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Fire Research
Abstracts and Reviews

Committee on Fire Research
and
Fire Research Conference

FOREWORD

It is a pleasure to report that encouraging progress is being made in the arranging of formal and informal discussions on fire research problems. The Committee on Fire Research is now holding periodic seminars in specific research areas. The seminars are intended as meeting places where current problems can be discussed prior to their formal publication in scientific journals. No record is made of the presentations or of the discussions. Their purpose is to stimulate exchange of information among persons with common interests. At a meeting devoted to Flame Inhibition, the following subjects were discussed:

Mechanism of Influence of Inorganic Salts on Combustion. (A. Broido)

Combustion Inhibition by Volatile Hydrogen-containing Compounds and by Finely Divided Powders. (W. A. Rosser, Jr.)

Inhibition of Ignition and Flame with Chemicals. (R. M. Fristrom and P. Breisacher)

Use of Basic and Applied Research in Evaluating Extinguishing Agents and Equipment. (Arthur B. Guise)

Inhibition of Diffusion Flames by Methyl Bromide and Trifluoromethyl Bromide Applied to the Fuel and Oxygen Sides of the Reaction Zone. (E. C. Creitz)

Research on Mechanism of Fire Extinguishment by Alkali Metal Salts. (J. B. Levy and Raymond Friedman)

Probing of Reaction Zones in Lean HBr-inhibited Methane Flames and Studies on Inhibition in Binary-fuel Mixtures. (Arthur Levy)

The Mode of Action of Dry Fire Extinguishing Agents. (Raymond R. Neill)

A Symposium on Fire Control Research, sponsored jointly by the Division of Fuel Chemistry of the American Chemical Society and the Committee on Fire Research of the National Academy of Sciences-National Research Council, will be held as a part of the Fall Meeting of the American Chemical Society, September 3–8, 1961, in Chicago, Illinois. A considerable number of invited papers will be presented, including four from abroad. If any reader of this Journal has contributions which he wishes to have considered for this Symposium, he should get in touch with Dr. R. Friedman, Atlantic Research Corporation, Alexandria, Virginia, or with the Editor of *Fire Research Abstracts and Reviews*. Papers which contain new information relative to fire control and flame inhibition (preferably from a chemical viewpoint) are being solicited.

The Proceedings of the International Symposium on "The Use of Models in Fire Research" held in Washington in November 1959 (NAS-NRC Publication 786) can be purchased from the Printing and Publishing Office, National Academy of Sciences, 2101 Constitution Avenue, Washington, D.C. at a cost of $5.00. This

i

book brings together, for the first time, the status of fire modeling principles and fire model experiments. The technical papers, supplemented by extensive commentaries and discussions, are as follows:

Fire under Influence of Natural Convection	G. I. Taylor
Fire Modeling	H. C. Hottel
Some Observations on Pool Burning	Howard W. Emmons
Burning Rates in Liquid Fuels in Large and Small Open Trays	David S. Burgess
Tests on Combustion Velocity of Liquid Fuel and Temperature Distribution in Flames and Beneath Surface of Burning Liquid	Gert Magnus
Effectiveness of Some Powdered Materials in Extinguishing Hydrocarbon Fires	T. G. Lee and A. F. Robertson
Study of Convection Currents Created by Fires of Large Area	J. Faure
Some Studies of Building Fires Using Models	P. H. Thomas
Upward Convection Current from a Burning Wooden House	Sizuo Yokoi
A Steady-State Technique for Studying Properties of Free-Burning Wood Fires	W. L. Fons
Experiments with Model Mine Fires	A. C. Rhodes and P. B. Smith
On the Self-Ignition of Wood Materials	Tosiro Kinbara
Natural Phenomena Exhibited by Forest Fires	J. S. Barrows
The St. Lawrence Burns	G. W. Shorter
Operation School-Burning	R. M. Hill

Continuing our plan of presenting programs carried out in Fire Research Laboratories throughout the world Professor T. Kinbara is reviewing in this issue the history and status of the Japanese work. We are grateful for his scholarly contribution. It is reprinted essentially as received.

WALTER G. BERL, Editor

Table of Contents

Volume 3   Number 1

Table of Contents—*Continued*

iv

Table of Contents—*Continued*

v

REVIEW

A Survey of Fire Research in Japan

T. Kinbara

University of Tokyo, Japan

I. Conflagrations in Japan in Old Times

As Japanese houses have been built of easily combustible materials—paper and wood—there have been numerous large fires since ancient times, and the records concerning them appear everywhere in the history of Japan. The reliable reports begin with the fire which occurred in 538, burning the imperial palace of that time.

Kyoto is one of the oldest cities, and as the capital of Japan it was the center of culture, policy, and commerce from 710 to 1603. Counting only those which have been recorded, the number of large fires during this period is 528, including the fire in 1434 by which more than 10,000 houses were burnt to ashes within a couple of days.

In 1603, Tokugawa Shogun (general) established a feudal government in Edo (the former name of Tokyo) which ruled over Japan until 1868. The political and cultural center was transferred to Edo, and Edo became the most prosperous city in Japan. The population was estimated to be about one million and the number of houses including large mansions of lords amounted to 250 thousands. All the buildings were built side by side in the commercial area and no powerful equipment for fire fighting was provided other than a pailful of water in front of each house, buckets for pouring water on the fire, and pickaxes to destroy the house.

So, if one failed to extinguish the fire in its initial stage, it rapidly grew beyond control and spread out until it came to the margin of the city or until it met with a severe rain. The number of outstandingly large fires in the history of Edo is 620, and conflagrations which ruined more than 3,000 houses occurred 101 times.

Among them, the conflagration in 1657 caused the largest damage. It spread out, with a strong northwest wind, over the most populated area of 6,200 acres and, after burning more than 100 thousand persons to miserable death, stopped at the coast of Tokyo Bay.

The second largest is the conflagration in 1772 which started from a point in the southwest suburbs. It spread in the blast of the strong southwest wind, and after burning the central part, extended as far as 14 km. to the northeast suburbs. It left a burnt area, very great in its length but very short (≈ 2 km.) in its breadth. Since it was unreasonable to make a frontal attack on a conflagration with the poor water-pouring methods, demolition gangs destroyed the houses on the fire front and prevented it from spreading perpendicular to the wind, leaving the lee untouched. This is the reason why many fires left long and narrow ruins among the fires of Edo. Narrow as the ruins of the conflagration of 1772 were, the

1

number of persons burnt to death has been reported to be 29,000. We can imagine how quickly the fire spread with the strong wind.

Other than these best-known conflagrations, there were fires of comparable scale which caused not only serious damage to property but immeasurable loss of human lives. The people who lived in the central part of Edo are said to have met conflagrations at least three times during their lives. It may be rather incomprehensible that there is no evidence that the Edo people tried to provide powerful scientific equipment for fire fighting, or to reconstruct the city with incombustible stone buildings, as western people did after conflagrations. This is because the Edo people were disciplined with a unique doctrine: "Have fortune under misfortune," and the person who made a fortune after his property had been completely burnt to ashes was thought to be most respectful. A fire was called even a "Flower of Edo" and was not considered to be disgusting by the Edo people.

From the numerous records of Edo conflagrations, we can study the spreading out of fires in a case where the spreading can not be prevented, or only partly prevented by fire fighting, and we can compare the propagation of fires with that of the experimental combustion along the surface of combustible materials in our laboratories.

In 1868, the Imperial regime was re-established and the name of Edo was changed to Tokyo. Soon afterward, manual fire pumps were introduced from Europe together with various innovations, and brick buildings began to appear. However, the damage caused by fires has not decreased remarkably. In the era called Meiji (1868–1911), there still occurred ten large fires which destroyed more than 3,000 houses each, including three which caused more than 10,000 houses to be burnt.

There was no very marked trend toward changing Japanese houses to stone or brick buildings. This was not only because of the economic reasons, but because of the fact that the Japanese showed especially deep attachment to the traditional wood buildings. This stimulated scientists to find chemicals which make paper and wood materials resistive to fire. The studies on these chemicals as well as fire resistive paint have appeared since the beginning of the 20th century.

Entering into the Taisho era (1912–1926), many buildings in the busiest parts of Tokyo had changed to the incombustible type, and the fire-fighting power had grown remarkably. Studies about chemicals to be dissolved in water, powders, and even chemical foams for extinguishing fire had been carried out since 1916. Thus the damage due to large fires greatly decreased and fires spreading over more than 1,000 houses completely disappeared.

II.   Fire Research 1923 to World War II

Just as this improved state had been reached the "Kanto Earthquake Fire" broke out following the earthquake on September 1, 1923. This caused serious damage in the wide Kanto area around Tokyo including Yokohama and other cities. Writing only of the City of Tokyo, fires broke out from more than 80 points of origin distributed all over the city, and spread without resistance, because the city-water system had lost its function due to the earthquake. The fire lasted for more than 3 days and propagated over 12,000 acres of the central part of Tokyo, covering 4.5 times as large an area as was ruined in the Chicago Fire in 1871. The number of people burnt to miserable death has been reported to be about 58,000.

2

ABSTRACTS AND REVIEWS

Prompted by a desire to exterminate such disasters forever, the late Professors T. Terada and S. Nakamura of the University of Tokyo set about making inquiries on how fires spread in this conflagration. More than 20 physics students were put to work, and they asked around the city about several items such as the time a particular spot was burnt, the direction from which the fire came, etc. It took a very long time, but finally they completed a fire map which showed how fires propagated from more than 80 independent sources.[1] The map teaches us how propagation is prevented by a large concrete building, how a fire can extend across a river (Sumida) 150 m. broad, etc.

