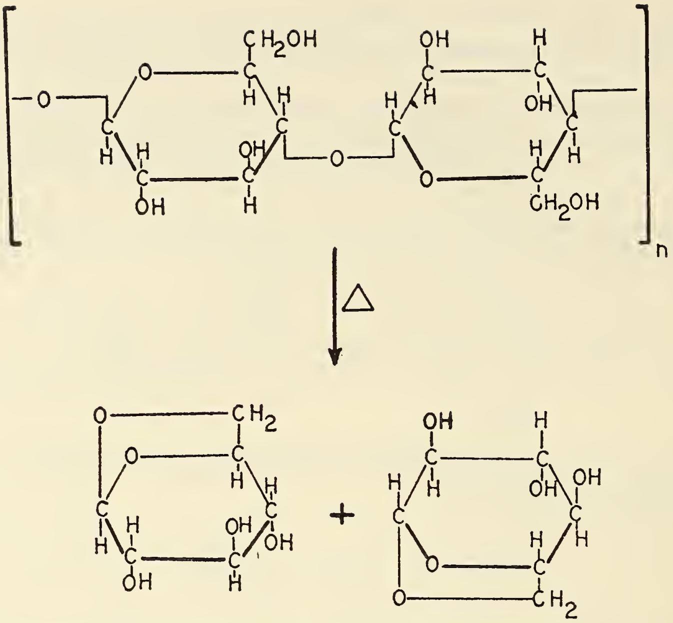


FIG. 10. Levoglucosan formation from cellulose.

Phosphoric acid is much more effective than sulfuric, sulfonic, and boric acids because it has sufficiently low volatility to remain in or near the site of combustion, is highly reactive, and is a mineral acid (pK, x ON).

Figure 10 illustrates the formation of levoglucosan from cellulose. Laible[60] concluded that the major cause of cellulose flammability is the tarry products being vaporized and thermally cracked into highly combustible gases. The major constituent of the tar is levoglucosan, which is formed as indicated in Fig. 10. It is noted that all organic fibers give off gaseous products during combustion or pyrolysis. Thus, if the textiles which are made from these fibers are to be fire retarded, the gaseous degradation products must be rendered nonflammable. There are three general approaches used to impart fire retardancy to this class of materials (or too many other polymeric materials):

1. To add a reactive fire retardant which becomes part of the chemical structure of the material;
2. To add an inert fire retardant which will function in a desired manner when required, but which is not part of the chemical structure of the material;
3. To deposit flame retardants or char precursors on the surface of the object to be protected.

Whatever the method of application, the fire retardant can act through one of two methods. In one the fire retardant causes the protective material to follow an abnormal course of decomposition, yielding less volatile and less combustible degradation products. In the second mechanism, which is effective with fibers and many polymers, the additive decomposes to gaseous products which mix with the normal gaseous products from the decomposing fiber to give a less-flammable gas mixture. Phosphorous containing fire retardants which generate phosphoric acid may be added to prevent the formation of levoglucosan and form instead a char percursor during combustion.

RETARDATION OF AFTERGLOW

The glowing reaction is a solid-phase oxidation of carbon to oxides, CO and CO_2. Phosphorous compounds are widely used to eliminate afterglow, but little information is known about this mechanism. Lyons[61] summarizes the possible role of the phosphorous compound in retardation of afterglow by stating that the polyacid, formed during the decomposition of the phosphorous compound, forms a physical barrier or in some way alters the oxidation process. Polyphosphoric acid is a very viscous, film-forming substance, which could coat the surface and retard oxygen diffusion into the reaction zone during combustion. The greater tendency for phosphorous compounds to form a gummy film as compared to sulfur or boron may explain the superiority of phosphorous compounds as glow-inhibitors. Alternative mechanisms such as favoring the production of CO_2 because of some as yet unknown catalysis effect attributable to the phosphorous acids and not from other acids are not as easily argued.

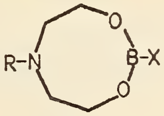
BORON FIRE RETARDANTS

The largest use of boron compounds as fire retardants is in wood and wood products. Eickner[62] published a comprehensive review covering the performance characteristics of fire-retardant wood. Borax, boric acid, and sodium borate are the most common boron compounds used in the treatment of wood.

McCluer[63] tested a number of inorganic boron salts as fire retardants for fabrics. The most effective of those compounds evaluated was sodium fluoborate.

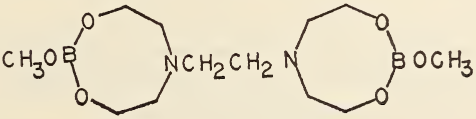
In general, organoboron derivatives (esters) are thought to be too hydrolytically unstable for general use as fire retardants. Knaggs[64] found that solutions of triamyl borate in an organic solvent with tritolyl phosphate and a fatty acid salt were effective in fire-retarding fibrous materials.

Cyclic boric acid esters derived from diethanolamines are stabilized towards hydrolysis by an intramolecular, boron-nitrogen coordinate bond



Rudner and Moores[65] utilized this structure to prepare direct polymers with cellulose that do not leach out on exposure to water.

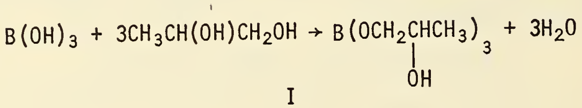
Cellulose fibers when treated with the following boron-containing compound were appreciably slower burning than control fabrics.



Rudner and Moores assumed that the methoxy groups were displaced by the hydroxyl groups of the cellulose to give an integrally bound boron-containing crosslinkage.

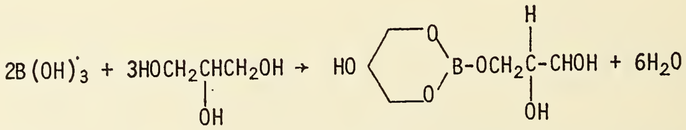
The mechanistic details of how boric acid and borate salts retard the combustion of cellulose are only partially understood. Schwenker and Beck[66] reported at least 37 products formed during the pyrolysis of cellulose. The major volatile primary product is thought to be levoglucosan (1,6-anhydro-β-D-glucopyranose). Levoglucosan is thought to arise by the thermal scission of the 1,4-glucoside bonds of cellulose.

A free primary hydroxyl group at C_6 is necessary for this depolymerization to occur. Levoglucosan is presumed to fragment to form the observed low molecular weight, volatile products. A second pathway for cellulose decomposition is simple dehydration to give water and dehydrocellulose. The dehydrocellulose is believed to be the principal source of char. Woods *et al.*[67] incorporated boron into the polyol moiety of rigid urethane foams. Several boron-containing compounds were synthesized as shown in Eqs. (35)–(38).

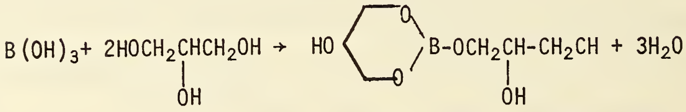


$$B(OH)_3 + 3CH_3CH(OH)CH_2OH \rightarrow B(OCH_2\underset{\overset{|}{OH}}{C}HCH_3)_3 + 3H_2O \qquad (35)$$

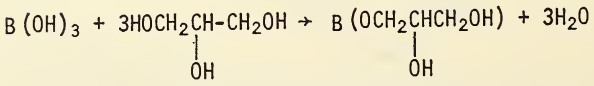
I

 (36)

II

 (37)

III



$$B(OH)_3 + 3HOCH_2\underset{\overset{|}{OH}}{C}H\text{-}CH_2OH \rightarrow B(OCH_2\underset{\overset{|}{OH}}{C}HCH_2OH) + 3H_2O \qquad (38)$$

IV

Structures I–IV are idealized; the actual products are probably mixtures of boron-polyol polymers. Prepolymers prepared with structures I, IV, or *tris*-(hydroxypropyl) glycerine and toluene diisocyanate produced foams of such poor quality that their evaluation was discontinued. Foams were prepared using polymethylene polyphenylpolyisocyanate and the boron containing polyols. Table 6 gives the formulations used by Woods in preparing these foams.

The formation of a complex (V) between the triethylenediamine catalysts and

TABLE 6

Polymethylene polyphenyl polyisocyanate boron–polyol foam formulations*

Foam No.	PAPI (wt. g)	Polyol used	Polyol (wt. g)	Catalyst System	Catalyst (wt. g)	F–11 (wt. g)
1	16.0	I	8.4	Triethylene diamine-hexanetriol†	0.4	6
2	16.0	II	19.1	Triethylene diamine-hexanetriol $(C_2H_5)_3H$	0.4 0.2	6
3	16.0	III	12.6	Triethylene diamine-hexanetriol $(C_2H_5)_3N$	0.4 0.2	6
4	13.1	IV	9.0	Triethylene diamine-hexanetriol	0.4	6
5	16.0	IV	9.3	Triethylene diamine-hexanetriol $(C_2H_5)_3N$	0.4 0.2	6
6	15.5	IV	9.3	Triethylene diamine-hexanetriol $(C_2H_5)_3N$	0.4 0.2	6
7	21.5	e**	15.1	*H,N,H',N'*-tetramethyl-1,3-butane diamine	0.2	5

* Each foam formulation contained 0.2 g of DC–113 silicone surfactant (Dow Corning Company).

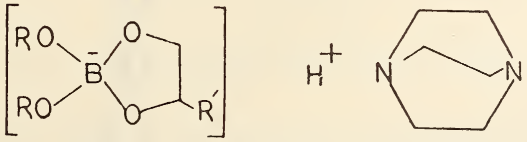
† A 112 mixture of triethylenediamine (DABCO–HOUDRY Process Company) and hexanetriol.

‡ Polymethylene polyphenylpolyisocyanate (Upjohn Corporation).

§ Trichlorofluoromethane.

** A mixture of VORANOL RS 530 (Dow Chemical Company) and I.

the acidic glycol borates resulted in retarded rates of rise during foam preparations.



Additional amine catalyst was required to produce satisfactory foam specimens. Table 7 presents the results of evaluations performed to determine the flammability characteristics of the boron modified foams.

Woods *et al.*[68] prepared several brominated boric acid esters as potential non-

TABLE 7

Flammability characteristics of boron-containing foams

Foam No.	Density (pcf)	% B	Burn rate,* (in./min.)	Observations
1	2.96	1.4	10.1±0.5	Shrinks
2	4.15	3.63	Immediate self-extinguishing	Melts
3	3.72	2.28	Self-extinguishing (7-sec)	Chars
4	16.9	1.4	Self-extinguishing (1–6 sec)	Chars, slight softening
5	3.54	1.26	Self-extinguishing (14-sec)	Chars, slight melting
6	3.36	1.3	Self-extinguishing (7–10 sec)	Chars, sags
7	3.69	0.89	7.3±0.3	Surface char, shrinks

* Modified ASTM D 635–56T.

reactive fire retardants. Rigid foams were prepared from a polyhydroxylpropylated sucrose-TDI prepolymer and polyether polyols. The additives were introduced at a level of 20 phr and the effect on burning rate determined. Some reductions in burning rates were achieved, but no self-extinguishing foams were obtained.

NEW CONCEPTS FOR THE DEVELOPMENT OF FIRE-RETARDANT PLASTICS

The use of recently developed techniques of thermal analysis to match the chemical and physical properties of candidate fire retardants with that of the polymer to

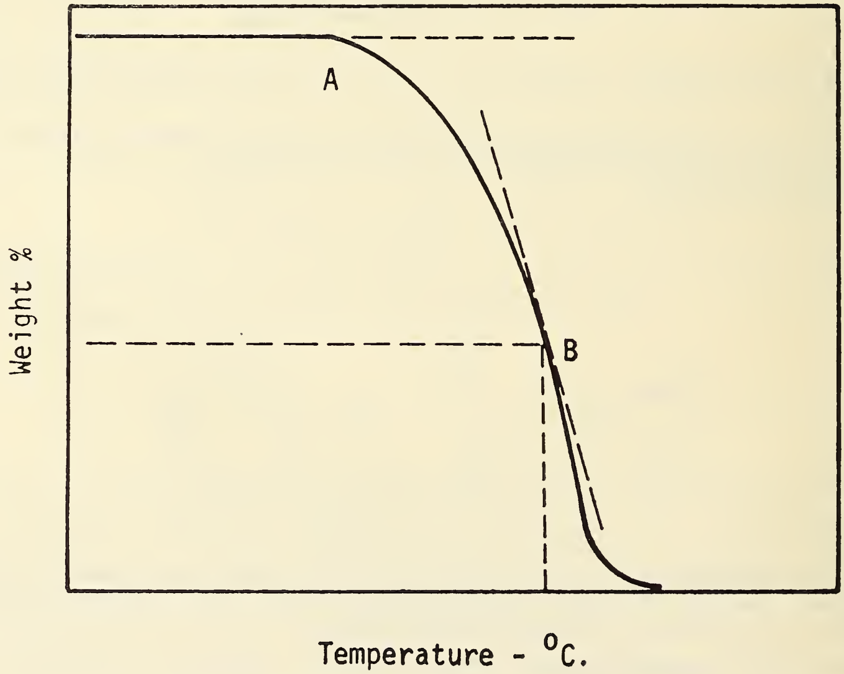


FIG. 11. Thermogram for a hypothetical polymer.

be stabilized has been reported by Einhorn.[59] Simultaneous differential thermal analysis (DTA), thermogravimetric analysis (TGA), and derivative thermogravimetric analysis (DTG) are carried out under dynamic conditions of a heating rate of 10°C/minute. Figure 11 presents the thermogram for a hypothetical polymer which exhibits a simple unimolecular degradation process. Point A represents the region of initial decomposition, point B represents the point of maximum degradation.