Together with this investigation, Terada made inquiries into the way the fire spread in the Edo conflagrations by means of old documents concerning them. All these studies made him feel convinced of the proposition that a conflagration was virtually the same phenomenon as the propagation of combustion along the surfaces of combustible materials. This motivated him to begin experimental researches in 1926, the results of which were reported in 1930.[2] One of the most interesting results obtained may be the following: when a sheet of paper, preferably cellophane, is stretched along an inclined plate having a suitable angle of inclination, leaving a space of a few mm. between the paper and the plate, and is kindled at its center, the flame spreads only downwards. The upper side of the flame front cannot keep burning, being choked by the burnt gas ascending from the front of the lower side. Thus there remains a reversed fan-shaped ruin. The phenomenon that combustion cannot propagate to the lee side or to the upper side of an inclined plane has been called "Terada's effect."

T. Kinbara extended Terada's study of the "combustion along surface," and clarified several characteristics of this phenomenon using liquid as well as solid fuels.[3] Since then, various papers by many authors have been published on this "combustion along surface."

A characteristic seen in the fires in Japan is that the frequency of their outbreak depends greatly upon the season. In the case of the Edo fires, they broke out as many as 61 times during the winter season of December through March, while only 2 times during the summer season of June through September. The statistics of Tokyo fires in recent years, show that the monthly outbreaks of fire during December through March number roughly 500 times, while only about 300 times during June through September. Two reasons for this are considered. The first reason is that heat is used more frequently in winter than in summer. The second is that materials such as wood, paper, fiber, etc. are more easily ignited in winter than in summer because the wind is stronger and the air is less moist in winter. The mean humidity of Tokyo is 60 per cent in winter and 80 per cent in summer.

It was Terada and S. Suzuki who first studied the relation between fires and the weather. Suzuki investigated the forest and prairie fires near railways caused by sparks from locomotives.[4] He paid attention to these fires because the occurrence of sparks being distributed in forests and ranges is constant throughout the day when the long range of railways is considered. The result showed that fires had broken out, by an overwhelming majority, mostly between 11 a.m. and 2 p.m., the period when the air is most dry. This is in good agreement with the outbreak of Edo conflagrations, most of which started between 12 noon and 4 p.m.

Suzuki also carried out experimental investigations [4] of the dependency of

3

flammability upon the four meteorological elements—wind velocity, humidity, temperature, and pressure—using incense sticks as fuels (1928). Since then many papers have appeared concerning fires and the weather, and it has been believed in our country that not only the spreading out of fires but the frequency of their outbreak depends mostly upon the weather. The difference in frequency of use of heat in winter and in summer has been considered so small that the frequency of outbreak is a function only of meteorological elements, among which humidity plays a most important role.

Two kinds of humidities have been thought to be related with the outbreak of fires, the one being the relative humidity with its usual meaning and the other being the effective humidity. The latter is a humidity in which not only the humidity of the day but the humidities of the past days are taken into consideration. It is expressed by the weighted mean of the humidities of today, yesterday, the day before yesterday, etc., their weights being considered to be 1, r, r², etc. respectively. Hatakeyama found statistically [5] that the number of daily outbreaks had closer relation with the mean humidity of that day when all fires were counted no matter how small, while it had closer relation with the effective humidity for r=0.7 when fires destroying more than half of a house were counted. Since then, the importance of the effective humidity has been recognized and it is now one of the elements forming a condition for fire warning (the authorities of cities, towns and villages give people a fire warning by means of radio, television, or other means when wind velocity, humidity, and effective humidity attain their critical values).

Relative to the weather, another interesting fact is that the number of outbreaks of large fires varies greatly according to the region. Large fires are concentrated in the eastern and northern parts of Japan, and only a few large fires have occurred in the region around the inland sea. Each prefecture has its own "months of fires" during which large fires are liable to develop.

In 1931, the Manchuria trouble broke out and Japan rushed into a state of war. People had come to be concerned with the prevention of fire. Thus, the first experimental burning of wooden houses was carried out in 1933 under the guidance of Y. Uchida and M. Hamada, professors of the University of Tokyo.[6] Following this, fire experiments were repeated once in 1934 and twice in 1938, and the temperature-time relation of a wood building fire has been clarified through a series of these experiments. The standard temperature-time relation which is used nowadays to evaluate the fire resistivity of building materials has been formulated in this way.

As the Manchuria trouble extended to the Japan-China War in 1937, fire fighting not only by professional troops but by people in general was greatly stressed. The Committee of Fire Prevention was established as a section of the Science Promotion Council to study ways of coping with fires expected to be caused by air raid. The large fire which occurred in Shizuoka on January 15, 1940 burning 300 acres including 5,500 houses became the stimulus for studying the manner of spreading out of fires. Many researchers such as Suzuki, Hatakeyama, Hamada, Kinbara, and others gathered in the city and made working surveys from several points of view.

As in many conflagrations, many fire sparks flew for some hundred meters to other houses and produced secondary sources. It was by studying this fire that the nature of sparks as well as the mechanism by which they fly across and cause new fires was clarified.[7]

4

As scientific researches were commenced following the Kanto fire, so they were pursued after this fire. A committee, the chairman of which was Professor A. Imanura, was organized in 1941 sponsored by the Tokyo Fire Fighting Research Association for the purpose of finding the spreading velocity of fires in the wind. The results obtained have been recognized as most reliable and are used in devising tactics of fire fighting.[8]

After 1941, Japan was in a complete state of war because of World War II, and the facilities for actual fire fighting were so busy that scientific researches were left behind. No methods could be devised to prevent conflagrations caused by countless incendiary bombs falling upon the veritable forest of wood buildings. The number of houses burned during the war was innumerable. It was reported that the number amounted to about 860,000 in Tokyo alone, and if the number was totaled for all the cities in Japan, it could amount to as many as 2,330,000.

III.   Establishment of Institutes of Fire Research after the War

Fires during wartime, together with the normal fire problems of peacetime, prompted the setting up of institutes for fire research after the War.

In 1948, the Fire Research Institute was established as a laboratory of the National Fire Defense Board. The work of this institute is divided into three parts: (1) both fundamental and practical researches, on the results of which improved techniques or equipment for fire protection may be developed, (2) grading of cities from the viewpoint of fire prevention and protection, and (3) testing for approval all kinds of equipment and devices for fire protection. The results of the work of this institute have been published in the *Report of the Fire Research Institute,* or in the *Bulletin of the Fire Prevention Society of Japan.* The titles of the articles are listed in section V. of this report.

The Building Research Institute, Ministry of Construction, was established in 1946. It has five sections, one being assigned to the functional study for fire protection. This section has carried on not only fundamental studies in laboratories, but fire tests of building materials by means of wall furnaces and experimental fires using concrete buildings especially built for this purpose. Most of the activities in the research field of this institute can be understood from the titles of papers listed as recent work in section V. The list omits the work conducted by K. Fujita because his work had been finished before 1954. His research started about 1940 with the confirmation that the radiation from a fire flame is black body radiation. He derived an expression for the intensity of radiation which is received by a building from burning wood buildings in its vicinity. On the other hand, he also obtained an expression for the maximum intensity of incident radiation at which wood materials will never catch fire even though small fire sparks approach them. From these two results, he concluded the safe distance beyond which wood buildings will never catch fire by radiation from neighboring burning buildings.[9]

The Tokyo Metropolitan Fire Board in 1948 established a small laboratory for tracking down the causes of fires which broke out in the Tokyo area. It is the duty of the Inquiry Section to investigate how fires break out, and several times it has been too difficult to find the causes of fires by mere inspections and laboratory studies have been needed. The Section has carried out researches on basic problems of how a fire originates and how it develops. The results obtained have been pub-

lished, as a rule, in the *Bulletin of the Fire Prevention Society of Japan* and are shown, so far as recent work is concerned, in the list of titles in section V.

The Industrial Safety Research Institute, Ministry of Labor, is an institute founded in 1942 for studying the prevention of various disasters in industrial fields. The Chemistry and Electricity Section have been studying the detonations of gases from the standpoint of industrial safety. They have conducted also several researches on factory fires caused by static electricity, and the Institute can be reckoned among institutes for fire researches.

Other than these institutes there have been established some committees or groups in which members discuss what they have studied, for the sake of furtherance of their studies. The committee formed in 1942 by professors and researchers of the above mentioned institutes, with M. Hamada as chairman, is one of them. It is sponsored by the Fire and Marine Insurance Rating Association and has its organ publication, *Research in Fires and Disasters*. A subcommittee for studying the relation between fires and the weather has been formed, with H. Hatakeyama as chairman.

The Fire Research Group of Japan which was established in 1948 with T. Kinbara as chairman, includes members from wide areas of fire researches. Discussions made in this group are not only about academic or technical problems but practical problems such as the way in which the cause of a fire was deduced.

As all the papers discussed in these committees and worth reporting have been published in the journals or publications cited in section V, it is needless to provide here space for writing about the activities of these committees and groups.

IV.   Fire Prevention Society of Japan

In addition to the researchers belonging to the above-mentioned institutes, in the period before 1950, there were still other university professors who had been studying the problems of fire prevention, mostly from academic interest. There were also some who were interested in fire prevention in the meteorological observatories, industrial and insurance companies, and fire departments in many cities. In November 1950, the Fire Prevention Society of Japan was set up, Y. Uchida as the president, and all these researchers, professors, and others, the number totaling about 800, were incorporated into the membership of this Society.

Journals

This society publishes the periodicals *KASAI* (*Fire Hazard*) and the *Bulletin of the Fire Prevention Society of Japan*, the former for the purpose of giving varied and general knowledge of fire prevention to all members and the latter being a journal for technical papers. The Bulletin is the most authoritative journal on fire research in Japan, and most researchers and professors, after publishing their paper in the reports of institutes to which they belong, publish again in this Bulletin in a refined and complete form. One can learn from this Bulletin what kinds of fire researches are now being conducted in Japan.

Meetings and Awarding of Prizes

The society holds general lecture meetings in spring and in autumn, at which time professors, researchers, and members concerned with fire-fighting matters meet together and discuss problems from various points of view.

ABSTRACTS AND REVIEWS

In the spring meeting, the society awards prizes to members who have completed eminent scientific work during the year. The articles for which prizes have been awarded are as follows (cf. section V), the figures shown in parentheses designate the years of award.

T. Sakurai: On a foaming fire-retardant paint (1954). This paint is a mixture of thiourea-melamin-formaldehyde resin, phosphoric acid-aniline and monoammonium phosphate. When heated, the paint of 0.5 mm. thickness expands as much as 8 to 10 cm. thick and prevents the wood from being burnt. This paint was invented independently of, and at almost the same time as American Albi-R, and has been proved to be very effective for fire prevention.

K. Hishida: On the quantitative estimation of fire risk in a district of a city (1954). Hishida considered that the fire risk in a district of a city depends, on the one hand, upon the "firing elements" such as structure, magnitude, and crowdedness of buildings in that district, and on the other hand, upon the "extinguishing elements" such as the numbers and capacities of fire departments, and the water supply system. Accordingly, he divided a city into sections within which all these elements are almost constant, and treated these sections as separate units. As the broadening of a fire depends also upon the wind, he took the wind velocity to be an additional element. Thus, by the statistical investigation of fires which had actually occurred in cities, he arrived at a method for making a quantitative estimate of the fire risk in a district of a city.

K. Usui: Studies on the extinction of a building fire (1955). Usui found first, by experiments, the quantities of water necessary for extinguishing several kinds of burning timbers which had been carbonized to various depths. He then calculated the surface areas of the combustible building materials such as pillars and beams of a dwelling or an office of the typical Japanese style. The depths of carbonization of timbers were estimated from the time elapsed since the outbreak of the fire. From these, he derived the quantities necessary for the extinction of building fires. The quantities used in actual fires were found to be as much as 100 times the theoretical ones thus obtained. He studied also about the extinction of fires by cutting off the air supply, and derived the criterion for judging a fire in a room of concrete building if it would grow or become extinct, provided the volume and the air-ventilation constant of the room were given.

K. Ogawa: Construction of building belt for resisting conflagrations in the City of Tottori (1955). Overcoming various difficulties after the conflagration in 1952, Ogawa planned (as the head of the building section in the prefectural office) and succeeded in constructing a building belt of concrete buildings for the purpose of stopping conflagrations by this belt in the City of Tottori in which wood buildings were predominant. This was the first such belt in our country and since then many belts have been constructed in many cities taking the one in Tottori as the model.

K. Okajima: Experimental investigations on the role of a water film for preventing heat and radiation (1956). He investigated experimentally the amount of water film needed to prevent various kinds of walls and roofs from carbonizing and burning when heated by flames or high temperature bodies. Then he studied the structure of a sprinkler head which would distribute the necessary amount of water most effectively to a building. His design has been applied to the drenchers at Horyuji-Temple, a national treasure built 1,300 years ago.

7

J. Miyama and K. Kita: An electrical analog method for calculating flow rate through a pipeline network (1957). The loss of pressure head of a water stream due to the resistance of pipes is, according to Hazen-Williams, proportional to (the rate of flow)$^{1.85}$, and so it is troublesome to find the flow rate at a given point of a pipeline network. The authors made special incandescent lamps for which applied voltage is proportional to (electric current)$^{1.85}$, and then invented electrical analog devices by which flow rate is read immediately in terms of an electric current.

S. Yokoi: On the upward current from a burning building (1958). Yokoi's research started with a theoretical calculation of the distribution of flow velocity and temperature in an upward current which ascends from a point or line heat source, which he then confirmed experimentally. He next succeeded in formulating the distribution when the current ascends from a heat source of circular or rectangular shape. His study extended also to clarification of the structure of the hot current emitted from a window of a burning building, and he determined the required dimension for a spandrel which can prevent a room from catching fire due to the hot current from the floor below.

K. Akita: Studies on the mechanism of the ignition of wood (1959). Akita studied, both theoretically and experimentally, the ignition and flashing of wood materials, dividing the process into 3 parts: thermal conduction, thermal decomposition, and the ignition of decomposed gases, and he succeeded in clarifying the mechanism and obtaining useful results. He also extended his research to the spontaneous ignition of wood materials. One of the interesting results obtained is that the heat of decomposition which is observed at the initial stage of ignition is produced when substances made by primary decomposition undergo secondary decomposition or polymerization. He then applied the results to estimate the time of spontaneous ignition and the relative combustibilities of fiber materials.

S. Nakauchi: A study on the pneumatic-tube-type fire detector (1959). In order to improve the reliability of pneumatic tube detectors, Nakauchi studied, both theoretically and experimentally, the optimum construction of various elements of the detector, such as the diameter and the total length of the tube, the resistance of the leak which is necessary to cancel the slow variations of room pressure, the diameter and the Young's modulus of the diaphragm, etc. His work consists of 3 parts: theoretical considerations on the working of the tube, theoretical and experimental studies on the change of temperature of the tube itself, and designing of the most economical and reliable detector. This study has contributed not only to the production of tube detectors, but to the rapid testing for approval of manufactured detectors.

Y. Izawa: Decrease of fire risk in a town when improvements in fire prevention are applied (1959). Following Hishida's idea, Izawa calculated the fire risk of a section of a town and of a building in it, using "firing elements" and "extinguishing elements" as stated in the description of his earlier work. He, then, calculated the change of fire risk in a section, when one of the wood buildings inside it is changed into a fire retardant structure, or into a concrete building, when a road 100 m. broad is constructed in this section, etc. This study contributes to city planning from the standpoint of fire prevention.

S. Horiuchi: A study for determining the optimum capacity of a municipal fire department (1960). Horiuchi first expressed the burnt area and the length of fire front of a city fire as functions of time assuming no fire fighting is undertaken. The fire front is the place where fire fighting should be carried out. Accordingly, if

8

the maximum permissible burnt area is given, both the time at which fire fighting should begin and the number of engines which should arrive at the fire front are known, and this gives the necessary distribution and capacities of fire departments. Thus he established a general method for determining the capacity of a fire department necessary to control fires within the maximum permissible burnt area.

Standing Committees

The society has several standing committees for studying causes of fires, teaching about fire prevention for elementary school pupils, fire fighting and water supply, city planning and fire fighting, fire fighting and extinguishing equipments, etc.

The committee studies are supported financially by the Fire and Marine Insurance Rating Association. The results which have been published by the society are as follows:

Redevelopment of city areas with fire-resistive buildings (1956).
Spontaneous Ignition. Its definition and examples (1956).
Fire fighting and city water (1957).
Teaching materials for fire prevention (1957).
Development of a city with fire belts. I (1958).
Development of a city with fire belts. II (1959).
Elimination of anxiety over fires (1960).
Planning for underground parking and equipment to be provided therein 1960).
Fires due to the leakage of electricity through building materials (now in press).

Although the society is a purely scientific association and does not advise the government officially, the government consults the results of these scientific researches in planning the development of cities and towns.

V.   Researches in Recent Years

Scientific fire researchers in Japan now number more than 50, excluding those in fire departments, insurance companies, and manufacturers of fire-fighting equipment and chemicals who are interested in this problem. However, the variety of problems in the research field is so large that 50 members can not cover all of the field. The subjects which have been studied in these five years are classified into 12 categories. The present author considers that the best way to describe the kinds of researches now being conducted in Japan is to list the titles of articles which have appeared in the journals since 1954. The following is a tabulation of these titles. In this list the names of journals are abbreviated. The abbreviation and the addresses of publishers are as follows:

F. P. S.: Bulletin of the Fire Prevention Society of Japan. Fire Prevention Society of Japan, c/o Prof. Hamada, University of Tokyo, Faculty of Engineering, Hongo, Bunkyo-ku, Tokyo.
F. R. I.: Report of the Fire Research Institute. Fire Research Institute, 700, Shinkawa, Mitaka, Tokyo.
B. R. I.: Report of the Building Research Institute (in English). Building Research Institute, 4-chome, Hyakunin-cho, Shinjuku-ku, Tokyo.

9

R. F. D.: Research on Fires and Disasters. Fire and Marine Insurance Rating Association of Japan, 2–9, Kanda Awaji-cho, Chiyoda-ku, Tokyo.

C. G. E.: Scientific Papers of the College of General Education. University of Tokyo, College of General Education, Komaba, Meguro-ku, Tokyo.

C. F.: Combustion & Flame. Butterworths Scientific Publications, London.

1. FUNDAMENTAL STUDIES ON COMBUSTION

K. Okazima, Y. Yazi: Shapes of flames. F.P.S. 5, 49–52 (1956)

K. Okazima, Y. Yazi: Shapes of flames in a wind. F.P.S. 6, 45–48 (1957)

K. Akita: Studies on the mechanism of the ignition of wood. F.R.I. 9, 1–106 (1959)

T. Moriya: Effect of water content on burning speed of wood. F.P.S. 5, 69–72 (1956)

K. Akita, S. Arai: Comparison of flammabilities of solid combustibles. R.F.D. 5, 212–220 (1959)

S. Hori: Spread of flame along paper. F.P.S. 4, 11–13 (1954), F.P.S. 5, 85–86 (1956), F.P.S. 6, 54–58 (1957)

Y. Yazi: Burning speed and the ignition temperature of cotton. F.P.S. 6, 23–26 (1956)

Y. Yazi: Burning speed along the surface of fiber materials. F.P.S. 7, 25–28 (1957)

Y. Yazi: Ignition temperature of fiber materials. F.P.S. 7, 51–54 (1958)

K. Akita: Ignition of various materials by strong radiation. R.F.D. 5, 208–211 (1959)

M. Hamada: Inclination of flames due to winds. R.F.D. 5, 141–148 (1959)

T. Kinbara, K. Akita: An approximate solution of the equation for self-ignition (in English). C.F. 4, 173–180 (1960)

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ABSTRACTS

I. Ignition

Thomas, P. H. (Joint Fire Research Organization, Boreham Wood, England) "Some Approximations in the Theory of Self-Heating and Thermal Explosions," *Transactions of the Faraday Society* **56**, 833–839 (1960)

This paper considers two approximate methods of effecting a solution of the partial differential equation arising in a system experiencing heat conduction, internal heat generation, and a increase in sensible heat to determine the value of reaction rate above which no steady-state heat transfer can occur. The heat generation is assumed to be due to a zero-order reaction obeying the Arrhenius law. The material is assumed to be isotropic with thermal and chemical properties non-temperature dependent. The material is further considered to be heated symmetrically and the usual boundary condition for surface cooling is used, i.e. the conduction in the system is equated to the radiative and convective heat loss. It is well to note that the usual approximation to the Arrhenius relation is used. While the equation has been solved exactly for arbitrary heating rates, a more flexible result is deemed desirable even though approximate in character.