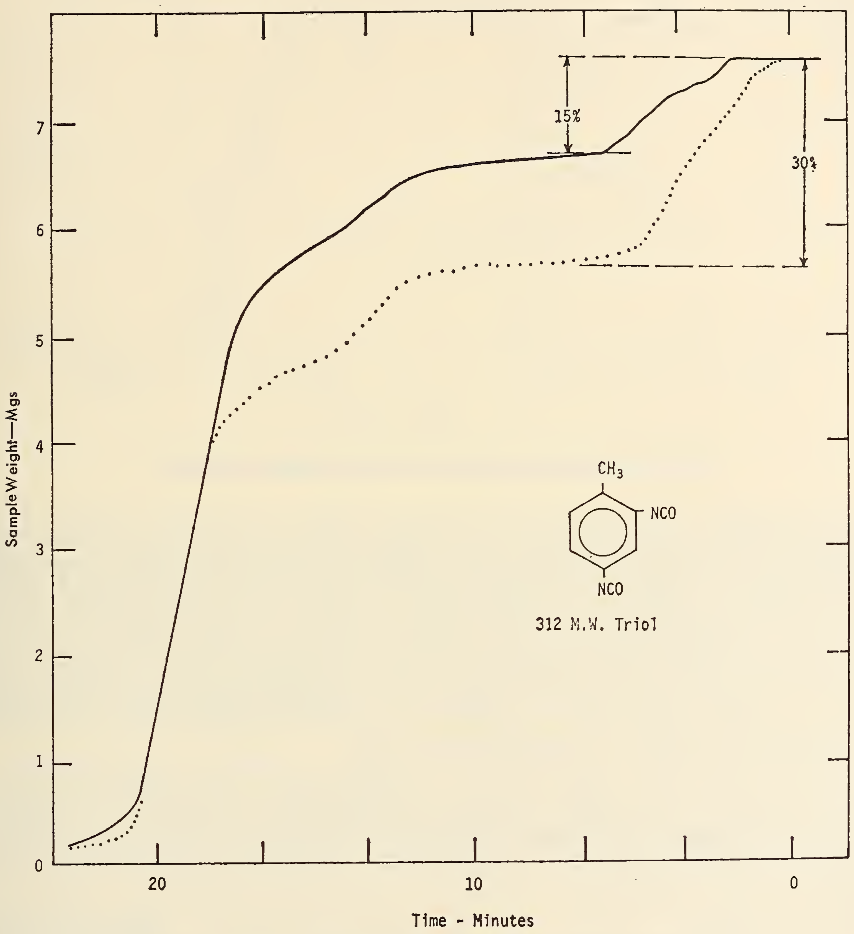


Fig. 12. Sublimination of fire retardant (vacuum).

Fire retardants are screened so as to select a material having thermal characteristics similar to those illustrated in Figure 11. A greater degree of stability can be obtained if two fire retardants are used: one fire retardant which changes state approximately 60° to 75°C lower in temperature than point A, and a second fire retardant which changes state in the temperature range of point B. For polymers which degrade by means of a complex or autocatalytic process, this technique may be used to select a balanced fire-retardant system using a combination of several retardants.

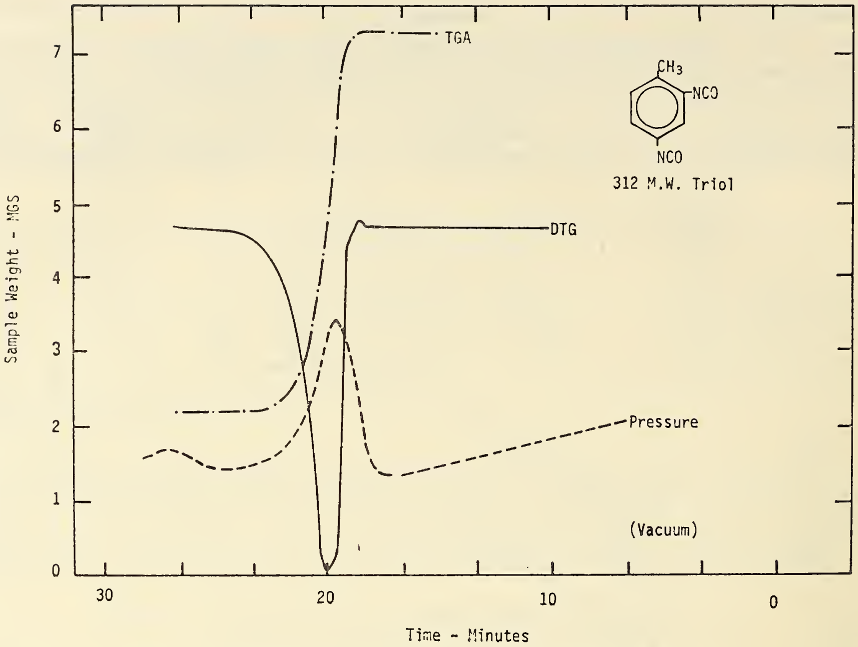


Fig. 13. Degradation nonfire-retarded urethane polymer.

The choice of fire retardants, is of course, dependent on the nature of the polymer, the method of processing, the proposed service conditions, and economic considerations. Generally, reactive fire retardants are more stable than inert systems. Numerous investigations of materials exposed in actual fires have indicated that the nonreactive retardants may sublime out of the polymer when exposed to the hot gases which normally proceed the flame front. Figure 12 illustrates weight losses equivalent to the weight of fire retardant in urethane polymers when the nonreactive *tris*-2,3-dibromopropyl phosphate was used.

Further studies were carried out in a vacuum of 10^{-7} torr. Figure 13 shows a single sharp weight-loss region when a nonfire-retarded urethane polymer was heated under dynamic conditions. The change in pressure was due to the evolution of gaseous degradation products at the time of thermal decomposition of the polymer.

Figure 14 shows a bimodal degradation process when the nonreactive fire-retardant *tris*-2,3-dibromopropyl phosphate was added to the model urethane. The initial weight loss (without an increase in pressure) was due to sublimation of the nonreactive fire retardant. The material which was lost initially was collected and identified by normal chemical analysis procedures as the fire retardant.

In the process of selecting fire retardants to improve the flammability characteristics of a polymer or plastic, consideration must be given to total fire response and not just a single parameter such as flame propagation, smoke development, or fire endurance. The final product must be subjected to evaluation standards which approximates actual service life. For example, it is not normally possible to fire-retard synthetic fibers, when they are produced, because of undesirable side effects

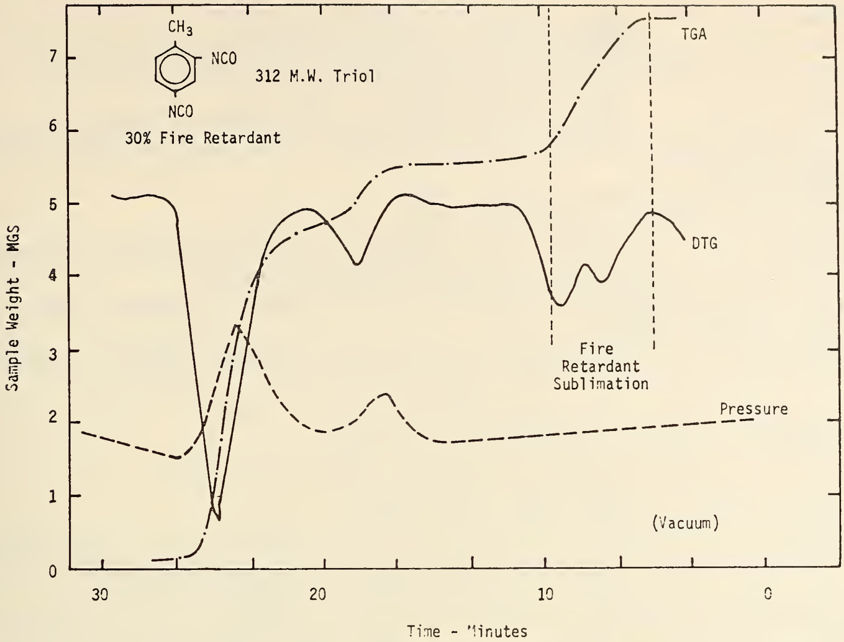


FIG. 14. Degradation of fire-retarded urethane polymer.

during coloring, weaving, or sizing operations. Nonreactive fire retardants may be added as an after treatment with only minor adverse effects to the process economics. Standardization tests usually are designed to rate the manufactured product. It is necessary to perform use-oriented tests so as to predict with the desired degree of confidence the performance of the finished product. Thus, in the case of fabrics, a given number of cycles of washing or dry cleaning may be used to evaluate the flammability characteristics after a preselected service life.

FUTURE TRENDS IN FIRE RETARDATION OF POLYMERS

Greater emphasis is now being directed toward modification of chemical structure in order to inhibit ignition and flame propagation. Einhorn has predicted that the second generation of fire retardants will not contain halogen atoms and thus reduce substantially the additional hazards to life support during the combustion of fire-retarded polymers.

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SUMMARY

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Trying to summarize such an excellent set of papers which already have been very brief summaries of an enormous background of work is not something that one can do very effectively except with a clear understanding of the purpose of that summary. The purpose of this meeting is to answer a certain very difficult question which, in spite of all the complexities that were discussed today, we have most successfully avoided. Namely, if you have N dollars, how many of them do you give to a chemist? This, it seems to me, is ultimately what we are trying to get out of this meeting.

I don't blame the previous speakers for avoiding this question. In fact, I would rather like to duck it myself, but in view of the fact that the Fire Research Committee's job is to come up with a suggested answer, I think I shouldn't duck it. To answer this question certain subjective information has to be added to what we have heard already.

A very quick overall summary as I heard it today is that chemistry does indeed play a significant and vital role in our ultimate real understanding of the ignition process, the smoke and toxicity problem, certainly the inhibition problem, and in the question of extinguishment. For the steady burning part of the fire, chemistry probably never will say very much of practical importance because of the fact that the fire is dynamically controlled by various dynamic factors, the chemistry being fast enough to be considered infinitely fast for practical purposes.

Now, if we take a look at how important chemistry really is, we have to note that at the high temperature oxidation level that we are concerned with in fire, all we need to do is to extend Dr. Einhorn's presentation a little bit and observe that if we really do get an inhibitor that prevents those reactions completely, the problem is gone. I don't have to worry about all of the various aspects of the administration of the fire services, and the economic factors, and the labor problems, and the operations research, and the various miscellaneous chemical problems like the thermodynamic data and the detailed kinetics, of the aerodynamic considerations, the heat transfer, the heat conduction, and all the rest. They all go away. When you have something that will really kill the problem completely, how could you possibly put your money anywhere else? If you find the perfect inhibitor the fire problem is gone. If, in the not too distant future, you think there is any prospect of finding that particular magic X that makes the problem go away, your money should be used to search for X.

I did not hear as I listened to the speakers today, and I do not believe from my own background that that particular magic X exists. Research in the detailed chemistry of inhibitors, in fact, may or may not get us anything. I do not know. It may well be that we already know all of the best inhibitors that exist, but perhaps we do not. We do need basic chemical research, therefore, to understand what these inhibitors are doing so that we can answer the question, "Do any better inhibitors exist than are already known?"

There are very important basic chemical questions in fires. However, that is not enough information to decide the issue of where to put our research money. Before deciding where to put our research money, we should not only answer the question, "Is chemistry important and exactly what is the detailed chemistry of this process?" but, should first answer the question, "What good will it do us if we understand them?" Fire chemical processes go on the same way whether or not we understand them. And if I do understand them, can I cope with the problem any better?

First, then, we ought to take a look at this last question and in order to do so, I think we have to break the issues down a little bit further because when I say chemistry, exactly what am I talking about. After all, I can say all fire is chemistry and therefore if you work in fire research, you are a chemist. No, that is not what we are here for today. We have to break it down more. I am going to break fire chemistry down into certain pieces in a very crude qualitative fashion which will help us decide where to put our research money. I am going to talk about chemistry first at the overall thermodynamic level. That is level number one; at an overall kinetic level, level two; and at a detailed atomic mechanism level, level three. These three levels of chemical knowledge are differently needed in different aspects of the practical fire problem.

We do not know at what level the chemistry of any particular nameable fire problem is important. Certainly, the overall thermodynamics is important in the steady burning fire, even though dynamics control all the detailed rate processes. We still need the overall thermodynamics in the ignition, in the suppression, and in the inhibition area. How much chemistry do we need? Do I have to know how the electron wiggles? Or is some overall picture of the kinetics sufficient? We do not know the answer to that question. And as always therefore, if we are going to do research (research means looking into the unknown), there is no guaranteed way by which we can say, "Ah, there is the problem I ought to work on. There is where I ought to put my money." Since the answers are unknown to all of the various problems that are now open, there is no way in which anybody can arrive at a number which he can defend against those who have a different point of view. And so the best I can do is to give you my point of view as to how I summarize this story today; the chemical needs for research, compared with the total fire problem needs for research, as I see it.

In the first place, I mentioned a few moments ago administration, economic factors, labor relations, operations research, physical phenomena, chemical phenomena, the parts that make up the fire problem. The scientific and technological research area is, in my thinking, something like 10 percent to 20 percent of that total problem. The social and humanistic parts of our problem ultimately need most of the money. However, these problems cannot be solved without an adequate technological base. It seems to me in view of our major ignorance in very important scientific and technical areas, that 10 to 20 percent put on those parts of the fire problem at a national level, is something like a sensible level at the present time. Our firemen friends and people in other areas will very likely challenge my number as too big. However, they generally do not realize how abysmal our present scientific knowledge is compared to what needs to be and can rather easily be known. My appraisal is 10 to 20 percent for science and technology of fire at the present time.

The earlier speakers have indicated the part that the chemistry is going to play, and I agree that today we did hear important reasons why ignition and extinguishment and other aspects of the fire raise very important chemical questions. That still does not really get at the question of where we should put our money because we have yet to answer the second question, "What do we think our chances are of doing something about it?" If you think that the probability of getting something useful out of a given piece of research is near zero, then near zero is the amount of effort you should put into that part as compared to something else that would have a more immediate and greater payoff.

In order to discuss this, I think that we have to look for the long-term answer and the short-term answer. These are not necessarily the same answer. And as a matter of fact, one's division of research effort would be expected to vary as we make progress with various parts. And so, let me try to look at it in this fashion.

Research in the chemical area, payoff, long-term, short-term fires. A study of the *detailed chemical mechanisms*, how important is it? Long-term, it is certainly very important both from the philosophical, aesthetic point of view and from a practical point of view. My answer to "research support" is yes, some. Since it is just as likely that in the long term all of these little details are really "little details" and do not really determine any of the practical fire processes, I cannot recommend large support. Even the inhibition process may come out as I imagined above, namely, that we already know the best inhibitors. So, for long-term chemical research support, some; short-term, none. Now, obviously "none" with that kind of finality is not right, but I think that is the first approximation.

Second, I will consider the need to know the *overall kinetic mechanisms*. They may have real detail significance in ignition and extinguishment problems and are very necessary for development of, for example, flammability ratings which do not vary from test to test as so often they do at present.

Short-term research on overall effective chemical kinetic rates should receive some support. I have to put the support on the low side because I do not believe it very likely that a significant improvement in our procedures and techniques will come out of a given effort put into this area as compared to the benefits attained by the same amount of effort in other areas which have been clearly neglected, are clearly growing at an enormous rate, and clearly have great prospect for practical results. I, personally, rate these other things the dynamics of fire, as of the moment, as of rather more importance than an overall understanding of the kinetic mechanism. Thus overall chemical kinetic studies deserve some support on the short term and these will go over to some support of the study of detailed kinetics in the long term.

Third, overall thermodynamics, in the long term, must be supported. For the short term, you probably expect me to recommend support also. However I am going to say no support. And I will tell you why. I think we already probably know all of the thermodynamic data that we really need. Now again, that is not a hard and fast rule. There are some things that we really do need to know in the area of basic thermodynamic data with the chemical processes of fire in order to do our combustion correctly. But the majority of that data is already available. It is necessary for us to do as Dr. Stull has done with certain reactions, make use of it. It is there and goodness knows we have not used it the way it should be used. But do we need a lot more? Probably a little more, but I think not much. So for thermodynamic data for the long term, some support; for the short term, none.

So where should we put our money? Well, I kind of think that of the 10 percent or 20 percent for fire science and technology we, in the long run, are going to have to invest a fair amount in the chemical area. Perhaps as much as 15 percent to 25 percent of the fire science pie. Maybe that is not enough, maybe it is too much, only the future can decide.

In the short term we need some support or we have not got any long-term work. For the actual needs in the short term, very little support can be justified but if we do not get started, we are never going to have any long-term answers. And so maybe as much as 5 percent of the fire science portion.

These chemical problems of fire, as noted in the preceding papers, are almost universally terribly difficult. They are tough. And I believe these should be approached as an aerodynamicist would approach the turbulence problem. Turbulent flow is terribly important in the fire area also. Why do we not do a lot of basic turbulence research? I do not think any turbulence research is justified as a part of fire research. This is not because it is not important, but because no one has a really breakthrough idea of what to do. Such ideas are awfully few and far between in the area of turbulence research and in listening to the discussion this morning I see that the same is true of the detailed chemical kinetics. If we have to wait twenty years for the determination of a hundred of the thousand or so important reactions in the two percent precision category, only a very small but continuous support is justified.

Let me comment on the way fire research should be done. Let us consider ignition research, or flammability research. We need to tackle the whole problem in a way that has some real prospects for getting immediate answers to the question of how easily this material will ignite in this room with all the synergistic effects present. Walter Berl considered a room that was utterly hopeless. He put everything in his room that he could think of. But it was typical of the rooms that we use and, unless we can define a test for flammability that is correct in this room as we sit here now, it is a fake. In fact, almost 100 percent of our tests are partially fakes because of the fact that the various tests devised by equally competent people give contradictory results. And so long as we get contradictory results, we have not simulated what we are really trying to test. In order to find what test is really significant we have to have a research approach which contains team work, and that team must have in it a first-rate experimental physicist, an applied mathematician, and a first-rate chemist.

The experimentalist must indeed be expert in the aerodynamics and the heat transfer areas, not atomic physics of high energy particles. He must be good in classical physics which are the key ones to the fire problem.

The applied mathematician must know the most modern analysis techniques and computational techniques. He must be interested in the physical answer to the relevant physical problems of fire and not concerned exclusively with the techniques themselves. He must work with the experimentalist in trying to understand the data by setting up the basic laws as we know them and calculating what the answer should be. He must compare the computed and measured results and then return to the experimentalist to improve the agreement. It is only by thus working together that the basic mechanisms can be understood.

Where does the chemist come in? The chemist is needed here, too. We have to develop overall reaction mechanisms at the essential level to understand what is going on. What is the essential level? I do not know. If we leave the chemistry to an aerodynamicist, we are going to use some very crude chemical mechanisms.

We will have one or two simple one-step reactions. The chemist's help is essential, not to come up with a detailed knowledge of every reaction step but rather with the right mix of controlling steps. What we have to do is increase step-by-step in complexity until we find out what degree of complexity is absolutely essential to understand ignition and other fire problems.

And so the first-rate chemist will know all the detail background that is currently available, but will, like the physicist and his high-speed particles, set the detail aside for the moment and work with the other two fellows as a team of three trying to bring in only what is absolutely essential and only increasing the complexity of the chemical understanding as it is essential to the understanding of the fire problem. None of our three-member team may put in everything he can think of. If he does he is not going to help us much. The analyst, if he does it, is going to pose a problem too difficult for the computing machine. It is not nearly big enough. The experimentalist, if he does it, is going to measure so many things that we are not going to untangle very much. And the chemist must be willing to do the same thing.

THE ROLE OF CHEMISTRY IN FIRE PROBLEMS—A CHEMIST'S SUMMARY

R. FRISTROM

Applied Physics Laboratory, The Johns Hopkins University

This symposium has presented a series of papers outlining the contributions which chemistry has made and continues to make in the areas of: Combustion, Thermodynamics, Chemical Kinetics, Analytical Chemistry, Polymer Chemistry, and the Chemistry of Fire Retardance and Suppression. Both the potentialities and the limitations of chemical information have been discussed.

Chemistry is, of course, only one of several sciences which play important roles in fire problems and the interactions between these are strong. Nevertheless, it is a useful exercise to consider the contributions of chemistry as an entity although it should be kept in mind that it is the marriage of information from these various disciplines which leads to the complete understanding of the fire problem which we seek.

This paper will provide a summary of the contributions of chemistry; not from the standpoint of the individual chemical disciplines, an approach which has already been well done by our speakers, but from the standpoint of the various problem areas. This gives a different and hopefully productive perspective on the problems of fires and the role which chemistry can play. To a degree, the classification of fire problems is a matter of taste; for discussion we will arbitrarily divide fire problems into five categories corresponding to the time sequence during a fire.

I. FIRE HAZARD PROBLEMS—What should be done before the fire.
II. FIRE DETECTION PROBLEMS—How to discover the problem before it gets out of hand.
III. FIRE PROPAGATION—How rapidly will a fire progress.
IV. FIRE SUPPRESSION PROBLEMS—What can be done to curb a fire.
V. FIRE SALVAGE PROBLEMS—What can be done to reduce the loss.

Each of these problems has two aspects:

A. Evaluation of the problem.
B. The countermeasures to the problem.

Fire Hazard Problems

The evaluation of fire hazard requires an understanding of chemistry. This involves both a qualitative and quantitative problem: (1) can a material be oxidized, (2) if ignited, what heat is released and what compounds are produced, (3) how easily is it ignited and how rapidly will it progress.

In the fuel-oxidizer loading problem, thermodynamics furnishes a powerful tool which Dr. Stull has discussed in some detail. Fuel loading is commonly considered the major problem but it is a two-fold problem; fuel and air availability. The usual assumption is that the oxidizer is the air and that it has unlimited availability. This is not always the case and often this can be of practical use or be a serious problem. For example, in a 15′×20′×10′ room there is only oxygen and only a third of this is available before a fire extinguishes itself for lack of oxygen. This is not a large amount so that if it were possible to isolate such a room, a fire would consume only a few pounds of fuel. Thus, one approach to fire suppression can be isolation. There are two problems with this approach, one is the life hazard in such an environment and the other is the flare-up hazard to firemen entering such a compartment and allowing air to suddenly contact hot, combustible gases. An added problem is the increased use of oxidizing substances—ammonium nitrate fertilizers—perchlorates for swimming pools, two potent sources of oxygen. Despite these complications, it is well within the capabilities of modern chemistry, using modern computing techniques, to furnish a meaningful answer to this problem. If the problem is organized and questions posed correctly, meaningful answers can be provided economically.

The second problem in hazard evaluation is ignitability, and here it is possible to divide materials into classes chemically but effects of geometry and position must also be considered. Ignition has been treated as an empirical problem, but it is high time that this empiricism is rationalized by the introduction of basic chemistry and the physical heat transfer. I feel that this is both feasible and necessary. It often involves both gas phase chemistry and solid phase chemistry which you have heard discussed by Drs. Berl, Friedman and Wall.

The third question is propagation probability. This is a complex problem which is not completely divorced from ignitability. Here again chemistry has basic inputs in the form of chemical kinetic constants and reaction mechanisms. Again a strong effort to connect the empiricism of the tests with the basic chemical and physical information is long overdue. Much of the basic information is already available and much of the information which is presently not available would be forthcoming if it were clear that the information would be used. The basic research worker can furnish relevant information if an outline of the areas of need is made. Again, this requires a viable theory connecting the empirical descriptions with the elementary processes.

The fourth area is life hazard toxicology. Here chemistry can furnish information on possible products and conditions for their formation which in turn must be evaluated toxicologically. A wealth of information is available, but the area has not been systematized. Again the relation between practice and available basic information is the weak link.

Following this evaluation, methods for reducing the hazard should be explored. The use of fire retardants is an important area. This is a predominantly chemical problem involving complex solid and heterogeneous phase chemistry. Here much information is available, but it requires more systematic evaluation. Both Dr. Wall and Professor Einhorn discussed these problems. Trade-offs between flammability and toxic combustion products may be necessary. This, I feel, is a particularly fruitful area for a chemist to make contributions to the fire problem. Automatic suppression systems can be improved by an understanding of chemistry. Both the combustion chemistry itself and the chemistry connected with flame extinguishment offer a wide area for chemical contributions.

Code recommendations are a powerful tool in reducing fire hazards and an understanding of the chemistry involved in hazard evaluation should be an important contribution.

Fire Detection Systems

Fire detection can in principle be based on chemical information. My own feeling is that it is urgent that fire detection be investigated relative to the question of saving life. Most fire detectors were designed for property safeguarding and heat sensors are commonly used. Life protection makes the chemical methods of detecting and warning methods of particular importance, since the smoke and toxic gases are the major life hazard in a fire. With the exception of smoke detectors, chemical detectors have not been widely used. It is possible that chemical detectors for CO, Hydrocarbons, CO_2, HCN etc. may be practical and offer an important addition to the detection systems—perhaps not as a complete substitute for heat and smoke detectors, but as alternate detectors to increase sensitivity and reduce false alarms.

Fire Suppression Problems

The chemistry of fire propagation and inhibition plays a key role in the choice and understanding of suppression systems. Much progress has been made in understanding gas phase chemistry, and you have heard the wealth of work on pyrolysis of solids and heterogenous oxidation processes. Much work still remains to be done, but information is available. What is needed is to organize the information, and understand the problem to the degree where we can systematically ask the chemist the key questions. This requires models of a sophistication not yet available, but this is a goal worth striving for. Some attempts have been made and this is an area where basic chemistry can offer vital information on mechanisms. When these roles are understood, basic rate and thermodynamic information can be utilized. If we knew the correct questions, it is probably well within the present capabilities of chemical researchers to furnish the required information on a reasonable time scale for practical use.

Fire Salvage

This is an area where research has made little contribution but it would appear to be a fruitful area to investigate. Chemistry could suggest where damage is potentially reversible and give a value judgment on the economics of such measures.

An understanding of this field involves almost the whole of industrial chemistry. In this context one should consider both people and property. It would be desirable to develop an understanding of the health hazard which exposure fire entails so that recommendations can be made to physicians and administrators on likely post fire problems. This understanding is coupled with the evaluation of the original hazards coupled with a knowledge of what actually was burned.

Summary

Fire problems are varied and many of them involve chemistry in some form The efficient use of chemical information will only come about by a marriage of the empiricism which has dominated the fire field with an intelligent use of basic information. A wealth of information is available, but it is not clear which pieces of information are required, which pieces are available and what basic information is still required. What is necessary is a dialogue between the practitioner and the research worker so that the critical pieces of information can be located, described and developed systematically. The contributions of chemistry to the overall problems of fire can and should be important, but a sympathetic understanding and exchange of information is required between the practitioner and the basic researcher.

COMMENT

CHARLES W. BECKETT

National Bureau of Standards

1) Upper bounds upon the quantity of energy released in thermal decomposition or combustion reactions give a measure of potential hazards. This can be calculated for many substances as discussed by Dr. Stull and also Dr. Wall. Estimation of the concentration of toxic products is less accurate because the concentration may differ by very large amounts from the thermodynamic value [e.g. rapid quenching of nitrogen–oxygen mixtures from high temperatures yields nitrogen–oxygen in concentrations of several per cent much higher than the thermodynamic equilibrium value (0.004% at 1000 K).] Since some decomposition products may be lethal in very low dosages, I would recommend caution in the use of thermodynamic estimates as a measure of potential toxic hazard. However, there are many ways in which thermodynamic methods can be applied in fire research as in other fields of high temperature research and technology.

2) Applied kinetic calculations now are possible for many high temperature processes using computer programs that include thermodynamic, kinetic, radiation, and some hydrodynamic processes. In some cases, these programs are being used in air pollution problems that are related to combustion. They can also be used in fire research where the same phenomena occur.

3) The current status of basic chemical kinetic data on substances containing the elements H C N O is sufficient now to permit chemical kinetic modeling of fire processes. This would include cellulose as indicated by papers given in the recent symposium on the thermal decomposition and combustion of cellulose, American Chemical Society Meeting in Washington, September, 1971.

4) Data on substances containing halogens; fluorine, chlorine, and bromine probably is less extensive and reliable. A recent review by Creitz does include a fair amount of data related to flame inhibition by bromine and chlorine compounds.

5) Studies of the kinetics of gas phase oxidation reactions involving compounds of antimony, iron, molybdenum, and barium now are in progress. Although some of these studies are not directed toward fire research, they may contribute significant information.

6) I recommend that the fire research committee prepare a list of substances (100 or less) that are most likely to be important in future work. This list could then be sent to specialists in various fields who may be able to contribute relevant research on the properties of these substances.

ABSTRACTS AND REVIEWS

A. Prevention of Fires and Fire Safety Measures

Law, M. (Joint Fire Research Organization, Boreham Wood, England) "A Relationship Between Fire Grading and Building Design and Contents," *Joint Fire Research Organization Fire Research Note No. 877* (January 1971)

Section: A
Subjects: Building Correlation; Fire grading; Structural elements

Author's Summary

This paper shows how temperature and rate of burning data from an international program of experiments[1] on the behavior of fully developed fires in compartments can be used to calculate, for each fire, the thermal properties of a protected steel column which just attains a critical temperature. It demonstrates how the time t_f for the same column to reach this temperature in the standard fire resistance test can be calculated. A correlation is then obtained for a range of scales, shapes, fire loads, ventilation areas and fuel thickness in the form $t_f = K(A_W A_T)^{-1/2}$ where L, A_W, A_T denote respectively fire load, window area and the sum of wall and ceiling area. The value of K varies slightly with fuel spacing. Data from other experimental fires in larger scale brick and concrete compartments, including those by Odeen with forced ventilation, have been examined and give a somewhat lower value of K. Reasons for this are discussed. The calculations are compared with those of Kawagoe and Sekine, Lie, Pettersson and Odeen, and the relation to Ingberg's early experiments is examined.

Reference

1. Thomas, P. H. and Heselden, A. J. M. CIB International Co-operative program on fully-developed fires in single compartments. Comprehensive analysis of results. Joint Fire Research Organization Internal Note No. 374, 1970.