The first approximation—quasi-stationary solution—is obtained by substituting a conduction term based on mean temperatures for the conduction terms of the differential equation. The general differential equation is solved for a no-reaction state and the long time solution equated to the approximate form of the equation obtained by the mean temperature substitution (no-reaction condition assumed) to relate the effective transfer coefficient to the coefficient in the long-time solution of the general equation. The case of the sphere, cylinder, and plane slab is treated.

The second approximate method—effective transfer method—proceeds by substitution of the maximum dimensionless temperature at the line or point of symmetry in the general solution in the generation term. The equation is solved and the steady-state solution used to evaluate the effective transfer coefficient. The temperature distribution (steady state) is obtained from the general equation. The surface temperatures obtained by the approximate solution are compared with the exact values and the agreement is found to be good.

The values of critical reaction rate obtained with the two approximate methods are compared graphically for various values of dimensionless surface cooling. This latter quantity is analogous to the Nusselt parameter. The geometry of a sphere, cylinder, and slab is considered. The comparison shows the first approximation to yield high values of critical reaction rate, while the second approximation is slightly low compared to the exact solution. The first approximation may in fact be more accurate than its value appears, since the conventional (exact) theory gives slightly low predictions. The use of the approximate methods allows treat-

13

ment of transient self-heating or thermal explosion problems by use of a transfer coefficient which can be expressed in terms of problem surface conditions.

Subject Headings: *Explosions, theory of self-heating.*

H. N. McManus, Jr.

Martin, S. B. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "The Mechanisms of Ignition of Cellulosic Materials by Intense Thermal Radiation," *Research and Development Technical Report USNRDL–TR–102, AFSWP–799* (February 1956)

The report interprets the scientific literature (78 references) concerning the ignition of cellulosic materials by thermal radiation. The distribution of radiant flux in cellulosic materials, which are diathermanous scattering solids, when exposed to radiant energy of known spectral distribution and irradiance as a function of time, can be calculated and, in combination with the heat conduction equation, yields the time-temperature-depth history for the solid. The calculated temperature profiles are modified by the heat of changes in state of the solid for which theoretical treatments are available although lack of thermochemical data prevents complete understanding. The pyrolytic rate behavior of cellulose has been shown to be "diffusion-controlled" (determined by the rate of energy transfer within the body) but this still fails to reveal the mechanisms that lead to ignition.

Combustion of cellulosic material involves first, decomposition of the solid into simpler volatile products and second, gas phase oxidation of the products after mixing with air at some distance from the solid. Ignition requires (1) sufficient reactivity of the gaseous fuel, and (2) a ratio of fuel to air within the upper and lower limits of flammability.

Low-rate pyrolysis of cellulosic material subject to a low level of irradiance at one surface proceeds in a relatively orderly fashion. Zone A at the surface while rising to 200°C loses weight by dehydration, evolving water vapor. Next, zone A penetrates deeper and is succeeded at the surface by zone B (200° to 280°C) from which mostly nonflammable gaseous products are evolved copiously, consisting of carbon dioxide, water, acetic acid, and some carbon monoxide. Zone B at the surface is succeeded by zone C (280° to 500°C) in which pyrolysis is more rapid and exothermic. The abundant gases evolved are rich in flammable materials, hydrogen, hydrocarbons, and condensable vapors of acetic and formic acids, ethanol, acetaldehyde, acetone, diacetyl, methylethyl ketone, ethyl acetate, and tars. The surface becomes black char, which is more absorptive of radiant energy, heats rapidly, and steepens the temperature gradient. Within the solid the carbon dioxide and water evolved from zones A and B pass out through zone C where they react with hot carbon to form flammable hydrogen, carbon monoxide, and formaldehyde. When zone D (above 500°C) succeeds zone C at the surface it evolves chiefly extremely flammable hydrogen and carbon monoxide. When the surface temperature exceeds 1000°C char is lost as fast as the reaction zones progress into the solid and the pyrolysis becomes self-sustaining.

High-rate pyrolysis proceeds differently. Highly flammable gases are evolved promptly, much less carbonaceous char is left, and a thin surface layer may become thoroughly charred before underlying material is observably affected.

14

ABSTRACTS AND REVIEWS

Molecular disruption is so violent that fragments are expelled too rapidly to permit the successive adjustments of molecules that lead to formation of the carbon structure of char. Macromolecules of cellulose undergo several disruptive processes simultaneously. While linkages along the molecule are being cleaved by hydrolysis, polyhydric alcohol groups are dehydrated and carbon-to-carbon and carbon-to-oxygen bonds are cleaved. Both the rate and the mechanism of pyrolysis change with the intensity of irradiation. Flameproofing treatments apparently retain the mechanism of low-rate pyrolysis up to higher temperature levels.

Two competitive reactions may be postulated (1) pyrolysis to carbon and oxygenated volatile products with negative heats of formation, dominant at low heating rate, and (2) pyrolysis entirely to volatile products largely oxygen-free and of positive heat of formation, dominant at high heating rates. The reactions seem to follow first-order kinetics. The specific rate constant may be considered the sum of the constants k_1 and k_2 for the low- and high-rate pyrolyses, respectively, whence

$$-\frac{dw}{dt} = (k_1+k_2)w = (A_1e^{-E_1/RT}+A_2e^{-E_2/RT})w$$

Below 300°C, k_1 may exceed k_2 greatly and above 400°C, k_2 may predominate. E_1 has been found to be about 30 kilocalories per mole and A_1 about 10^9 per second. Perhaps E_2 is about 50 kilocalories per mole and A_2 about 10^{20} per second.

The mechanism of pyrolysis of cellulose is almost entirely unknown. Hydrolysis at the acetal linkage between glucosan units may well be the first step. Its extent may well affect further pyrolysis profoundly because each hydrolytic cleavage produces two new end groups, one with reducing properties, the other without, and both unlike the interior glucosan units. Interior units and each kind of end unit may direct subsequent pyrolysis in different directions. Possible important products that have rarely been considered are the highly unsaturated and reactive ketenes, which could be derived from the abundant $CHOH \cdot CHOH$ groups in glucosan units, and free radicals such as CHO, CH_2, H, OH, and CH_3, which are important in many chain reactions.

Ignition in the gas phase results from coincidence in time and space of levels of kinetic energy and concentrations of active species and oxygen for which steady-state processes are impossible. The hot surface of the solid cannot serve as ignitor because it is always engulfed in gases free from oxygen. Hot fragments of solid torn from the surface and carried by the rush of gases into the region of suitable admixture with air may be considered. To serve as ignitors, solid particles must be far above the ignition temperature of the gaseous mixture and their necessary temperature increases rapidly as their size diminishes or as their velocity increases. Experimental evidence affords little support for the hot-particle theory of ignition.

Upper and lower flammability limits for mixtures of 33 gases and vapors with air and their ignition temperatures, which range from 189° to 632°C, are tabulated. The region of flammability is that within which enough reactive collisions between molecules of fuel and oxygen occur to evolve heat faster than it is dissipated by nonreactive collisions with cooler molecules and by radiation. Ignition temperatures depend on time as well as on temperature; the induction period or "lag in ignition" diminishes rapidly as the temperature increases.

The purely empirical ignition behavior, i.e. ignition temperature with its

15

associated time lag and limits of flammability, can now be expressed mathe-
matically. In recent years classical reaction kinetics has been combined with
principles of heat and mass transfer in a procedure called macroscopic kinetics
which proves very successful in uncovering the intimate mechanisms of combus-
tion processes. The procedures are considered for an idealized model of a semi-
infinite solid undergoing radiant energy pyrolysis. For the real case of ignition of
cellulosic materials the application of the method is complicated and requires
knowledge of the composition of the gaseous products as a function of time under
a given set of conditions.

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

F. L. Browne

Martin, S. B. (U.S. Naval Radiological Defense Laboratory, San Francisco, Cali-
fornia) "On Predicting the Ignition Susceptibility of Typical Kindling Fuels
to Ignition by the Thermal Radiation from Nuclear Detonations," *Research
and Development Technical Report USNRDL–TR–367, AFSWP–1135* (April
1959)

Utilizing the results of earlier investigations,[1-3] a method is presented for
calculating the effects of nuclear weapons on the ignition of a number of kindling
fuels representative of materials found in urban and wildland areas. It is based
on a generalized behavior pattern of ignition represented by curves plotted in
terms of a modified energy modulus $aQ/\rho L(c_o+m)$ and a weapon yield modulus
$W(a/L^2)^2$. The symbols are: a=radiant absorptance, Q=radiant energy per unit
area required for ignition (sustained flaming, transient flaming, and sustained
glowing); ρ=density; L=thickness of irradiated fuel; c_o=specific heat capacity
of oven-dry fuel; m=moisture content; W=weapon yield; a=thermal diffusivity.

Calculations are simplified by the assumption that material properties ap-
pearing in the two moduli which are difficult to measure can be determined with
sufficient reliability from the thickness and unit area weight of the materials and
relative humidity. Results are presented in two groups of charts. One shows radi-
ant energies required to ignite the representative kindling fuels for weapon yields
ranging from 10^{-3} to 10^2 megatons. The other group gives the corresponding range
of ignition for the same weapon yields.