B. Ignition of Fires

Chandler, S. E. (Joint Fire Research Organization, Boreham Wood, England) "The Ignition of Plastic Materials in Dwellings," *Joint Fire Research Organization Fire Research Note No. 883* (July 1971)

Section: B
Subjects: Ignition of Plastics; Fire statistics

Author's Summary

An analysis has been made of the statistics of incidents involving the ignition of plastics in dwellings. The estimated number of incidents in 1969 (based on a 1 in 2 sample of reports) was 396. This total does not include fires in which plastics were not the materials ignited first or fires involving woven fabrics. One hundred and sixty eight incidents occurred in kitchens, 54 in living rooms and 52 in bedrooms. The items most frequently ignited were bowls, buckets, containers, furniture, toys and games. In only 12 incidents were structural materials (e.g. walls and ceilings) ignited. Cooking appliances provided the source of ignition in 100 incidents, and space heaters in 80. In the 1 in 2 sample of reports, seven incidents involved rescues and casualties (7 non-fatal, 5 fatal). All but one of these occurred in the bedroom.

C. Detection of Fires

O'Dogherty, M. J., Young, R. A. and Lange, A. (Fire Research Station, Boreham Wood, England) "Detection of Fires in Cable Tunnels," *Electrical Review* (February 26, 1971)

Section: C
Subjects: Fire detectors; Spacings of detectors

Abstracted by G. Fristrom

Experiments were conducted to investigate positioning of smoke and heat detectors in cable tunnels and subways. Response times of both detectors at various spacings to a pan fire of 0.37 m^2 with and without forced ventilation were compared. The heat detector system spaced at 3.7 meters gave a maximum detection time of 30 seconds to 1 minute 12 seconds without forced ventilation while an ionization chamber smoke detector at 10 meters spacings required 31 seconds response time. With forced ventilation these times are reduced to 40 and 40 seconds respectively. Smaller fires were not detected by the heat sensitive detectors at ambient temperature of 0°C.

D. Propagation of Fires

Malhotra, H. L., Morris, W. A. and Hopkinson, J. S. (Joint Fire Research Organization, Boreham Wood, England) "The Fire Propagation Test as a Measure of Fire Spread Correlation with Full Scale Fires in Corridors," *Joint Fire Research Organization Fire Research Note No. 876* (June 1971)

Section: D
Subjects: Fire propagation test; Fire spread

Authors' Summary

Tests have been carried out to observe the spread of fire along a corridor of 13 m length with different lining materials on the walls and the ceiling. The tests established that the performance of the lining systems in the Fire Propagation Test (B.S. 476: Part 6)[1] provided a reliable guide to their behavior under fire conditions.

Reference

1. British Standard 476: Part 6 (1968).

E. Suppression of Fires

Nash, P., Bridge, N. W. and Young, R. A. (Joint Fire Research Organization, Boreham Wood, England) "Some Experimental Studies of the Control of Developing Fires in High-Racked Storages by a Sprinkler System," *Joint Fire Research Organization Fire Research Note No. 866* (April 1971)

Section: E
Subjects: Detector, fire; Fire spread; Sprinklers

Authors' Summary

This report gives an account of six large scale tests on goods stored on pallets in a system of racking at 6 levels. The storage was protected by a sprinkler system

mounted centrally within the racking at each level. The effect of varying the numbers of sprinklers per pallet cell, the use of each and alternate sprinkler levels and the size of the sprinklers (10 or 15 mm bore) on the development of the fires was studied.

This arrangement was found to give good general protection to the racking and goods, in that the fire would have been contained and subdued, but in all but one experiment the fire spread throughout the height of the racking. Lateral spread was restricted to the width of the cell of origin.

Automatic detection equipment was found to operate about two minutes before the operation of the first sprinkler. The operation of the sprinklers caused the production of a certain amount of cool smoke which sank to ground level.

Corrie, J. G. and Griffiths, D. J. (Joint Fire Research Organization, Boreham Wood, England) "Extinction of Laboratory Hydrocarbon Fires with a Synthetic Foam," *Joint Fire Research Organization Fire Research Note No. 894* (October 1971)

Section: E
Subjects: Extinction, hydrocarbon fires; Foam tests

Authors' Summary

The extinction performance of a proprietary synthetic foam liquid, normally used for the production of high expansion foams, has been measured on 0.279 m^2 petrol fires, the foam being applied with expansion of about 10 at a rate of 0.04 $1/m^2/s$. Control time was found to be a function of expansion as well as of shear stress.

With optimum foam characteristics, control time was equal to that obtained with fluorochemical foams, and superior to all other types of foam which have been tested. Under the test conditions used, best results were obtained at an expansion of 12 and a shear stress close to 10 N/m^2.

Thorne, P. F. and Young, R. A. (Joint Fire Research Organization, Boreham Wood, England) "The Application of High Expansion Foam to Wood Crib Fires," *Joint Fire Research Organization Fire Research Note No. 887* (August 1971)

Section: E
Subjects: Extinguishing foam; Wood crib fire

Authors' Summary

Experiments have shown that when applied at an adequate rate, high expansion foam can readily extinguish flaming combustion in wood crib fires. The complete extinction of smouldering combustion, however, did not always occur and it was often necessary to top-up with fresh foam in order to minimise smouldering beneath the foam.

Buckley, J. L. (Factory Mutual Research Corporation, Norwood, Massachusetts) "Evaluation of a Novel, Slurry Type Fire Extinguishing Agent," *Factory Mutual Research Corporation Report FMRC Serial No. 19969, RC71-T-31* (September 1971)

Section: E
Subject: Fire extinguishing agent, evaluation

Author's Abstract

An experimental program was conducted wherein mixtures of two fire suppressing agents, and a gelling agent (bromotrifluoromethane, $CBrF_3$, ammonium dihydrogen phosphate (ADP) and Cab-O-Sil) were prepared as a potential suppressing agent for habitable aircraft interiors. These mixtures, although capable of extinguishing a combination class A and B fire, yielded a large quantity of particulates causing a high degree of obscuration and were, therefore, considered unsuitable for this application. A mixture of Halon 2402, ADP and Cab-O-Sil was prepared and found to be an excellent suppressing agent against the combination class A and B fire. This agent may be suitable for this application after certain toxicological questions are resolved.

Thorne, P. F. (Fire Research Station, Boreham Wood, England) "The Vibrations to Which Dry Powder Extinguishers May be Subjected During Storage," *Fire*, February, 1971

Section: E
Subject: Powder extinguishers, storage vibration

Reviewed by G.Fristrom

A study of the level of vibrations likely to be encountered in various locations where fire extinguishers are stored was made. The following table summarized the results.

Levels of vibrations found in various locations

Location	Frequency (c/s)	Amplitude (cm)	Peak acceleration (gn)	Reference
Buildings				
1) Near road and rail transport	10–60	Up to 0.001	Up to 0.2	(2)
2) Near heavy machinery	8–35	Up to 0.023	Up to 1.0	(2)
Large Ships (eg, aircraft carrier)				
1) Stern	2	±0.38	~0.1	(1)
2) Waist and forecastle	50	±0.0076	0.8	(1)
	5	±0.064	~0.01	(1)
Small Water Craft				
1) Stern	5–15	±0.0305	~0.2	(1)
2) Waist and forecastle	5–15	±0.013	~0.1	(1)
	80	±0.0051	~1.5	(1)
Unspecified Road Vehicles				
1) Goods in transit	1–3		<3.0	(1)
	15–40		1.0	(1)
2) Suspension	2–4		3.0–5.0	(1)
3) Body	8–15		1.0	(1)
4) Engine	20–60			(1)
30 *cwt to* 10 *ton Lorries*				
Floor over rear axle	Continuous spectra peaking at 3 c/s, 20 c/s and 70 c/s		1.0 to 1.5 r.m.s.	(4)
Unspecified Road Vehicles				
1) Suspension	2–3		Mean value of ~0.4 Maximum value ~1.0	(5)
2) Wheel hop	10–20			(5)
3) Body	30–50			(5)

(*Continued*)

Location	Frequency (c/s)	Amplitude (cm)	Peak acceleration (gn)	Reference
Vehicle based on 6×6 *Chassis and Suspension* This forms the basis of some air-field fire crash tenders				
1) Front and sides of body	6–60		max. 1.2	(3)
	1		max. 1.4	(3)
2) Centre of floor at rear	5–8		max. 2.0	(3)
	18		max. 1.0	(3)
Rail Transport				
Goods in transit	2		±1.5	(1)
	100	±0.005	±2.0	(1)
Unspecified Aircraft				
1) Central fuselage	3–150	±0.025 to ±0.0076	up to 5	(1)
2) Near engine nacelles	10–500	±0.038 to ±0.0025	up to 20	(1)
3) Tailplane and extremities	3–150	±0.076 to ±0.0076	up to 5	(1)

Baldwin, R. and North, M. A. (Joint Fire Research Organization, Boreham Wood, England) "The Number of Sprinkler Heads Opening in Fires," *Joint Fire Research Organization Fire Research Note No. 886* (August 1971)

Section: E
Subjects: Fire statistics; Sprinklers

Authors' Summary

Statistics of the number of sprinkler heads opening in fires are used to investigate the influence of various factors on sprinkler behavior. It is shown that fewer sprinklers open in older premises, but there are insufficient data to investigate the reasons. More heads open in dry sprinkler systems, presumably because of delays in tripping the dry pipe valve, and these delays are estimated by means of a simple theoretical model of the early stages of the fire.

Nash, P., and Fittes, D. W. (Joint Fire Research Organization, Boreham Wood, England) "Extinction of Industrial Fires by Foams," *Fire Research Technical Paper No. 24, London: Her Majesty's Stationery Office: 1970*

Section: E
Subjects: Extinguishment; Foams; Industrial fires

Reviewed by R. L. Tuve

This paper of general scope gives the applications, characteristics, necessary equipment needed (and its fundamentals of design), and U.K. specification test methods, for producing and using fire-fighting foams of the following types: Chemical foam. Mechanical or air foams. Fortified mechanical foams (Fluoroprotein). All-purpose foams (Alcohol foams). "Light Water" foams. High expansion foams.

The performance of ordinary protein based foams, all-purpose alcohol type foams and "Light Water" foams when applied to the burning surface of NBP (Narrow boiling range petrol), AVTUR (Aviation kerosene, JP1), AVTAG (Wide-cut fuel, JP4), AVGAS (Aviation gasoline), AVPIN (Aviation starter fuel), and to burning surfaces of Industrial methylated spirit, methanol, isopropanol, acetone and methyl ethyl ketone are also given. Comparative standards of 90 percent fire control time, the critical and optimum rates of application, and the minimum quantities (in gallons per sq. ft.) necessary to control the test fires are used.

The uses and governing characteristics which are involved with the surface application of mechanical foams and their subsurface application (injection) in burning flammable fuel storage tanks are outlined as are the elementary requirements and uses of medium and high expansion foams (50 to 500 expansion range and 500 to 1200 expansion range respectively) for fire protection of fires within buildings of mixed Classes A and B.

The following comments are stated in this paper as general guide lines in the consideration of foams for multiple uses in fire extinguishment:

> The water retention of foam is a measure of its stability during and after extinction of fire and hence gives a guide to post-extinction protection provided by the foam.
>
> The simplest type of foam-making equipment for mechanical, all-purpose or "Light Water" foams is the hand-held air induction branch pipe producing foams in the expansion range of 4 to 10 with a critical shear stress of 100–200 dynes per sq. cm. "Forcing type" aspirating foam makers operate at higher water pressures. Other foam makers producing foam under pressure utilize separate pumps for air and foaming solution or vane-type, positive displacement rotating pumps.
>
> High expansion foams are produced in much larger self-aspirating portable branch pipes and in motor-driven air blower ducts where a mesh screen forms the separate bubbles. The design of the screen must be such that the air velocity through it does not exceed 1.5 meters per second.
>
> Normal air foams are suitable for application to the burning surface of gasolines, kerosines, light diesel and lubricating oils and other non-water-miscible fuels.

All-purpose (alcohol) foams must be employed for extinction of water-miscible fuels (polar solvents).

Foams must be applied at optimum rates of two to four times the "critical" rate (i.e., that rate at which its fire destruction is balanced by its input volume per unit time). Critical rates vary from about 0.02 gpm per sq. ft. to 0.05 gmp per sq. ft., dependent on the type of fuel.

Sub-surface applied (injected) foam promotes cold fuel circulation in tanks and can be equally efficient as surface applied foam. A low expansion foam must be used for this process and fuel pick-up during transit must not exceed 10% of the volume of liquid in the foam layer. Fortified foams (fluoroprotein) are more tolerant of these factors and operate more successfully.

"Light Water" foams perform more efficiently than other foams by factors of 2× to 4× (depending on the fuel used) and improve in performance with expansion. (An expansion of 20 is 2× more efficient than an expansion of 4.) They may be used on both water-miscible and immiscible fuels.

"Light Water" foams will not resist "burn-back" of extinguished fuels as well as protein type foams but will seal and close small fuel areas more readily.

Medium high expansion foams (50× to 500×) are best for extinction of flammable liquid fires, particularly for outdoor use.

High expansion foams (500× to 1200×) are suitable for fires in compartments and their "critical application rates" may be measured in terms of minimum rate of increase in depth to extinguish the fire. These foams require special methods of distribution and where high level flames are encountered in high storage compartments the critical rates will be increased by at least a factor of five.

H. Chemical Aspects of Fires

Woolley, W. D. and Wrist, F. N. (Joint Fire Research Organization, Boreham Wood, England) "Coupled Gas Chromatography—Mass Spectrometry and Its Application to the Thermal Decomposition Products of Cellulose," *Joint Fire Research Organization Fire Research Note No. 870* (April 1971)

Section: H
Subjects: Cellulose pyrolysis; Gas chromatography; mass spectrometry; Pyrolysis study

Authors' Summary

An analytical system, consisting of a coupled gas chromatograph—mass spectrometer unit linked to an on-line decomposition furnace has been constructed for studies of the thermal decomposition products of organic materials. The system has been evaluated by a quantitative study of the decomposition products of

cellulose in nitrogen and air atmospheres. Some chromatographic experiments using flame retarded cellulose (mono ammonium phosphate) are given and some general observations on the action of this flame retardant are recorded.

Lipska, A. E. and Martin, S. B. (Stanford Research Institute, Menlo Park, California) "The Effect of Flame Retardants on Thermal Degradation of α-Cellulose in Nitrogen," *Final Report, August 1970–August 1971, under Contract No. DAHC20-70-C-0219 for Office of Civil Defense* (August 1971)

Section: H
Subjects: Cellulose pyrolysis; Effect of inorganic additives

Authors' Summary

The Problem

Cellulose is a major constituent of the bulk of combustible materials available as fuel in destructive fires. For more effective prediction, control, and prevention of urban fires, it is necessary to learn more about the rate and mode of decomposition of cellulosic materials. Additionally, to develop more effective flame retardants, it is important to understand how these retardants interact with the decomposition process in cellulose to reduce its flammability. The present study seeks to develop a self-consistent model of the decomposition of cellulose and the effect of flame-retardant treatments. It reviews current theories of cellulose decomposition, including the Parker–Lipska model previously developed by one of the authors.[1] New data are presented and used to test the capability of the current theoretical models to predict the pyrolytic behavior of cellulose.

The Findings

A significant finding of this research is that the specially purified cellulose, a commercial filter paper, used in contemporary studies in other laboratories behaves in isothermal pyrolysis in a manner similar to that of acid-salt-treated alpha cellulose used in this laboratory. This finding suggests that the specially purified material, known to have been treated with strong acids in the purification process, is substantially degraded by the purification process in a manner resembling the degradation induced by the addition of acids or salts of weak bases to alpha cellulose. With this in mind, it is reasonable to attribute at least part of the differences in mechanisms of decomposition of cellulose to varying procedures used in the preparation of the material as well as to their residual mineral content. Molecular weight determinations of the acid-purified filter paper offer further evidence of the validity of this explanation.

The second highly significant finding of the current experimental work deals with the important effect of low concentrations of oxygen on the rate of decomposition of cellulose. Comparative measurements of rates of decomposition of thick and thin samples indicate no effect of sample thickness if oxygen is carefully excluded. On the other hand, surface adsorption of low concentrations of oxygen appears to increase the rate of decomposition in the initial phase of pyrolysis of the thin (0.0043-in.) samples by a factor of three, whereas no appreciable effect was noted in the case of thick (0.030-in.) samples. The results (1) suggest that the previously observed initial rapid decomposition phase is caused, at least in part, by effects of surface-absorbed oxygen and (2) indicate that there is no appreciable surface effect resulting from interaction between the particles of the fluidized bed and the surface of the cellulose, thereby proving the effectiveness of the fluidized-bed technique for isothermal-kinetic studies.

The experimental results further indicate that the overall pattern for the weight and monomer loss of neutral-salt-treated cellulose is similar to that of untreated samples, but with the rates of weight and monomer loss being, respectively, 25.8 and 25.2 times faster than the untreated samples. Observed rates of weight loss agree well with values predicted by the Parker–Lipska model. Molecular-weight measurements of the neutral-salt-treated cellulose combined with the corresponding data on monomer loss suggest that the dominant reaction that governs the decomposition is simultaneous unzipping of the majority of the molecules.

Rates of weight loss for the acidic-salt-treated samples are often orders of magnitude faster than those of untreated samples; for example, the whole degradation process is finished after 1 minute at a temperature of 276°C in cellulose containing small amounts of ammonium sulfate. In contrast to untreated cellulose, weight loss is not linear with time over most of the duration of active pyrolysis, similar to the case for acid-purified cellulose. Monomer loss is also changed, asymptotically approaching a limiting value rather than suffering depletion in value with the length of pyrolysis as with neutral and basic retardants. Molecular-weight measurements of the acid-salt-treated cellulose show a rapid decrease in the degree of polymerization at the beginning of pyrolysis, asymptotically approaching a $\langle DP \rangle$ value of 10 with subsequent heating. This suggests that acidic salts increase the rate of degradation through hydronium-ion-catalyzed hydrolysis. This hydrolytic effect seems to be the primary reason for the failure of the Parker–Lipska model to predict effectively the rates of weight loss of cellulose treated with acid retardants.

The pattern for the rates of weight and monomer loss of basic-salt-treated cellulose is similar to that of the untreated cellulose, but with rates of weight and monomer loss being 19 and 50.05 times faster, respectively, than for the untreated samples. Results of the molecular weight measurements show a rapid drop in the average degree of polymerization after the initial heating, and, just as in KBr-treated samples, a slow progressive decrease in the length of the molecules on subsequent heating.

Degradation products from acid-, neutral-, and basic-salt-treated cellulose were analyzed with the gc/ms combination instrument and with an infrared spectrometer. Results indicated that the basic salt treatments eliminate the production of levoglucosan, whereas neutral and acidic salt additions decrease the amount of levoglucosan but do not eliminate it entirely. Acidic treatment significantly increases the amount of the furanose derivative, previously identified, while decreasing the number of degradation products. The neutral retardant increases the amount of water, furfural, 5-methyl-2-furfural, 5-hydroxymethylfurfural, and the furanose derivative and either eliminates or decreases all others. The basic retardant increases the amount of water, the furanose derivative, and both unsubstituted and substituted phenols.

These treatments also affect the carbon monoxide-carbon dioxide ratio. Its value of 1.14 in basic, 0.16 in neutral, and 0.33 in untreated samples has been reported by other researchers. For a related acidic salt, the carbon monoxide-carbon dioxide ratio is 0.42.

The degradation products of pure levoglucosan are similar to those of untreated cellulose. Addition of a basic salt increases the total number of gc peaks as well as the amount of the furanose derivative. Acidic additives increase the amount of furanose derivative even more than basic ones and are most successful in decreasing the number of degradation produts.

The furanose derivative degrades primarily into oxides of carbon, water, and char. Both basic and acidic additives increase the amount of water and char, which confirms SRI's earlier data. These findings, combined with those of the effects of additives on cellulose and levoglucosan, support the contention that the observed degradation products result from decomposition of these intermediate pyrolysis products of cellulose, and that the additional char from the retardant-treated cellulose is produced by the degradation of these products of cellulose decomposition rather than of the cellulose molecule itself.

Although the Parker–Lipska model represents a significant contribution to the state of the art, it has significant shortcomings that preclude its use for the prediction of ultimate improvement in fire and ignition retardance for cellulose. The most notable failing is its inability to predict char yields from readily characterizable properties of retardant molecules. However, it does provide some general guidance toward prescribing optimal retardance treatment. Until further major advances are made in analytical models of cellulose pyrolysis, the Parker–Lipska model will serve many useful interim purposes.

Woolley, W. D. and Field, P. (Joint Fire Research Organization, Boreham Wood England) "A Preliminary Study of the Thermal Decomposition of Polyurethane Foams by Elemental Ultramicroanalysis," *Joint Fire Research Organization Fire Research Note No. 880* (July 1971)

Section: H
Subjects: Plastics; Polyurethane foam; Pyrolysis; Analysis

Authors' Summary

A study of the thermal decomposition of certain rigid and flexible polyurethane foams has been undertaken by monitoring the nitrogen content of the residues from decomposition experiments using elemental ultramicroanalysis. With the rigid foams the nitrogen content is lost in each case by a general temperature dependent fragmentation process whereas the flexible foams each show a rapid complete loss of nitrogen at low temperatures.

Packham, D. and Pompe, A. (CSIRO Division of Applied Chemistry, Melbourne Australia) "Radiation Temperatures of Forest Fires," *Australian Forest Research* 5, (3), 1–8

Section: H
Subjects: Radiation temperature; Forest fires

Authors' Summary

This paper describes an experiment conducted to measure the radiation temperatures of free burning, forest type fires. Radiation falling on a vertical receiver 25 feet from a flame front was measured and, when combined with a configuration factor obtained from a photograph, this permitted a calculation of effective radiation temperature. Effective radiation temperatures were compared with estimates obtained at the same time using a radiation pyrometer. The results suggest that effective radiation temperatures of forest fires in Australia may reach 1200°K in many cases.

Wiltshire, L. L. and Alger, R. S. (Naval Ordnance Laboratory, Silver Spring, Maryland) "Carbon Monoxide Production in Charcoal Briquette Fires," *Naval Ordnance Laboratory Report NOLTR 71-104* (July 1971)

Section: H
Subjects: Charcoal combustion; Carbon monoxide production

Authors' Abstract

Yields of carbon monoxide and carbon dioxide from burning charcoal were measured under various conditions typical of recreational fires. The experimental parameters were quantity of charcoal, air supply, arrangement of the briquettes, and the method of ignition. Carbon monoxide yields were found to depend primarily on factors that effect the reaction temperature, i.e., the availability of oxygen and fuel arrangements that generate the hottest fires. In a sealed compartment the carbon monoxide concentration reached a saturation level of about 0.5 to 0.7 percent. Prior to equilibrium the maximum yield was about 0.3 gram of CO per gram of charcoal consumed.

I. Physical Aspects of Fires

Heselden, A. J. M., Theobald, C. R. and Bedford, G. K. (Joint Fire Research Organization, Boreham Wood, England) "Thermal Measurements on Unprotected Steel Columns Exposed to Wood and Petrol Fires," *Joint Fire Research Organization Fire Research Note No. 874* (May 1971)

Section: I
Subjects: Heat transfer, steel columns; Fire temperature of steel columns

Authors' Summary

This note describes measurements of temperature attained by an unprotected steel column heated by wood and petrol fires. From the rate of temperature rise of the column and its dimensions and thermal capacity, rates of heat transfer from the flame to the column were obtained. The petrol fires gave higher column temperature and higher rates of heat transfer.

Silcock, A. and Hinkley, P. L. (Joint Fire Research Organization, Boreham Wood, England) "Fire at Wulfrun Shopping Centre, Wolverhampton, December 24, 1970," *Joint Fire Research Organization Fire Research Note No. 878* (July 1971)

Section: I
Subjects: Fire account; Fire spread; Smoke

Authors' Summary

This note gives details of a fire which occurred in a shop facing on to a covered shopping arcade in a modern shopping centre. A number of features are of interest.

Calculations show that a layer of gases at a high temperature extended beneath the ceiling of the covered arcade for its entire length and that this condition and smoke logging of the arcade must have become established in about a minute from the time when the fire in the shops flashed over. It appears that the fire brigade were called just in time to prevent extensive fire spread.

Wiersma, S. J. and Martin, S. B. (Stanford Research Institute, Menlo Park, California) "Measurements of the Dynamics of Structural Fires," *Annual Report, August 1970–August 1971, under Contract No. CAHC20-70-C-0219 for Office of Civil Defense* (August 1971)

Section: I
Subjects: Structural fires, dynamic behavior; Measurements in structural fires

Authors' Abstract

The dynamic behavior of structural fires in the context of civil defense implications following nuclear attack is experimentally evaluated. The second year's effort has studied the interactive effects of pairs of structures that were burned simultaneously and the effects of wind on individual burning structures. The buildings burned were similar to the one story wooden buildings used in the first year's program, so comparisons could be made. Also during the year, an opportunity to measure radiant fluxes from burning buildings of masonry exterior was afforded by an urban renewal project.

In comparison to the single burns of the previous year, the pair burns exhibit measurable interactive effects; however, these effects are modest. Burning rates are slightly enhanced by the interaction of simultaneous fires in nearby structures; however, no measurable increase in induced inflow velocities is found. A high wind substantially increases the burning rate of an individual structure, and also the area in which fires can be ignited by radiation and firebrands. Radiant-flux levels are well correlated with flame areas. A simple empirical equation fits reasonably well to the pulse of radiant energy from a burning building. The results of this year's work offer further evidence of the possibility of generalizing at least some of the dynamic characteristics of structural fires.

Simard, A. J. (Forest Fire Research Institute, Ottawa, Canada) "Calibration of Surface Wind Speed Observations in Canada," *Information Report FF-X-30, Forest Fire Research Institute, Department of Fisheries and Forestry* (April 1971)

Section: J
Subject: Wind speed

Author's Abstract

Implementation of Forest Fire Weather Forecasting requires the development of a procedure for obtaining representative wind speed observations for large areas. In this paper, a procedure is outlined whereby surface observations can be used to obtain area averages. The procedure involves the calibration of each station with respect to a standard value, and then relating the calibrated value to a wind speed distribution which is applicable to the Forest Fire Weather Index. A map showing wind speeds across Canada which can be used to calibrate any station is also presented.

Kishitani, Koichi (University of Tokyo, Tokyo, Japan) "Study on Injurious Properties of Combustion Products of Building Materials at Initial Stage of Fire," *Journal of the Faculty of Engineering, University of Tokyo,* Vol XXXI, No. 1 (1971)

Section: K
Subjects: Lethal combustion products; Carbon monoxide; Lethal products of building materials

Abstracted by B. M. Halpin

Many fatalities that result from exposure to a fire environment are not understood. The victims are not able to escape even though they do not have any visible physical handicaps, and in many instances the victims have not been touched by the fire. The primary theory is that carbon monoxide gas is the basic cause of the problem. However, there is very little known about the interactions of the carbon monoxide, other gases, smoke and heat which are prevalent during a fire. The study discussed in the report provides what could be some important findings about fire fatalities and when the gases begin to cause problems. The experiments seem to be well designed, and the report provides good documentation of the results.

The purpose of Dr. Kishitani's study was to attempt to gain an understanding of the cause of death in fires where gases are involved. In particular, he hoped to determine if the cause of death in this type of case was due to carbon monoxide and other gases paralyzing the muscles of the human body such that escape was made impossible. Experiments were conducted in an attempt to determine "the harmful nature of a building material at the time of its combustion." They were biological experiments involving male mice of the strain dd. The behavior of the mice up to the time of death were observed and recorded, and the cause of death was determined.

The study had two distinct phases. The toxicity of carbon monoxide was examined in the one phase. The other phase introduced building materials under combustion. In both phases electrocardiograms were obtained for each subject.

In the initial phase of the study the lethal quantities of carbon monoxide and the behaviour of the mice resulting from carbon monoxide poisoning were obtained. These data were obtained for constant concentrations and rising concentrations of "pure" carbon monoxide. Sixteen levels of CO were used varying from 0.1% to 1.8% in steps of 0.1% during the experiments with constant concentrations. In the rising concentration experiments a mixed gas of CO–air was introduced at a given rate. The relationship between the time elapsed and the concentration is given by

$$C = a[1 - \exp(-vt/V)]$$

where

C = concentration of CO at time t
v = rate of introduction of mixed gas = 2 l/min
V = volumes of the test chamber = 56 l
a = concentration of the mixed gas = 0.1 to 2.2% in steps of 0.1%.

The results of this phase are presented in five tables in the report.

Conclusions from this phase of the study in which only CO and air are used were:

1. The toxicity of CO is due to the hindrance of the oxygen carrying capacity of the blood causing internal suffocation.
2. The degree of CO poisoning is given by the quantitative measurement of the carboxyhemoglobin in the blood.
3. No abnormalities were found in the tissue specimens on autopsy.
4. The lethal amount of carboxyhemoglobin for the mice was at about the 40% level.

The second phase of the study involved burning building materials and exposing the mice to the gases. The test materials included cedar, woodwool– cement board, fire retardant plywood, melamine finishing board, PVC, polyurethane, polystyrene, phenol resin and acrylic resin. These were chosen since they are used as interior finishing materials, and they are considered to produce large quantities of smoke and noxious gases when burned. A good summary of the test results is provided in tabular form. A record of the cardiogram traces, pictures of the smoke condition at specific times and the CO concentration as a function of time are also presented. An autopsy soot was found in the trachea of the mice after the cedar and PVC were burned. Damage to the eyes was noted with PVC and polystyrene.