The author points out that the calculations have not been substantiated by
direct experimentation.

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   (December 1958)

Subject Headings: *Fuels, ignition of, by nuclear radiation; Radiation, ignition of
fuels; Ignition, of fuels, by nuclear radiation.*

G. M. Byram

Laughlin, K. P. (Office of Civil and Defense Mobilization, Battle Creek, Michigan) "Thermal Ignition and Response of Materials," *Project 31.5 Operation Teapot Civil Effects Test Group* (February-May 1955)

This report presents the results of six separate tests conducted in conjunction with the open atomic shot of Operation Teapot. The test objectives were to determine the extent of damage due to thermal radiation on stakes, pilings, fabrics, plastics, oxyacetylene units, and drums containing flammable liquids, and to determine how much protection could be obtained from normal window hangings. Damage at various points was correlated with thermal energies obtained from a curve of thermal flux as a function of distance reproduced from an earlier report. The author stressed that in many cases the conclusions are general because of such factors as the variation in intensity of thermal radiation with haze characteristics of the atmosphere and angle of incidence, and the effect of aging, atmospheric conditions, etc., on the materials tested.

Stake-Line Test Untreated stakes of ponderosa pine and Douglas fir (2 inches x 6 inches x 3 feet) were placed at 500 yard intervals radially from 1000 to 12,000 feet from Ground Zero (GZ). The depth of char was measured and plotted versus the incident radiant energy. The results were generally reasonable. By correlating the degree of char with data on ignition energies for kindling fuels, an estimate can be made of the possibility of smoldering and other primary fires in these materials. No stakes continued to burn after the thermal pulse passed. On this basis, it seems that continuing fires will be started principally by thermal radiation on kindling fuel, i.e. combustibles that are thin or of low density. There were no differences due to the type of wood. Surprisingly, the effect of char and scorch was less up to 3500 feet from GZ than between 3500 and 6500 feet. Apparently the blast wind at close range effectively terminates the thermal action before its normal completion.

Treated-Timber Piling Test Currently, timbers used in bridge construction are treated with creosote, either pure, or in mixtures with coal tar or Bunker C fuel oil. Southern yellow pine and Douglas fir were treated with these preservatives to various yield retentions. Specimens underwent laboratory fire-testing which indicated that species of wood, type of preservative, and degree of retention all affect fire behavior.

In the field test, ten feet pile stubs were placed at 4700, 6800, and 10,500 feet from GZ. At each position there was one untreated, unpainted piling and three groups of three treated pilings. One group was left unpainted, one was painted black and the last group was painted white.

The pilings at 10,500 feet from GZ showed no damage. At 6800 feet, the unpainted controls were only superficially charred, the black painted pilings suffered thermal damage on the frontal surfaces and there was no apparent damage to the white painted pilings. These were also undamaged at 4700 feet, whereas damage was intensified in the other pilings. In any given case, the creosote-treated piling showed the least damage. Coupled with white paint, it offered almost complete protection at the test conditions.

Window Protective Test Beyond the range of major blast damage, kindling fuels such as upholstery, bedding, and draperies within a dwelling can be ignited by thermal radiation. Consequently tests were carried out to find out to what extent heat penetration could be reduced by some common window coverings or by coatings that could be applied to window glass under emergency conditions.

17

Racks were set up at 4700, 5500, 6800, 8500 and 10,500 feet from GZ. Each rack had the following specimens; control, window glass, aluminum sheet, various aluminum screens, and venetian blinds, and window glass covered with three mixtures—whiting and water, Bon Ami cleanser and water, and opaque paint. A range of heat sensitive papers were arrayed behind each specimen. These papers were later calibrated in the Naval Materials Laboratory. They indicated that closed venetian blinds will preclude radiation completely, various screenings will cut radiation by from 35 to 65 per cent, whiting reduced radiation 90 per cent while Bon Ami halved it and the paint was only 35 per cent effective.

Fabrics Test This test was designed to study the effect of thermal radiation on textiles used in civilian wearing apparel in terms of physical changes such as scorching, melting, burning, and particularly in terms of the effect of several layers. Fully clothed mannequins and plaques of more than twenty different fabrics were set up at 7000, 8000, and 9000 feet from GZ. Several paper indicators printed with heat sensitive materials were pasted on each support plaque, half of which was recessed so that half of the fabric lay directly on the paper and half of it was separated by an air space. Effects differed only in degree at the three stations. Color was most important. At 7000 feet, black wool was severely damaged while the white wool showed little effect. The heavier natural fibers were better than the lighter ones but most of the synthetic-fiber fabrics melted or fused. Layers of fabrics increased protection and the mannequin clothing was generally less damaged because of folds and air spaces. A white cotton bed sheet wrapped around the mannequins offered complete protection.

Oxyacetylene and Flammable-Liquid Drum Test To determine if thermal radiation will damage or explode oxygen and acetylene units, standard units plus accessories were placed at 4700, 5700, and 8000 feet from GZ with valves closed. The equipment was not damaged by the blast.

Since vented chemical storage tanks can be exploded by lightning, etc., both vented atmospheric and pressurized 55 gal. steel drums containing explosive vapor-air mixtures were placed at 5700 and 8000 feet from GZ. There were no explosions and no damage to the tanks.

Plastics Test In this test, 680 samples of commercially available plastics varying in thickness, color, and type were placed at three positions, 6600, 7660, and 8690 feet from GZ. Damage to the samples was evaluated visually. In general, the thermal radiation had more effect on the thermoplastics than on the thermosetting plastics and on the darker materials. The vinyls were most affected. Among the undamaged plastics were teflon, polyester molded parts, melamine dinner ware, molded phenolic pieces, epoxy high-heat-resistance laminates, polystyrene and acrylics sheeting, and most of the high pressure laminates. Damage to other families of plastics including nylon, polyethylene, mylar, and cellulose acetates varied greatly.

Subject Headings: *Thermal ignition, of materials; Ignition, thermal, of materials.*

Gladys M. Steffan

ABSTRACTS AND REVIEWS

Kollman, F. (University of Munich, Munich, Germany) "Occurrence of Exothermic Reactions with Wood," *Holz als Roh-und Werkstoff* 18, 193–200 (1960)

This study deals with a series of temperature measurements in the center of wood cubes (70 mm. diameter, 70 mm. long) supported in a furnace whose temperature is raised (at an unspecified rate) to above 200°C. Differential temperatures are recorded between wood and gas. An exothermic reaction sets in at about 230°C. Beechwood cubes, with a higher content of thermally labile pentosan sugars, start to react at a somewhat lower temperature than fir wood.

In the absence of a quantitative analytical treatment of the data in terms of heat balance and heat transfer, this work is of little value in obtaining a more than qualitative picture of the processes involved.

Subject Headings: *Wood, thermal decomposition of.*

W. G. Berl

Wolfhard, H. G. (Thiokol Chemical Corporation, Denville, New Jersey) "Problems Connected with Afterburning of Rocket Exhausts," *ARS Propellant Thermodynamic and Handling Conference, Columbus, Ohio*, 457–472 (1959)

This is one of a series of papers by the author dealing with ignition of combustible mixtures by hot gases. The present paper is concerned primarily with the source of light emission from rocket exhausts and in particular with the specific case in which the rocket exhaust contains combustible gases which ignite and burn outside the rocket chamber. Methods of ignition of these gases and possible ways of inhibiting this ignition are considered.

Ignition properties of both laminar and turbulent jets are investigated. Laminar jets were produced by passing the gas through a small bore ceramic tube immersed in a furnace. Turbulent jets were produced by allowing gases from a confined methane-oxygen-nitrogen explosion to escape through a short length of small bore tubing. In both cases the heated jet emerged into a vessel through which an explosive mixture was circulated and the temperature of the jet necessary to cause ignition was recorded.

Results showed that the relative ignitibility of fuels depends to a large extent on whether the jet is laminar or turbulent, with ignition occurring more readily with a laminar jet. The amount of fuel in the exhaust stream does not seem to be critical in deciding whether ignition occurs or not, although the type of fuel present is of overriding importance. Lead tetraethyl and iron carbonyl, usual additives for preventing knock, showed little influence on "hot gas" ignition while methyl bromide had a strong inhibiting effect, indicating afterburning may be influenced appreciably with the use of additives. Hot jets of both hydrogen and carbon monoxide ignite at low jet temperatures when injected into air—much lower than hydrocarbons—indicating that the important question in afterburning is whether the unburnt fuel in rocket exhausts "degradates" in the chamber to form hydrogen and carbon monoxide or whether a simple pyrolysis leads rather to methane and carbon particles. In any event, the study indicates that after due study it may be possible to reduce, if not completely eliminate, afterburning in rocket exhausts.

Subject Headings: *Rockets, afterburning of exhausts of; Ignition, of rocket exhausts.*

I. R. King

19

Zabetakis, M. G. and Burgess, D. A. (U.S. Bureau of Mines, Pittsburgh Pennsylvania) "Research on the Hazards Associated with the Production and Handling of Liquid Hydrogen," *Wright Air Development Division, WADD TR 60–141* (June 1960)

The use of liquid hydrogen as a fuel has introduced hazards which required the obtaining of basic data to permit definition of procedures to protect personnel and equipment if spillage of this fuel occurred and to establish distance requirements for the storage of varied quantities of the fuel from other structures. The results of this work briefly are:

1) In addition to the known hazards associated with hydrogen vapor, the hazard of the condensation of oxygen from air in liquid hydrogen is present. Mixtures of oxygen and hydrogen are shock sensitive and therefore require special precautions to exclude oxygen from hydrogen storage facilities.