The following conclusions were presented for the phase using building materials:

1. Carbon monoxide poisoning was the cause of death for the wood, woodwool-cement board, plywood, melamine finishing board and acrylic resin. The average values of the COHb in the mice ranged from 39% to 49%.
2. With PVC and polyurethane the cause of death is thought to be the combined effects of CO and some other noxious gases. The average COHb level for the PVC cases was 21% and for the polyurethane it was 24% which are significantly lower than those levels mentioned above.
3. The gas generated prior to any noticeable smoke caused irregularities in the cardiograms for all materials. A "considerable amount of effect" is prevalent before the concentration of smoke becomes thick. In other words, "harmful gases produced at the time of combustion caused fairly great damage to human bodies at the early stages of fire."

The report includes some incidental information such as the breakdown of fire fatalities in Japan during 1967–1968. There were 2266 fire fatalities for the two years of which 55 to 60% were considered to be caused by CO poisoning and suffocation. There are references cited to other Japanese work in the toxicity field which are published in the Japanese literature.

L. Operations Research, Mathematical Methods, and Statistics

North, M. A. and Baldwin, R. (Joint Fire Research Organization, Boreham Wood, England) "An Association Between Fire Spread and Casualties in Fire," *Joint Fire Research Organization Fire Research Note No. 893* (October 1971)

Section: L
Subjects: Fire statistics; Fire spread

Authors' Summary

Fire statistics for multi-storey houses indicate a possible association between the incidence of fires causing casualties and fire spread, even allowing for the presumed state of awareness of the victims at the time of the fire. This association is quite strong for fires involving fatalities and seems to indicate a strong correlation between fatalities and spread, but the association is relatively weak for fires involving non-fatal casualties whose frequency appears to be correlated more with the frequency of outbreaks of fire.

It is pointed out that no causal relationship has been established and that there is more than one explanation for this association.

Chandler, S. E. (Joint Fire Research Organization, Boreham Wood, England) "Fire Deaths in the First Quarter of 1971," *Joint Fire Research Organization Fire Research Note No. 873* (May 1971)

Section: L
Subjects: Fatalities; Fire statistics

Author's Summary

A preliminary survey shows that there were 147 fatal casualties in fires attended by fire brigades in England and Wales during the first quarter of 1971. The corresponding figures for Scotland and Northern Ireland were 31 and 2 respectively. It is likely that because of an industrial dispute involving the fire services these figures are underestimates of the true figures.

Chandler, S. E. (Joint Fire Research Organization, Boreham Wood, England) "Fire Deaths in the Second Quarter of 1971," *Joint Fire Research Organization Fire Research Note No. 885* (August 1971)

Section: L
Subjects: Fatalities; Fire statistics

Author's Summary

A preliminary analysis shows that 133 persons died in fires in the period April–June 1971. Of these 118 were in England and Wales and 15 in Scotland. The most serious incident was at a London hotel when nine people died in a fire attributed to arson.

Gaudette, J. J., Jr. and Harrington, J. J. (Harvard University, Cambridge, Massachusetts) "Information Systems for Urban Fire Protection Planning: A Case Study," *Environmental Systems Program, Harvard University, Discussion Paper No. 71–3* (August 1971)

Section: L
Subject: Fire protection information

Authors' Abstract

The technical and economic feasibility of an information system for fire protection planning is demonstrated by developing such a system for Cambridge, Massachusetts. Municipal, federal and private data are merged, permitting analysis of factors influencing alarm rates such as time, construction class, occupancy, and socio-economic and demographic forces. Some 29,000 alarm records for five years and 13,000 individual structural data from the primary data base. Data collection strategies, processing approaches and verification procedures are discussed.

Results from preliminary analyses suggest the power of the information system. Statistical analyses are possible on both an individual structure or areal bases. Computer mapping display programs detect patterns in contiguous areas. The direction of future work is discussed.

Lee, B. T. (Stanford Research Institute, Menlo Park, California) "Modeling the Dynamic Behavior of Building Fires," *Final Report, August 1970–August 1971, under Contract No. DAHC20-70-C-0219 for Office of Civil Defense* (August 1971)

Section: L
Subjects: Modeling fire behavior; Scaling methods

Author's Abstract

The practical modeling of fire behavior in a burning building requires separate techniques for simulation of the convective and radiative fields about the fire. Previously derived scaling methods for modeling the fluid flow environment in mass fires appear applicable to 1/16 scale structural fires. The time duration of a fire can be scaled as the square root of a characteristic dimension of the burning structure upon satisfaction of geometric similarity with the model to which it is being compared. The perturbation of the flow, e.g., the smoke column, by the ambient wind is shown to depend on wind velocity, burning rate, and fire size.

If the material thickness in a model is increased to about the thickness of combustible sheathing in full size buildings, the resulting model will exhibit the radiative characteristics of large fires at the low viewing angles pertinent to evaluation of building to building fire spread. Although study of ambient wind enhancement of fuel consumption rate and room to room fire spread appear to require altogether different modeling techniques, the above model for radiative simulation has potential in these two areas as well.

Chandler, S. E. (Joint Fire Research Organization, Boreham Wood, England) "Fires in Hospitals," *Department of the Environment and Fire Offices' Committee Joint Fire Research Organization Fire Research Technical Paper No. 27* (March 1971)

Section: L
Subject: Fire in hospitals

Author's Discussion

Fires in hospitals have been increasing at about the same rate as all fires in buildings, rising from 590 in 1963 to 684 in 1968 (estimated from a one-in-four sample of reports).

Mental hospitals do not appear to be more fire-prone than other hospitals, although the types of fire which occur in them are different in some respects. There are more fires in wards and less in kitchens, and fires are more often thought to be due to smoking materials and malicious ignition in mental than in other hospitals. At present there is no statistical evidence that the fire risk to patients in hospital differs appreciably from that to people in their own homes.

Sixty-eight per cent of the fires in hospitals occur between 0900 and 2100 and 20 per cent between 2100 and 0300. The places where fires occur most frequently are wards (144), stores (80) and kitchens (76). Malicious ignition and smoking materials are the two most prominent causes of fires in wards and stores. Rules on smoking vary from hospital to hospital and it is possible that some of the fires in wards could be attributed to hospital visitors. There are few fires in operating theatres (the estimated frequency in 1968 was only 8).

Only 6½ per cent of fires in hospitals spread beyond the room of origin, compared with 28 per cent in all buildings. This can be attributed to prompt detection and fire-fighting activity before the arrival of the fire brigade. About 80 per cent of hospital fires are tackled before the arrival of the brigade and about 60 per cent of the fires reported are extinguished before it arrives. It appears that water is more often used successfully than extinguishers. Internal hose reels are used on 15 per cent of fires, and on half of these occasions they are successful.

During the period 1963–1968, 38 fires gave rise to 62 fatal casualties, 24 of these were in the Shelton Mental Hospital fire in which there was a delay in calling the fire brigade. During 1969, the problems of mental hospitals were again highlighted by the Carlton Hayes Hospital fire in which there were four deaths. Here, however, prompt evacuation saved many lives.

Ramachandran, G., Kirsop, P. and Eveleigh, C. (Joint Fire Research Organization, Boreham Wood, England) "Large Fires During 1970," *Joint Fire Research Organization Fire Research Note No. 891* (September 1971)

Section: L
Subjects: Fire, loss; Fire statistics

Authors' Summary

This note contains an analysis of large fires during 1970. These were fires which were estimated to have cost £10,000 or more in direct damage. There were 1115 such fires during 1970 resulting in a total loss of £69.9 million. Of these, 75 started in outdoor hazards, 56 per cent of which spread to buildings. The average loss in these "outdoor" fires was twice the average in the 1041 fires that started in buildings.

Butcher, E. G. (Joint Fire Research Organization, Boreham Wood, England) and **Hall, M.** (Directorate of Building Development, Department of the Environment, England) "Smoke Tests in New Law Courts Building," *Joint Fire Research Organization Fire Research Note No. 889* (September 1971)

Section: L
Subjects: Building, pressurization; Smoke, test

Authors' Summary

The system of pressurization which forms part of the smoke control arrangements in the New Law Courts Building is described. The results of smoke tests carried out in the building show that the pressurization not only prevents smoke penetrating to the two staircases but also acts to clear smoke which has been allowed to penetrate into the lobbies.

Jessop, C. M. and Chambers, E. D. (Joint Fire Research Organization, Boreham Wood, England) "Auto Diallers in the United Kingdom," *Joint Fire Research Organization Fire Research Note No. 888* (September 1971)

Section: L
Subjects: Alarm, automatic; Statistics

Reviewed by G. Fristrom

A survey was made of the number of operable auto diallers in the United Kingdom. Auto diallers normally pass a recorded message via a manned telephone exchange to a fire brigade control room. From a random sampling, the total number of such systems in the United Kingdom was calculated.

O. Miscellaneous

Hinkley, P. L. (Joint Fire Research Organization, Boreham Wood, England) "Some Notes on the Control of Smoke in Enclosed Shopping Centres," *Joint Fire Research Organization Fire Research Note No. 875* (May 1971)

Section: O
Subjects: Smoke; Ventilation

Author's Summary

This note considers ways in which the spread of hot gases and smoke from a fire in an enclosed shopping centre may be limited. If the shop fronts are fire resisting the hot smoky gases may be confined to the shops of origin. Otherwise the size of the fire and hence the rate of 'production' of hot smoky gases must be limited (preferably by sprinklers) and it is then possible to confine the hot smoky gases to a stratified layer beneath the ceiling while the air beneath them is relatively cool and clear. The extent of the layer should be limited by dividing the space beneath the ceiling into smoke reservoirs by screens extending part of the way towards the floor. Screens by themselves are ineffective; hot gases must be extracted from a smoke reservoir at at least the same rate as they flow into it while fresh air must be introduced or allowed to flow into the building to replace the extracted hot gases. Theoretically the principle can be used to confine hot smoky gases to the space beneath the ceiling of the shop of origin but the rates of extract required can seldom be achieved on practice in the confines of a small shop and it is generally necessary to allow the smoky gases to flow into smoke reservoirs beneath the ceiling of the mall. The requirements of both natural and powered systems for extracting smoke from the smoke reservoirs are considered.

It is essential that smoke control measures should be considered at any early stage in the design of the building as they may be difficult to incorporate as a later modification.

Miller, C. F. (URS Research Company, San Mateo, California) "Fire Fighting Operations in Hamburg, Germany During World War II," *Report under Contract No. DAHC20-70-C-0307 for Office of Civil Defense* (June 1971)

Section: O
Subject: Fire Fighting, Hamburg

Author's Abstract

Information recorded by the Hamburg Fire Department during World War II has been summarized and analyzed to evaluate several operational parameters relating to the performance of the various fire fighting organizations under conditions of stress from air attacks on the city. Prior to the large scale attacks, the professional fire fighting units fought at about 38 percent of the fire sites while the Self-Protection Service squads fought at about 59 percent of the fire sites.

Finally, in the major air attacks during the period 7/25/43 to 8/4/43, when the capabilities of both the professional and Self-Protection Units were exceeded, a maximum performance or effort level was reached for the Self-Protection Services at about 2 fire sites per squad per attack and, for the Fire Department Units at 6 fire sites per squad per attack. Because of the failure of the municipal water system and the evacuation (forced and voluntary) of large numbers of people, the Self-Protection Service did not function to any great extent after the first of these large scale attacks on 7/25/43. However, at the above indicated rate, the Self-Protection Service was credited with extinguishing fires in about 20,000 residential buildings over the 11 day period. The Hamburg Fire Department units, on the other hand, performed more or less continuously over the 11 day period with a continuously decreasing efficiency; its units either extinguished fires or prevented the spread of fires at about 4,300 fire sites. Water volume use rates by the Fire Department units was found to increase with fire fighting effort (i.e., in man hours) to the 3/2 power.

The major constraint in deploying the fire fighting units to fire sites, according to the reports, was debris in the streets. Once at a fire site, the most often mentioned difficulties were those of supplying water, the heat and spark showers and smoke, and of maintaining the hose lines. The main difficulties faced by the district headquarters were in locating the major fire areas as rapidly as possible and in finding out the whereabouts of the fire fighting squads who, without communications assigned themselves to fire sites (as per directive).

The reports indicate that no person in the bunkers died from fire effects, as had been reported previously. No specific survival rate data for either shelter or fire conditions are given in the Hamburg Fire Department documents. Outside survival within the fire areas appeared to be possible for an extended period only when the radius of the open area was 75 meters or more. In the extreme case, escape from the fire storm area by crawling on the street near the curb appeared to be feasible where the streets were at least 8 meters wide (curb to curb) and when safety could be reached in about 15 minutes.

Clark, C. C. (Worcester Polytechnic Institute, Worcester, Massachusetts), **Musson, M. E.** and **Horlick, J.** (National Bureau of Standards, Washington, D.C.), editors, "Flammable Fabrics Data Sources, An Information System Printout," *Product Evaluation Technology Division, National Bureau of Standards, Document 411.00 CM070*

Section: O
Subjects: Flammable fabrics, data sources

Authors' Abstract

To aid in the retrieval of the diverse sources of public information on flammable fabrics, and the important work of the Information Council on Fabric Flammability, a computer information system on Flammable Fabrics Data Sources has been developed at the National Bureau of Standards.

The Flammable Fabrics Data Sources November 1971 printout utilizes many of the information categories and techniques developed for the Consumer Product Safety Index of the National Commission on Product Safety, which is available from the National Technical Information Service, Springfield, Virginia 22151, 703-321-8543. The Flammable Fabrics Data Sources printout provides extensive cross-referencing, and in some cases excerpts of material presented, so that it is a beginning encyclopedia rather than just a bibliography or index. The document contains lists of definitions, economic data, events, some 600 groups and addresses, hearings with some excerpts, injury data, journal sources, laws and legislation, some 370 manufacturers and addresses, some 1,000 names of people professionally involved with their addresses, research programs, standards and test methods, some 260 technical references with some excerpts, and applicable university programs.

To obtain a copy of this unpublished work, write to the

Product Evaluation Technology Division
National Bureau of Standards
Washington, D.C. 20234

Department of the Environment and Fire Research Offices' Committee Joint Fire Research Organization List of Reports Published 1958 to March 1971, Her Majesty's Stationery Office, London, England (March 1971) 20 pp.

Contents

I. Stationery Office Publications
  - Fire Research Annual Reports
  - Fire Research Technical Papers
  - Fire Notes
  - Special Reports
  - United Kingdom Fire Statistics
  - Proceedings of Symposia
  - Miscellaneous

II. Other Publications
  - Occurrence of Fire
  - Fire Hazards
  - Initiation and Development of Combustion
  - Fire Resistance
  - Fire Fighting: Detection
  - General; works of reference, etc.
  - Instruments

National Data Needs: Fire Service Statistics, U.S. Department of Commerce, Bureau of the Census (1971) 42 pp.

This report on the informational needs of the fire service was prepared by the staff of the Government Division, Bureau of the Census. It is intended to serve as a comprehensive statement of data considered necessary for the development of a national fire service data reporting system. The report is available from the U.S. Department of Commerce, Bureau of the Census, Washington, D.C. 20233.

BOOKS

IFSTA Catalog of Publications and Training Aids, International Fire Service Training Association, Fire Protection Publications, Oklahoma State University, Stillwater, Oklahoma

Titles of Manuals Published

Forcible Entry, Rope and Portable Extinguisher Practices
Fire Service Ladder Practices
Fire Hose Practices
Salvage and Overhaul Practices
Fire Stream Practices
Fire Apparatus Practices
Fire Ventilation Practices
Fire Service Rescue and Protective Breathing Practices
Fire Service First Aid Practices
Fire Inspection Practices
Fire Service Practices for Volunteer Fire Departments
An Introduction to the Fire Service
Fire Service Training Programs
Fire Department Support of Automatic Sprinkler Systems
Water Supplies for Fire Protection
Aircraft Fire Protection and Rescue Procedures
The Fire Department Officer
Fire Department Facilities, Planning and Procedures
Fire Service Instructor Training
Fundamental Principles of Mathematics
Fundamental Principles of Science
Leadership in the Fire Service

References to Scientific Literature on Fire, Part XX 1969 by J. Crees, Published by Department of the Environment and Fire Offices' Committee Joint Fire Research Organization, Boreham Wood, England

Contents

Occurrence of Fire: Incidents; casualties; material loss; statistics
Fire Hazards and Fire Precautions: Industries and materials
Initiation and Development of Combustion: Experimental studies
Fire Resistance: Structures; building materials; fire retardant treatments
Fire Detection and Fire Fighting: Appliances; equipment, including technique; extinguishing media; personnel protection
Nuclear Energy: Hazards and precautions
General: Works of Reference, etc.
The 411 page compilation contains 3450 references chiefly to information published during the year 1969. Information on availability; contact J. Crees, Fire Research Station, Boreham Wood, Herts., England

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United Kingdom Fire and Loss Statistics 1969, Department of the Environment and Fire Offices' Committee Joint Fire Research Organization, Published by Her Majesty's Stationery Office, London, England 1971, 150 pp. Price £1.30

PERIODICALS

Factory Mutual Record: Property Conservation Engineering and Management. Published bimonthly by Factory Mutual Engineering Corporation, Norwood, Massachusetts

Contents

Volume 48, No. 5 (1971)
    The Role of Basic Research in Fire Protection
    Now, Protection Standards for Rack Storage up to Twenty-five Feet
    Tornadoes! Hurricanes—Ready Your Plant Emergency Organization for Action
  Boiler and Machinery
  Factory Mutual Services
  What Has Happened Can Happen
  Conservation Sampler

Copies of Record may be obtained from Factory Mutual Engineering Corporation, Factory Mutual Systems, 1151 Boston-Providence Turnpike, Norwood, Massachusetts, 02062.

Fire Control Notes. Published quarterly by the U.S. Department of Agriculture, Forest Service

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Volume 32, No. 3 (Summer 1971)
    Prevention—E. F. McNamara
    Pieces of Paper Protect You. Specifications—B. J. Graves
    New Compact Simulator Provides New Versatility—H. E. Ball
    Fires Burn Trees . . . and Other Things
    Smoke Dispersal Determines When to Burn
    Films to Fight Fires By
    Symbols for Prevention Signs—F. O. Carroll
    Exhaust Particles. How Many Fires Do They Start?—J. L. Hickman
    Simulator Training is Refined in Florida
    You Can Measure Salt Content of Retardants
    Field First Aid Station—R. L. Marsalis and R. G. Beasley
    Progress Sparks Remote Sensing Seminars

Fire Research 1970. Published annually by the Department of the Environment and Fire Offices' Committee Joint Fire Research Organization, Her Majesty's Stationery Office, London, England 1971, 120 pp.

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Report of the Director of Fire Research for 1970

Statistics and Economics
Building Development and Regulations
Structural and Material Fire Tests
Extinguishing Materials and Equipment
Detection and Electrotechnics
Industrial and Toxic Hazards
Technical Inquiries
Overseas Activities
Library and Publications
Lectures and Exhibitions
Symposium
General Committees
Available from Her Majesty's Stationery Office, 49 High Holborn, London, England, Price 95 p

TRANSLATION

Trabaud, Louis (Phyto-écologiste, docteur en Écologie, C.E.P.E., Montpellier, France) "Some Measurements and Observation on the Phytodynamics of Burnt Areas in Bas-Languedoc (Southern France)," *Naturalia monspeliensia, sér. Bot.*, 21 231 (1970)* In French.

Subject: Burnt area phytodynamics

Translated by G. L. Ordway

Summary

In the Mediterranean region fire can be considered as an important factor of the dynamics of vegetation. With this in mind we have made some observation on the regeneration of burnt areas in the Bas-Languedoc (Southern France). Observations were carried out *in situ* on a burnt-out zone comprising side by side a thicket of kermès oak (*Quercus coccifera*) and a stand of Aleppo pine (*Pinus halepensis*). In this zone, soil samples were taken in order to study the contents of seeds that were able to germinate.

Under natural conditions the area is immediately occupied by preexisting species endowed with an important capacity of resprouting from the stump. In the samples numerous species, mainly annuals, appear that were not inventoried *in situ*.

* The results presented in this paper were obtained as part of a study of the action of fires on vegetation in Bas-Languedoc. This program is a part of the research of the dynamics of a thicket of *Quercus coccifera* planted by the Division of Phytoecology of the Centre d'Etudes phytosociologiques et écologiques of Montpellier.

INTRODUCTION

Fire is a definitive factor in the dynamics of plant life in the woods of the Mediterranean region.

In France numerous authors have studied the fire factor and its devastating effects; notably, for the Midi, Ribbe (1866, 1869), Jacquemet (1907), Ducamp (1932), Laurent (1937). Nevertheless, none of these made precise observations on the development of vegetation after a fire. And unfortunately there are few ecological data available on the causes and effects of fires. Only a few authors, such as Kühnholtz-Lordat (1938, 1952, 1958), Braun-Blanquet (1935, 1936), Kornas (1958), have approached the problem with somewhat more rigor.

Braun-Blanquet described several stages of vegetative degradation, but he did not analyze what determines the regressive sequence. According to him, a number of phenomena, which are generally associated with each other (cutting, fire, and pasturage) have brought vegetation to an advanced state of degradation such as can currently be seen in certain areas.

Kornas indicates the causes of the retrogressive sequence. Comparing parcels subjected to fires, he tries to describe the series of successive stages, but he does not analyze the actual process of plant dynamics after the fire. He indicates that with the dominance of *Quercus ilex* in the forest (which would be according to him the climax) the cycle of progressive evolution would be closed.

Kühnholtz-Lordat, who is one of our best specialists on the subject, describes the various stages of progressive or retrogressive sequences. He estimates the approximate time required to reconstitute a stand of *Q. ilex*. He names the species (*Q. coccifera, Arbutus unedo, Cistus* sp., *Pinus* sp.) currently best recognized as pyrophytes, and indicates the plant characteristics that permit them to survive and to spread over burnt areas.

Before proceeding, we should like to make a brief parenthetical remark on the meaning of the term "pyrophyte," which is actually ambiguous and covers several meanings. Herewith is a critical review:

Grand Larousse encyclopédique (1963): "said of a plant that easily repairs injuries brought about by fire thanks to its mode of reproduction by rhizome."
Grand Littré (1962): does not include the term.
Carpenter (*An Ecological Glossary 1956, New York, Hafner,* 306 pp.): "a tree having a thick fire-resistant bark, which thus escapes damage caused by forest fires."
P. Gray (*Dictionary of Biological Sciences, 1967, Reinhold*): "a plant having a bark resistant to forest fires."
Kühnholtz-Lordat (*L'ecran vert, Mem. Mus. Nat. Hist. Nat., IX, 1958*): This in our opinion is an excellent definition of pyrophytes—"There are plants that are more or less resistant to flame; there are even those whose propagation or reproduction appears to be stimulated by fire; these are pyrophytes." He refers to numerous examples of pyrophytes having different kinds of resistance.

One could thus have two large types of pyrophytes: pyrophytes resisting fire, and others that are not fire-resistant but whose regeneration would be promoted by fire (e.g., the rockroses). The resistant pyrophytes could also either be favored, thanks to their underground organs of survival (kermès oak), or else not favored, but having two different survival systems: resistant underground (live oak) or resistant aboveground (cork oak).

We shall use the definition of "pyrophyte" proposed by Kühnholtz-Lordat. However, we shall add that a *true pyrophyte* should be one that at the same time is resistant to fire and whose regeneration is promoted by fire.

In the works cited the authors describe the effects of fires recurring at more or less regular intervals, but they do not follow the development. The descriptions are made starting with stages that are supposed *a priori* to belong to the pyrophyte sequence. It would appear from our observations and will be seen later on that burnt vegetation, at least in certain natural situations, rather rapidly regains its structure and composition almost as they were initially. Furthermore, these authors provide no information on the variation of intensity of the fire, physical mechanisms, degradation due to heat, or the biological condition of the plants.

Abroad, however, studies of this type are rather numerous. Among others, Ahlgren (1960) describes the effects of fire on the reproduction and growth of plants in forests of *Pinus banksiana* in Minnesota. He cites species that arise and their development after the fire, indicating the ecological characteristics and the means of reproduction for each of them. Floyd (1966) in Australia describes the effect of fire on the seeds of pioneer species, particularly woody plants, that germinate en masse after a fire. Each species behaves differently with respect to the mechanism of the fire and the temperatures reached. Oppenheimer (1961) referring to the studies of Went in the United States, and Specht in Australia, states that raised temperatures stimulate the germination potential of many seeds, which in fact are already very resistant to heat.

In France the absence of exact data on plant regeneration immediately after the passage of a fire has encouraged us to undertake some preliminary observations on a recently burned area.

Description of the Burnt Area

On June 16, 1967, a fierce fire burned 15 hectares of oak thicket and of pine stands in the commune of Buzignargues (Hérault) at a place called Pic du Prieur. The fire starting from the edge of a vineyard, grew rapidly worse and climbed to the top of the hill. The grades, variable but fairly regular, are of the order of 7 to 15 percent. The exposure is S and SW. The substrate is marl and limestone. The soil is sparse of a brown limestone type.

We did not make a survey of the vegetation before the fire. Two types of plant formation cover the hill—at the foot on the marl a stand of pine of *Pinus halepensis*,* which ringed the hill, and on the limestone at the top a thicket of *Quercus coccifera*. The principal species in the pine stand that were recognizable after the fire were *Pinus halepensis*, *Rosmarinus officinalis*, *Lavandula latifolia*, *Juniperus oxycedrus;* those at the top were *Quercus coccifera*, *Quercus ilex*, *Juniperus oxycedrus*, *Pinus halepensis*. The most frequently found grass in the two groups was *Brachypodium ramosum*. In the pines the top stratum was formed of Aleppo pines alone. These were about 8 m high and had a coverage of 60% (crowns). Thin undergrowth occupied about 40% of the surface. The thicket of kermès oak was dotted here and

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* The specific names are those given in *Les Quatre Flores de France* by P. Fournier (Lechevallier, 1961, 405 pp.).

there with Aleppo pines about 4 m tall but of low coverage since the kermès oak occupied 95% of the surface.

Methods of Observing the Regeneration of Vegetation

We used two methods to follow the process and regeneration:

(1) the first consisted of periodic observations made directly on the burnt areas,
(2) the second consisted of laboratory observations of the germination of seeds contained in samples from layers of surface soil taken from the burnt plots and put under glass.

In order to follow the conditions of regeneration on the ground, plant censuses were made on three successive dates: June 30, 1967 (14 days after the fire), September 18, 1867 (three months after the fire), and April 23, 1968 (ten months after the fire). The surveys were made at sites immediately adjacent to those from which the samples had been removed.

On June 20, 1967 (four days after the fire) we gathered in each initial population two soil samples of a quarter of a square meter (50 cm×50 cm) and 5 cm thick; these samples were immediately put in a greenhouse in large plastic trays on a bed of fine sterile sand. The trays were misted regularly with ordinary water.

The first germinations took place June 26. Few in number at first, they became very numerous in the course of the first year and then decreased. Towards the end of the period of observation the soil was turned to let the last seeds germinate. The last germination took place August 6, 1968 (i.e., 14 months after the sampling). The experiment was ended the end of October 1968. The count of the germinated seeds was made in total for the two samples from each location.

It is important to emphasize that only plants coming from seeds could develop in the trays, because we took the precaution of not transplanting roots or rhizomes; this would have allowed certain perennials to develop by vegetative reproduction.

TABLE 1
Survey of species of the pinewood and oak thicket

	Pinewood		Oak thicket			Type regeneration after fire	
	9/18/67	4/23/68	9/18/67	4/23/68	Type		
Phillyrea angustifolia	X	X	X	X	V	R	
Dorycnium suffruticosum	X	X	X	X	V	R	S
Brachypodium ramosum		X	X	X	V	R	S
Rubia peregrina	X	X		X	V	R	S
Asparagus acutifolius	X	X	X	X	V	R	
Pistacia lentiscus	X	X	X	X	V	R	
Quercus coccifera	X	X	X	X	V	R	
Fumana coridifolia		X		X	V	R	S
Leuzea conifera	X	X		X	V	R	S
Bupleurum rigidum	X	X	X	X	V	R	S
Smilax aspera	X	X	X	X	V	R	
Genista scorpius	X	X		X	V	R	
Rhamnus alaternus	X	X		X	V	R	

TABLE 1 (*Continued*)

	Pinewood		Oak thicket			Type regeneration after fire	
	9/18/67	4/23/68	9/18/67	4/23/68	Type		
Carex halleriana	X	X	X	X	V	R	S
Aphyllanthes monspeliensis	X	X	X	X	V	R	
Quercus ilex	X	X		X	V	R	
Lonicera implexa		X		X	V	R	
Aristolochia pistolochia	X	X		X	V	R	S
Sonchus oleraceus		X		X	A		S
Scorpiurus subvillosus		X		X	A		S
Argyrolobium linnaeanum		X		X	V		S
Thymus vulgaris		X		X	V	R	S
Cistus monspeliensis		X		X	V		S
Psoralea bituminosa	X	X			V	R	
Brachypodium phoenicoides	X	X			V	R	
Euphorbia serrata		X			V		S
Rubus ulmifolius	X	X			V	R	
Torilis arvensis		X			A		S
Ononis minutissima		X			V	R	S
Rosmarinus officinalis		X			V		S
Pinus halepensis		X			V		S
Anagallis arvensis		X			A		S
Lagoseris sancta		X			A		S
Eryngium campestre		X			V		S
Shoenus nigricans	X	X			V	R	
Sanguisorba minor		X			V		S
Crepis taraxacifolia		X			V		S
Galium sp.		X			A		S
Seseli elatum		X			V		S
Muscari racemosum		X			V	R	S
Bromus erectus		X			V	R	
Hieracium murorum	X	X			V	R	
Coris monspeliensis		X			V	R	
Andropogon ischaemum		X			V	R	S
Daphne gnidium	X	X			V	R	
Euphorbia exigua		X			A		S
Carex glauca		X			V	R	
Clematis flammula	X	X			V	R	
Sonchus tenerrimus		X			A		S
Hieracium pilosella		X			V	R	
Narcissus juncifolius				X	V	R	S
Seseli montanum				X	V	R	
Juniperus oxycedrus				X	V	R	
Festuca ovina				X	V	R	
Teucrium chamaedrys				X	V	R	
Staehelina dubia				X	V	R	
Allium sp.				X	V	R	S

The species are listed in order of decreasing frequency: Type V = perennial; A = annual. Type of regeneration after the fire: R = regrowth in general from the stump; S = seeds.