2) The rate of liquid hydrogen evaporation has been satisfactorily expressed, by relating the decrease in liquid level (Δy) with time (t) where heat conduction is limited to conduction through the surface of contact, by the following equation:

$$\Delta y = \frac{(R)(2K)(T_i - T_o)t^{1/2}}{\rho L(\pi k)^{1/2}}$$

where $R = \dfrac{\text{total surface area}}{\text{projected area}} \geqq 1$

K = thermal conductivity of the surface material

ρ = liquid-hydrogen density

L = latent heat of vaporization of hydrogen

$T_i - T_o$ = difference in initial and cooled temperature of surface material

k = thermal diffusivity of the insulating material

This relationship has been shown to fall in the range of experimental data obtained from large-scale evaporation tests from a moist sandy soil.

The initial flash vaporization rates of liquid hydrogen were determined experimentally to obtain a crude indication of these rates on smooth macadam, steel, and gravel surfaces. The effect of the high specific surface area of the gravel on the evaporation rate was quite marked.

3) The distribution of the flammable volumes formed by spilling 0.5 to 7.4 liters of hydrogen was found dependent upon the rate of vaporization and the rate of mixing with the surrounding air. The former depends upon the rates of liquid spillage and heat transfer to the liquid. The latter depends upon the rates of heat transfer and air mixing with the hydrogen vapor. The experimental data showed that

a) the liquid vaporized sporadically initially and thus produced nonuniform vapor-air mixtures, and

b) the heights of the visible vapor clouds which formed above the liquid spill area were less than the heights of the flammable spaces. The differences in these heights varied with the relative humidity, air movement, and the time elapsed after spillage.

4) Ignition of the combustible mixtures above a liquid-spill area produced flames with dimensions that depended upon spill quantity, spill rate, nature of the surface upon which spillage occurred, and the location and time of ignition. Under conditions where 8 to 89 liters of liquid were spilled rapidly on a gravel

20

surface which was twenty inches below an open flame, it was found that the maximum flame dimensions were related to the quantity of liquid hydrogen as follows:

$$H_{max.} = W_{max.} = 7\sqrt{V_1} = 17.8\sqrt{M}$$

where $H_{max.}$ and $W_{max.}$ = max. flame height and width in feet
V_1 = liquid volume in liters
M = liquid weight in pounds

Under conditions where the ignition times varied from zero to 15.8 seconds, the maximum flame volume $V_{f\,max.}$ (cu. ft.) was found to be related to the liquid spill volume V_1 (liters) in this manner:

$$V_{f\,max.} \approx 750 V_1$$

The radiant energy emitted by these hydrogen spill fires were determined over the ignition time range of zero to 6.3 seconds. These data showed that

a) the total radiant energy generated depended upon the quantity of the liquid and the time delay before ignition,

b) the rate of energy release depended markedly on the ignition time delay, and

c) a considerable proportion of the radiant energy was absorbed by the moisture in the air. The fraction of radiation intensity (I/I_o) at any distance (r, feet) was found to be

$$I/I_o = e^{-0.015wr}$$

where w = per cent water vapor in the air.

The blast, or "over pressures" produced by the hydrogen vapors above the liquid hydrogen pools showed that the "over pressure" was proportional to

a) 1/D for distances (D) between 20 to 80 feet from the fire source and gave pressures in the range of 0.3 down to 0.07 psi.

b) $1/D^2$ for distances (D) between 80 and 200 feet and gave pressures in the range of 0.07 down to 0.01.

5) It was shown that hydrogen did not require a "burning in" period as is common for hydrocarbons since normally the liquid is kept at its boiling point by conductive heat transfer from the ground. To estimate the burning rates of hydrogen for large diameter pools, ½ to 4 ft. diameter pool fires of butane and hexane were used to test a mathematical analysis of liquid regression rate versus tray diameter by H. C. Hottel.[1] This equation represented the experimental data of these compounds satisfactorily and as a consequence, this equation was used to extrapolate the hydrogen data for fires of less than one ft. diameter to the "limiting" burning rate for large (infinitely large) pool diameters. The "limiting" burning rate for hydrogen was thus found to be ca. 0.6 in/min. For comparative purposes, the "limiting" rates for butane, heptane, and benzene were 0.32, 0.28, and 0.24, respectively. As a point of supplementary interest, the steady burning rates for 4 ft. diameter tray fires are only slightly less than the "limiting" rates. The correctness of the "limiting" rate of liquid hydrogen was verified by a straight-line extrapolation though data points of methanol, UDMH, benzene, hexane, and

21

butane which related "limiting" burning rate to the ratio of heat of combustion to the heat of vaporization of the liquid.

Reference

1. Hottel, H. C. Review of "Certain Laws Governing Diffusive Burning of Liquids," by V. I. Blinov and G. N. Khudiakov *Fire Research Abstracts and Reviews* 1, 41–44 (1958)

Subject Headings: Hydrogen, liquid, hazards associated with handling of.

R. A. Gorski

Coleman, E. H. (Joint Fire Research Organization, Boreham Wood, England) "Effects of Compressed and Oxygen-Enriched Air on the Flammability of Fabrics," *British Welding Journal* 6, 406–410 (1959)

While flammability of fabrics has been studied extensively and specifications have been established for testing and evaluating flameproofing of materials, the author points out that current flameproofing tests and methods are not appropriate to those industrial processes in which compressed or oxygen-enriched air are used. In such processes as welding where fire hazards exist, workers customarily wear clothing of low flammability such as asbestos, thick wool, or leather and in addition overalls treated with flame retardants. The purpose of this study was to determine quantitatively the extent of reduction in protection provided by flame retardants on fabrics in both oxygen-enriched and compressed air environments.

Two experiments were conducted: one, to determine the effect of oxygen enrichment on the flame speed of untreated and treated fabrics; the other, to determine the effects of compressed air on flammability and compare the results with oxygen enrichment. The oxygen enrichment experiment consisted of suspending narrow, long strips of fabric from an arm of a torsion balance within a cabinet in which a slow flow of oxygen-enriched air was admitted. Ignited at the bottom, the vertical flame speed was calculated from a photographic record of weight loss with time. It was noted that with slight oxygen enrichment the luminous flame separated into two zones which moved at different rates over the fabric tested; at higher oxygen concentration, the flames merged. This behavior was attributed to different modes of burning and thought to be responsible for an inflection of the burning rate curve plotted against oxygen concentration.

The compressed air experiment used small fabric specimens suspended in a pressurized cylinder, combustion being initiated electrically with Nichrome wire and a celluloid strip at the bottom of the specimen. Burning time for complete combustion measured visually was used to compare the effect of varying pressure.

The results of these experiments show that there are limits of oxygen concentration or air pressure above which fabrics burn regardless of the quantity of flame retardant added, and also that there are limits of flame retardant beyond which further additive has little or no effect. The limits vary with different fabrics and retardants, the best flame retardant of those studied being a boric acid, borax (30%:70%) mixture which provided protection with relatively low retardant concentration (10%) to about 32% oxygen concentration in air by volume and in compressed air to over 75 psig. The effect of oxygen enrichment was considerably greater than that of air pressure, in reducing the protection afforded by flameproofing.

22

ABSTRACTS AND REVIEWS

The results of this work should be beneficial in establishing adequate flame-proofing for fabrics used for personnel protection in gas welding and similar industries.

Subject Headings: *Fabrics, flammability of; Flammability, of fabrics.*

D. Dembrow

Zeplichel, F., Wegener, W., and Peters, H. (Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, Germany) "Flammability and Combustibility of Organic Foam Materials," *Materialprüfung* 1, 297–302 (1959)

The complex problems of flammability and combustibility of materials can best be solved by testing methods that are clearly and exactly defined with the added demand that the results be reproducible.

The authors, in conjunction with the German Association for Materials Testing, describe two test devices which were developed to determine (1) the flammability, (2) the velocity of flame propagation on foam plastics and some non-foam materials.

It is necessary to know something about the thermal conductance of the new man-made materials since inflammation often is associated with direct contact of a hot area. The flammability of foam plastic is defined as the ability to burn without additional heat supply after ignition.

One of the test devices described is the so-called flame-pendulum method. The test specimen is attached to a pendulum which swings through a flame of definite size. Employing counterweights, the swing-time of the pendulum can be varied in different ways until finally the inflammation of the material results in the course of only one swing of the pendulum. Problems associated with this device include the interference of air convection currents which tend to prevent inflammation or cause immediate extinguishment. This test device was abandoned.

Another apparatus consists of a notched rotating disk set between sample and burner. The revolution rate of the plate determines the length of time the flame is in contact with the test samples. The notches are enlarged until at least 80 per cent of the samples are ignited during one spin of the disk.

Other apparatus are described to determine the rate of flame propagation through test samples. These tests proved inadequate due to varied heat losses which contributed to the extinguishment of the burning sample. Flame propagation velocity measurements are made by positioning the sample at 90° and 45° to the ignition source. The dimensions of the samples are carefully regulated. The number of tests where ignition occurred also are closely monitored.

Subject Headings: *Flammability, of organic foams.*

P. Breisacher

Stott, J. B. (University of Otago, Dunedin, New Zealand) "Influence of Moisture on Spontaneous Heating of Coal," *Nature* 188, 54 (1960)

In recent experiments the loss of heat by evaporation of moisture from sub-bituminous coals subjected to a dry air stream has been shown to be greater than the heat produced by oxidation. It is suggested that the transfer of heat by evaporation of moisture can be of overriding importance in spontaneous heating.

23

The moisture was removed from a crushed sample of sub-bituminous coal at 105°C in a vacuum of 0.05 mm. Hg. When oxygen saturated with moisture was passed through a 3 kgm sample so treated at the rate of 1 l/min, ignition occurred after 30 minutes. Using dry oxygen, ignition occurred after 12 hours. Experimental details are presented.

Subject Headings: *Coal, moisture effect on spontaneous heating.*

G. L. Isles

II. Thermal Decomposition

Martin, S. B. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "Gas Chromatography Application to the Study of Rapid Degradative Reactions in Solids," *Journal of Chromatography* **2**, 272–283 (1959)

With convincing experimental evidence, this paper describes a method which allows the kinetics of many chemical reactions to be studied. Some of the very important reactions to which this technique may be applied are the ignition of explosives, the burning of solid propellants, the degradative processes induced in solids by ionizing radiations, and the rapid pyrolysis of organic compounds. The author states that the method is applicable to reactions of any substance whose vapor pressure is small. The material must decompose (at least partially) to gaseous products under the influence of applied stimuli. Not the least of the requirements for the qualifying substance is its ability to decompose fast enough so that the reaction runs its course (or nearly so) in one minute or less.

The method involves primarily the exposure of an organic solid, suspended in helium carrier gas, to very intense radiant energy. So powerful is this source that the energy is similar in spectral distribution and radiant power to that which is emitted during nuclear weapon detonation. Such intense radiant energy is produced in the laboratory by high-current carbon arcs. High temperatures are developed in a very short time in a solid when it is exposed to this radiation. Depending upon the intensity of the energy source, the solid may be decomposed to vapors in a small part of a second.

The study described in this paper is the rapid pyrolysis of a-cellulose in thin sheet form. The material was cut in a circular wafer no larger in diameter than the field of uniform irradiance provided by the source. The wafer was suspended behind a quartz window in the center of the carrier gas (helium) stream. Since vapors resulting from an irradiated sample must be carried away quickly and uniformly with little or no "lag," this necessitated high carrier gas flow rates throughout the system, including the chromatography column. To achieve this flow rate, it was necessary to use "larger-than-ordinary" diameter copper tubing for the column and reduced pressure at the column exit.

The analytical procedure used to characterize the resulting vapors due to pyrolysis consisted of the use of two different systems. The first separated the condensibles into rough fractions with dynamic cold traps and analyzed the non-condensibles with suitable solid adsorption chromatography columns. Later, the materials condensed in the cold traps were analyzed by liquid partition methods. The author suggests that liquids or any substances which can not be readily pro-

24

ABSTRACTS AND REVIEWS

duced in sheet form could be handled by impregnating asbestos or quartz fiber paper with the substance, and proceeding as in the case of the thin sheet material.

Cold traps were designed to produce turbulent gas flow along the full length of the immersed tubing. Cold trap media were selected according to the particular column packing in use at the time. The following drawbacks are pointed out about this type of vapor separation: since the system is not at rest there is always a finite equilibrium vapor pressure; secondly, the trap efficiency can never be 100 per cent for any substance; no matter how small the vapor pressure becomes it is always finite at any real temperature; lastly, materials which are supposed to pass the trap may be carried down and occluded with condensibles despite the fact that at the trap temperature their vapor pressure may exceed greatly their partial pressure in the gas phase. Recognizing these potential sources of error, the author outlines three steps which were taken to avoid or at least evaluate their effect.

A special design of a chromatography unit to analyze the noncondensibles which incorporated a single detector was utilized. The detector unit was enclosed in a massive brass block which was immersed in a constant-temperature water bath. The element formed one arm of a very stable bridge circuit. The unbalance of this bridge was recorded on a chart-type potentiometer recorder having 0.5, 2.5, 10, and 50 mV full-scale sensitivities. A calibration was obtained by introducing, with a hypodermic syringe, measured quantities of pure gases or gas mixtures whose composition had been previously measured with a mass spectrometer. A very useful table which gives combinations of cold traps and columns with comments as to their better utility is presented.

Analysis of the condensed fractions of the degradation products was accomplished by use of a gas-liquid partition chromatography apparatus immersed in a constant-temperature water bath. The unit could be operated in the temperature range of 10 to 90°C with a high degree of temperature control and constancy. Because of the high temperature limitation of the bath fluid, the system does not lend itself to analysis of tarry materials. Columns were interchangeable so that various lengths (1 to 20m) could be incorporated in the system. The condensate from cellulose pyrolysis could be analyzed with columns 2 meters long filled with dinonyl phthalate or polyethylene glycol. The carrier gas for the vaporized samples was, as before, helium. The detector unit in this case was a commercially available thermal conductivity cell.

The author concludes that the methods described in this report have proven quite satisfactory for the investigation of the reaction products of the pyrolysis of cellulosic solids irradiated by intense radiant energy. Products whose molecular weight is rather low (less than 50) can be analyzed directly by a chromatograph incorporated in the exposure equipment. The apparatus discussed in this report, when used in connection with the conventional chromatograph, permits complete separation of all products evolved in cellulose pyrolysis.

In the reviewer's opinion, this paper offers the combustion kineticist a very useful tool. Its application to the burning of rocket propellants could be quite rewarding, and may lead to a solution of the perplexing problem of rocket exhaust products.

Subject Headings: *Degradation, study of rapid by chromatography; Chromatography, study of degradation by.*

C. O'Neal

25

Higgins, H. G. (Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia) "The Degradation of Cellulose in Air at 250°C as Shown by Infrared Spectroscopic Examination," *Journal of Polymer Science* 28, 645–648 (1958)

Purified α-cellulose pulp, average degree of polymerization 310, prepared from eucalyptus wood was studied. For infrared examination finely ground samples were dispersed in potassium chloride as pressed disks.

Drying at 70°C for 17 hours at 0.5 mm. Hg. pressure left the spectrum between 2 and 14μ nearly unchanged, although a very weak, sharp, absorption band appeared at 7.15μ. The CH stretching band showed a subsidiary peak at 3.45μ, and a faint trace of the C=O stretching band appeared at 5.8μ. At 175°C there was slight C=O absorption after 3.5 hours but no other change. At 260° to 270°C the C=O band was stronger but the other main features of the spectrum remained. In air at 260° to 270°C for 2 hours the C=O band became very strong; after 17 hours it dominated the spectrum.

TABLE 1

CHANGES IN ABSORPTION WITH TIME OF HEATING OF α-CELLULOSE IN AIR AT 250°C

Approx. wave length μ	Assignment	Time of heating hours				
		0	3	6	17	30
3.4	CH stretch	0.17	0.09	0.04	0.02	0.03
7.0	HCH deformation	.08	.02	0	0	0
8.6	Glucopyranose ring vibration	.19	.08	.02	0	0
9.5	OH deformation (or C—OH stretch)	1.5	.75	.55	.11	.08
11.2	C_1—H deformation	.04	.03	.02	0	0
5.8	C=O stretch	0	.18	.47	.61	.44
8.1	OH deformation (carboxyl)	0	0	.09	.16	.11

Changes occurring in air at 250°C are shown in Table 1. In addition the OH stretching absorption ($2.9–3.0\mu$) decreased and the C=C absorption near 6.1μ increased but interference arose from bands attributable to adsorbed water. Rapid decline in the HCH deformation band suggests preferential oxidation of primary hydroxyl. Decline in the ring vibration does not necessarily imply ring cleavage (the band may be due to a hydroxyl group). After 6 hours only a vestige of cellulose structure remained. After 12 hours the cellulose-OH deformation absorption at $9–10\mu$ practically disappeared, the carboxyl-OH deformation band at 8.1μ became strong, and a band appeared at 3.8μ attributable to bonded OH stretching in the carboxyl group. On neutralizing with sodium hydroxide, most of the C=O band and the band at 8.1μ disappeared, indicating predominance of carboxyl over aldehyde or ketone groups, and new bands at 6.4 and 7.3μ due to symmetrical and antisymmetrical vibrations of the COO$^-$ group appeared. Acidification then reversed the changes caused by neutralization.

In 24 hours the composition of the residue changed from $C_{3.6}H_{6.5}O_{3.1}$ to $C_{5.0}H_{3.0}O_{2.3}$. The color changed to black. No aromatic nuclei appeared in the spectra of the residues nor in that of a trace of condensate collected in the cooler part of the apparatus.

The oxidative nature of initial degradation of cellulose in air appears in the

26

ABSTRACTS AND REVIEWS

development of C=O groups. The carbohydrate spectrum is soon lost. After 12 hours a relatively stable structure with aldehyde groups replaced by carboxyl develops. Decline in CH and OH, changes in elementary composition and color, and distribution of C=O stretching bands suggest the development of nonaromatic, but somewhat unsaturated cyclic structures.

Subject Headings: *Cellulose, degradation of; Thermal decomposition, of cellulose.*
F. L. Browne

Dacey, J. R. and Cadenhead, D. A. (The Royal Military College of Canada, Kingston, Ontario, Canada) "The Formation of Carbon from Polyvinylidene Chloride," *Proceedings of the Fourth Carbon Conference,* 315–319 (1960)

Polyvinylidene chloride (Saran) and partially carbonized polyvinylidene chloride were decomposed at various temperatures between 130° and 700°C. The purpose of the experiments was to clarify the mechanism of decomposition of Saran. Rates of decomposition, infrared spectra, density, and porosity were measured as functions of the extent of carbonization.

In the pyrolysis experiments, the weight loss or conversion to carbon and hydrogen chloride, as measured with a quartz helixal McBain-Baker balance, was found to be very small below 140°C. Above 140°C, the initial decomposition rate was rapid, then decreased exponentially with time. The initial decomposition rate increased with increasing temperature, while the plateau of slow decomposition rate was higher as the temperature of carbonization increased. The partially decomposed Saran samples had similar characteristics. The initial weight loss followed first-order kinetics. Computed activation energies for 0, 10, and 45 per cent decomposed samples were 28,000, 29,000, and 34,000 cal/mol, respectively. The plateau region of the decomposition rate curve was believed to be due to an equilibrium within the solid. It was suggested that the equilibrium would be shifted by a higher temperature, causing a loss of HCl and a new equilibrium plateau at the new temperature.

The infrared spectrum as obtained by the potassium bromide pellet technique showed that C-Cl bonds and aliphatic C-H bonds disappeared as carbonization progressed while double bonds and aromatic structure were formed. The data were not inconsistent with the conclusions of others that the Diels-Alder mechanism occurred during Saran decomposition.