OBSERVATIONS MADE AT THE SAMPLING SITES—TABLE 1.

June 30, 1967 (14 days after the fire) no plants had resprouted or germinated.

September 18, 1967, only a few perennials—those among the most abundant—had resprouted. It is noteworthy that it was the perennials alone that reoccupied the free space.

On April 23, 1968, the pinewood had 50 species of perennials and the oak thicket only 30 species.

In Table 1 the symbols R and S represent the type of regeneration after the fire: R, regrowth, in general from the stalk; S, seed.

It appears of interest to compare the two regions by keeping track of the type of regeneration of the species after the passage of the fire. Three classes have been considered: (a) perennial species in the strict sense that they are able to regenerate by regrowth but also by seed; (b) perennial species that can only regenerate by seed; (c) annual species in the strict sense.

Of the 50 species in the pinewood, 33 are perennials in the strict sense (66%), 9 are seeding perennials (18%), and 8 are true annuals (16%). The perennials of either kind are thus very numerous (more than half of the species present), but the proportion of species able to regenerate by seed alone, both annuals and perennials, 34% is nonetheless higher for the pine than for the kermès oak thicket. In fact, the oak has for the 30 species present, 26 true perennials (86.6%), 2 seeding perennials (6.7%) and 2 annuals (6.7%). There are thus very few annuals and seeding perennials. This is probably due to the competition caused especially by the kermès oak itself, which has exceptional regenerative powers and which resprouts quite vigorously.

The large proportion of species resprouting should be noted: 70% of the total of the species encountered in the two regions. Nevertheless only 66% of the species in the pinewood resprouted as opposed to 86% of species regrowing from stumps in the oak thicket.

Most of the perennial, woody, and suffrutescent species can resprout. Of these only *Argyrolobium linnaeanum*, *Cistus monspeliensis*, *Pinus halepensis*, and *Rosmarinus officinalis* reproduce by seeds alone. On this account, they appear only in the spring.

In general, the perennial species that reseed produce a large number of seeds, which permits them to fill in bare spaces rapidly. This does not appear to be the case here; on the other hand in an open stand of kermès oak and rockrose on gravel and marl at Castelnau-de-Guers, we were able to count up to 4,000 seedlings of *Cistus monspeliensis* per m^2.

Perennial species have the capability of reproducing after a fire either by resprouting or by seeding. Thus some species that can regenerate immediately by resprouting rapidly colonize the area and eliminate by competition foreign volunteer species that would attempt to occupy the space. The case of the kermès oak thicket is typical: 86% of the species counted were able to regenerate immediately by resprouting; the thicket thus reconstituted itself just as it was before the fire. This is a very important observation for an exact understanding of plant dynamics.

TABLE 2

Number of seedlings by species and by type (under glass): V = perennial; A = annual; and species normally absent in the plant population at the site.

Species	Pinewood *Pinus halepensus*	Oak thicket *Quercus coccifera*	Type
Erigeron naudini+	91	146	A
Sonchus tenerrimus+	36	43	A
Erigeron canadense+	8	21	A
Cistus monspeliensis	5	27	V
Rosmarinus officinalis	6	19	V
Crepis taraxacifolia+	1	1	V
Centaurium pulchellum+	63		A
Fumana coridifolia	54		V
Chlora perfoliata	51		A
Thymus vulgaris	3		V
Sonchus oleraceus+	3		A
Andropogon ischaemum	2		V
Brachypodium ramosum		6	V
Carex halleriana		5	V
Allium sp.		4	V
Scorpiurus subvillosus		2	A
Dorycnium suffruticosum		2	V
Pinus halepensis		2	V
Argyrolobium linnaeanum		1	V
Rubia peregrina		1	V
Epilobium tetragonum+		1	V
Total	323	281	

OBSERVATIONS MADE ON THE SOIL SAMPLE PUT UNDER GLASS—TABLE 2.

Table 2 gives a list of the species enumerated and of the number of plants per species according to region. Twelve species germinated for the pinewood sample and fifteen for the oak. However, if one considers the number of seedlings, the pine had many more seeds that germinated (323) than the oak (281). Thus, though having fewer species, the pinewood had a higher number of viable seeds.

Apart from some annuals (*Erigeron naudini*, *E. canadense*, *Sonchus tenerrimus*) and biennials (*Crepis taraxacifolia*) common to the two groups, which are species not normally found at these sites, but which are found in large numbers, it is said, after fires (cf. Floyd, 1966), there are only two common perennials: *Cistus monspeliensis* and *Rosmarinus officinalis*. It would appear that *Rosmarinus officinalis* is not peculiar to one of the two groupings rather than the other; on the other hand, *Cistus monspeliensis* is more frequent in the thicket of *Quercus coccifera*.

The remaining species, which are not common to the two groups, show that we have here two different plant communities.

The coefficient of similarity of the two groups, determined by considering the species of seedlings produced, is 28.6%; it is thus fairly small. The two lists of species produced from the soil samples do not have much in common.

In order to explain the germination, two possibilities can be considered: The seeds of annuals as well as perennials could have been carried in during the four days between the date of the fire and the date of sampling, or what is more likely, these seeds could have been stored in the soil (cf. Guyot, 1968) and been unaffected by the passage of the fire.

In the wood of *Pinus halepensis*, the total number of species that germinated in the course of the experiment is twelve, of which six were annuals and six perennials, giving a ratio of $A/P=6/6=1$; the annuals represent 50% of the germinating species and there are as many annuals as perennials. If one weights the calculation by taking into account the number of seedlings of each species, the variation of the numbers is more important. The total number of seedlings is 323, of which 252 are annuals and 71 perennials, giving a ratio of the number of germinations $G_A/G_p=252/71=3.54$.

The percentage of annual seedlings is 78.02%, while that of perennials is only 21.98%. One can thus see the preponderance of annuals. This is not surprising, since the fire leaves open spaces for plants to grow, and annual species have a great ability to produce seeds with a high germinating capacity. Furthermore, the pinewood is a population of low stability. In addition, the greenhouse species were not subjected to intraspecies and interspecies competition, so that the number of annual species is very important, since as has been seen elsewhere, in a natural medium there is competition that reduces the expansion of the annuals to the benefit of the perennials, which are apt to develop rapidly by resprouting from the stumps.

In the oak thicket the number of species germinating is larger than in the pinewood—namely, 15, of which four were annuals and eleven perennials. The ratio $A/P=4/11=0.36$; and the respective percentages are 26.6% annuals and 73.3% perennials. In distinction to the pinewood, the perennial species are predominant. However, the number of seedlings though different from the pinewood, is even higher for the annuals. Total number of seedlings, 281; number of annual seedlings, 212; number of perennials, 69. The coefficient $G_A/G_p=212/69=3.07$, or 75.44% of annuals against 24.55% of perennials.

Comparison of the Results Obtained from Experiments under Glass and the Surveys Made at the Sampling Sites

If we compare the coefficients of similarity of the results obtained by the experiments under glass and the surveys made on the sites, in which we not only account for those species able to reproduce from seed, we can say that there is a rather large connection between the samples and the surveys from each group.

In other words, the similarity is greater between the samples coming from the pinewood and the survey of the pinewood than between the samples from the pines and the survey of the oak; and the similarity is greater between the samples from the oak and the survey of the oak than between the samples of the oak and the survey of the pine (Table 3).

TABLE 3

Values of similarity coefficients between the experiments under glass and the surveys (Species reproducing by seed).

	Study under glass of pinewood samples	Study under glass of oak-thicket samples	Survey of oak thicket
Survey of pinewood	24.2 (8)	33.3 (11)	41.9 (13)
Survey of oak thicket	17.3 (4)	36.8 (8)	
Study under glass of oak thicket samples	28.6 (6)		

The numbers in parentheses are the numbers of species in common.

However, the coefficient of similarity of the oak samples and the pine survey (33.3) appears to be abnormally high. In addition, the coefficient of similarity of the pine survey and the oak survey (all species) is 40.3. This is rather high, in fact the two surveys have 23 species in common; and, what is more, if one compares the surveys in each case, only taking account of species that reproduce by seed, the coefficient becomes 41.9.

It thus appears, even more strongly for the burnt areas (surveys) than for the samples under glass, that the connection is rather large between the two groups. From the plant population view, the two groups belong to different formations, but they are neighbors ecologically, whence the presence of certain species common to the two. The pinewood pertains to the Rosmarineto-Lithospermetum pinetosum Br.-Bl. 1924 and the oak thicket to the Cocciferetum rosmaretosum Br.-Bl. 1924. In addition the pinewood is less stable and has a tendency to evolve towards the climax of the Quercetum ilicis (cf. the species of shrubs: *Phillyrea angustifolia*, *Quercus ilex*, *Rubia peregrina*, etc.) and on this account has species that will be the same as those of the oak thicket.

Discussion

The two plant groups are not too greatly different from each other, but they react differently to the action of fires. The number of species appearing on burnt areas is much greater for the pine than for the oak. In addition, the proportion of annuals is much greater for the pine than for the oak. This is connected with the fact that the competition between species and between individuals is not as strong in the pinewood, because there are fewer species that resprout from stumps and that thus very quickly fill the area. On account of this, a rather significant amount of space is available for the growth of foreign species. In fact, the proportion of species that propagate only by seed is higher for the pinewood (34%) than for the oak (13%).

However, the proportion of perennial species reproducing vegetatively is so important in the two groups that a series of intermediate transition stages is not observed in the burnt areas, although this would often be the case (Ahlgren, 1960; Floyd, 1966). Here, the species present before the fire are the ones repopulating the space left open after the passage of the fire.

This can be attributed to interspecies competition and to the immediate occupation of free space by species that send forth a large number of shoots. In fact, in the absence of this competition and repopulation by shoots (the case of the samples removed to a greenhouse), one finds that the number of annuals, including species that do not belong to the two groups, can be quite high.

But also the favoring of the original species is due to the fact that the soil is a buffer agent that protects the underground parts of the plants found there (rhizomes, roots, tubers). In fact, when preliminary experiments were made to study the action of fire on the kermès oak thicket, we used thermocouples to measure the temperatures reached during fires that were set, at the level of the plant mass, temperatures reached 750°C or even 800°C; on the other hand, the heat released by the burning had little effect on thermocouples buried in the soil: at a depth of 10 cm, there was no rise in temperature, while at 5 cm the mean temperature was 40°C. This temperature of 40°C is significantly below temperatures that kill plant tissues, and moreover it only lasted for a short time and did not have time to kill the regenerative organs. One can even assume that it served to activate the eventual germination of planted seeds.

Thus it is, thanks to the protective action of the top centimeters of soil that keeps seeds and underground organs alive, and also the great capacity of most of the species to resprout from stumps, that we have both germination under glass and the filling of bare and free areas on the site by the original species.

Conclusions

The survival of seeds and the special ability of a large number of species to put forth shoots are the two principal factors that have played a role in the reoccupation of the burnt areas that we have studied. It is especially the growth of the original species that has permitted a rapid regeneration of vegetation in the burnt zones. This filling of the area is determined by the plant dynamics, and it must be emphasized that there is a natural tendency to create rapidly an environment identical to the original one by impeding the growth of foreign species.

One can consider that the two plant formations studied are in fact relatively stable communities and not transition stages. The groups as they exist now are in equilibrium with the environment, so much so that one can assume that fire acts as a natural factor.

Other authors have on the other hand described stages; one can assume when this is the case that the species present before the fire do not have a great capacity for reoccupying the devastated area and that these plants do not vigorously put forth new shoots. Hence there is a possibility that new and transitional species will grow for a certain time.

For kinds of vegetation strongly affected in the past by the recurrence of fires, which we appear to have in general in our region, one can assume that the present state of the vegetation represents a relatively stable equilibrium in which fire is one of the determining factors.

We wish to thank M. Long, Underdirector of the Research Institute at C.N.R.S. and head of the Division of General Phytoecology of the C.E.P.E., for having guided us in performance of this research in its various stages and particularly for having helped with the final editing. Prof. Sauvage, Director of the C.E.P.E., examined the results closely; we thank him for his valuable advice.

International Symposium and 15th Nordic Fire Protection Day 1969—Proceedings of Lectures and Discussions on Plastics, Fire, Corrosion; published by The Swedish Fire Protection Association, Stockholm, Sweden

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Proceedings available from The Swedish Fire Protection Association, Kungsholms hamnplan 3, S-112 20, Stockholm, Sweden, Price 50 Sw. Cr.

Symposium on Employment of Air Operations in Fire Services—Argonne National Laboratory, Argonne, Illinois (June 9–10, 1971)

Contents

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The Fourteenth Symposium (International) on Combustion, Pennsylvania State Univ., University Park, Pennsylvania, August 20–25, 1972.

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CUMULATIVE CATEGORICAL INDEX FOR VOLUME 13

YEAR 1971

SPECIAL ARTICLES

ABSTRACTS AND REVIEWS

A. Prevention of Fires and Fire Safety Measures

B. Ignition of Fires

C. Detection of Fires

D. Propagation of Fires

E. Suppression of Fires

F. Fire Damage and Salvage

G. Combustion Engineering

H. Chemical Aspects of Fires

I. Physical Aspects of Fires

J. Meteorological Aspect of Fires

K. Physiological and Psychological Problems from Fires

L. Operations Research, Mathematical Methods and Statistics

M. Model Studies and Scaling Laws

N. Instrumentation and Fire Equipment

O. Miscellaneous

BOOKS

PERIODICALS

TRANSLATIONS

MEETINGS

CUMULATIVE INDEX OF AUTHORS FOR VOLUME 13

YEAR 1971

CUMULATIVE INDEX OF SUBJECTS FOR VOLUME 13

YEAR 1971

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ABSTRACTS AND REVIEWS

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THE COMMITTEE ON FIRE RESEARCH functions within the Division of Engineering to stimulate and advise on research directed toward the development of new knowledge and new techniques that may aid in preventing or controlling wartime and peacetime fires. The Committee was established in December of 1955 at the request of the Federal Civil Defense Administration. 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.