In the density and porosity measurements, both helium densities and apparent densities decreased as the extent of carbonization increased up to a weight loss of 40 per cent. Subsequent heating and further weight loss was accompanied by a rapid increase in the true density and in the porosity of the sample until complete expulsion of all the HCl. Pore volumes were calculated as the difference between apparent and helium densities. It was suggested that the condensed aromatic rings formed cage-like tunnels after about half of the HCl was removed, giving rise to a rigid porous graphitic structure.

Subject Headings: *Carbon, formation of, from polyvinylidene chloride.*
J. M. Singer

27

III. Heat and Material Transfer

Martin, S. B. (U.S. Naval Radiological Defense Laboratory, San Francisco, California) "A Simple Radiant Heating Method for Determining the Thermal Diffusivity of Cellulosic Materials," *Research and Development Technical Report USNRDL–TR—352, DASA–1136* (April 1959)

Thermal diffusivity, the ratio of thermal conductivity to volumetric heat capacity, is an important parameter in transient heat transfer work. In calculation of values of this parameter from its component properties, inadequacy of temperature dependent data often results in gross errors in diffusivity values. Hence, a method of direct determination of diffusivity values is desirable.

Prior methods of direct measurement of thermal diffusivity have employed sinusoidal surface heating with at least two inputs varying as to frequency. A more recent development succeeded in eliminating one of the sinusoidal inputs. Butler and Inn[1] developed a technique of computation based on the "long time solution" of the one-dimensional Fourier equation, which allowed the use of a steady-state input, thus simplifying experimental procedure and resultant calculations. The authors have adapted this method to use in measuring thermal diffusivity of alphacellulose paper. The method is general to other organic solids.

The experimental apparatus was designed necessarily to satisfy the boundary conditions of the governing equation, namely, that the heating rate was a constant and the temperature gradient at the distance L, i.e. the unheated sample face, from the heated face be equal to zero. The latter requirement was met by mounting a sample of 2L thickness in the center of an optical bench and heating at the same rate from both sides. The first condition was met by restricting the temperature range on the heated face.

The sample was prepared from six rectangles of a-cellulose sheet 0.031 inch thick and 3 inches by 3½ inches on a side. The sample was bonded together with aqueous methyl cellulose. Thermocouples with foil junctions 0.0010–0.0012 inch thick were bonded between the lamina near the sample center. The cellulose contained two per cent carbon black by weight. The heating sources were two lightly frosted commercial photoflood bulbs. Preliminary tests were run and adjustment of heating lamps made until the embedded thermocouples indicated equal heating rates from each side.

Experimental runs were performed with the lamps at varying distances from the respective surfaces and with different lamp voltages. This technique varied the irradiance level (constant voltage, varying distances) and color temperature (constant distance, varying voltage). In no case was a significant data trend observed. It is suggested that the use of glow bars would be superior to the photoflood lamps because of the selective transmission of the lamp glass. A mean value of thermal diffusivity in the temperature range 40° to 210°C is reported as $1.06 \pm 0.06 \times 10^{-3}$ cm²/sec. A maximum value was observed in the 60° to 100°C temperature range and is thought attributable to desorption of moisture.

Reference

1. Butler, C. P. and Inn, E. C. Y. "Thermal Diffusivity of Metals at Elevated Temperatures," *Thermodynamics and Transport Properties of Gases, Liquids and Solids* (McGraw-Hill Book Co., Inc.) 377–390 (1959)

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

H. N. McManus, Jr.

ABSTRACTS AND REVIEWS

Martin, S. B. and Ramstad, R. W. (U.S. Radiological Defense Laboratory, San Francisco, California) "Temperature Profiles in Thermally Irradiated Cellulose Accompanying its Spontaneous Ignition," *Research and Development Technical Report USNRDL–TR–353, DASA–1142* (May 1959)

At present the literature contains a variety of estimates of surface temperature for cellulosic materials at the time of ignition. These range in value from 250° to 600°C. The characteristic irradiance associated with these values has been less than or equal to 5 cal/cm² sec. Some measurements at radiant inputs up to 20 cal/cm² sec had suggested surface temperatures of between 700° and 800°C. The work outlined in this report was carried out on black (2 per cent by weight carbon black) α-cellulose at irradiance levels ranging from 5 to 16 cal/cm² sec with the intent of clarifying the situation.

The experimental portion of the work was performed on cellulose sheets formed from four lamina with thermocouples located at the interfaces. The irradiated lamina was of 0.011 cm. thickness and the others of 0.049 cm. thickness. Binding of the laminate was accomplished with an aqueous solution of methylcellulose. A monitoring thermocouple was located in front of and above the irradiation zone to detect ignition; a fifth thermocouple was located on the rear of the sample. Irradiation was accomplished with a focused carbon arc with a 0.9 inch diameter uniform spot and irradiance level variable up to 22 cal/cm² sec.

The temperature-time recordings showed a reduction in the rate of temperature rise at about 100°C which was thought to be due to moisture desorption. Additionally, between 400° and 500°C the shallow thermocouples indicated a drop in temperature of as much as 50°C. It is proposed by the authors that this drop in temperature is a manifestation of a change in the mechanism of flash pyrolysis from a slow, low temperature process controlled by exothermic reactions to a rapid, high temperature mechanism dominated by endothermic reactions. Prior investigations had attributed observed surface temperature fluctuations to convection surges.

Observations showed that, for the test range covered, no discernible temperature rise occurred on the back of the sample, hence, the sample could be likened to a semi-infinite solid. The experimental data was generalized by plotting the product of the observed temperature rise and the root of the ratio of the time to ignition to the observed time versus the dimensionless depth (root of the Fourier modulus). Extrapolation of the data to zero depth allowed estimation of the surface temperature at time of ignition. The uncertainty in the data led to the range of 600° to 900°C for the surface temperature. In view of the wide range of published surface temperatures at ignition and the variance in heating rate, it is suggested that "ignition temperature" is dependent on irradiance level.

Subject Headings: *Cellulose, ignited, temperature profile in.*

H. N. McManus, Jr.

IV. Diffusion Flames

Wood, B. J., Wise, H., and Inami, S. H. (Stanford Research Institute, Menlo Park, California) "Heterogeneous Combustion of Multicomponent Fuels," *Combustion and Flame* **4**, 235–242 (1960)

This paper summarizes much of the recent work of Wise and his collaborators on the burning of fuel droplets suspended on quartz fibers or porous spheres. Attention is focused mainly upon initially unmixed systems (diffusion flames) involving binary liquid fuel mixtures and air. The investigations may be divided into three main categories (a) measurement and analysis of the droplet burning rate, (b) measurement of the surface temperature of the droplet, and (c) observation and discussion of an unsteady "disruptive" mechanism of droplet burning.

Measurements made with heptane—butanol-1, 2,2,4-trimethylpentane—butanol-1, and dibutyl ether—pentanol-1 mixtures show that, while the burning rate coefficient K is constant (except during an ignition period comprising approximately 15 per cent of the total burning time), when either of the liquid fuel components is present in excess, at some intermediate liquid compositions K varies with time. Here $K = dD^2/dt$ for a droplet in which no fuel is added internally, D = droplet diameter, and t = time; established quasi-steady-state spherically-symmetrical theories predict K = constant for burning droplets. The authors postulate that the quasi-steady-state approximation remains valid and chemical reactions within the droplets are of negligible importance in their experiments; instead, they propose to account for the variation in K by assuming that an equilibrium fractional distillation process occurs at the droplet surface. This would lead to a variation in the average composition of the droplet (and hence in the burning rate) with time. A batch-distillation calculation of the liquid and equilibrium vapor compositions as functions of time (for the droplets used), by means of liquid-vapor equilibrium diagrams measured by the authors, yielded reasonably good agreement between measured K values and those computed from a quasi-steady-state theory. Hence the surface interface condition is probably one of phase equilibrium for these experiments. The fact that many multicomponent mixtures (e.g. kerosene) have K≈constant is explicable on the grounds that the individual components are so similar in their important properties (namely, densities and heats of vaporization) that the change in K as a consequence of fractional distillation is negligibly small.

Measurements of surface temperatures of burning droplets were made by attaching a thermocouple to a fuel-wetted porous sphere and also by suspending fuel droplets from a thermocouple junction. The measured temperatures, which are tabulated for ethanol, butanol-1, pentanol-1, octanol-1, 2,2′-oxydiethanol, heptane, octane, and kerosene, are consistently 10 to 15 per cent below the normal boiling point of the liquid (in °C). Theoretical surface temperatures, which are on the average about 5 per cent below the experimental values, are also quoted, but it is not made clear in the paper or the reference cited exactly how the theoretical results were obtained. It is interesting to note that application of the (equilibrium) Clapeyron equation at the liquid-gas interface (in conjunction with the usual theoretical analysis of the gas-phase processes, as described in Ref. 1) for the fuels studied here yields surface temperatures approximately in agreement with these measurements. This result provides further evidence for phase equilibrium at the droplet surface.

30

ABSTRACTS AND REVIEWS

With some binary mixtures of aliphatic hydrocarbons, e.g. a 50–50 mole per cent heptane-hexadecane mixture, it was observed from motion pictures and burning rate measurements that bubbles tend to form inside the droplet and burst, ejecting small sprays of liquid, thus producing continual disruptions in the burning rate curve. It was postulated that radiative heat transfer to the interior of the droplet is responsible for this effect, a conclusion which was supported by the observation that the addition of small quantities of black (absorbing) material to the liquid enhanced the tendency toward "disruptive" burning while the addition of small amounts of white (reflecting) particles had no effect. It was also suggested that large differences in the boiling points of the components of the fuel mixture would favor "disruptive" combustion, since local inhomogeneities may then produce regions with a lower boiling temperature, i.e. an increased tendency toward vaporization or bubble formation. The authors speculate upon the existence and possible effects of "disruptive" burning in practical combustion chambers, but are unable to reach definite conclusions because of the different radiative environment and smaller droplet sizes in practical systems.

Reference

1. Williams, F. A. *Journal of Chemical Physics* 33, 122–144 (1960)

Subject Headings: *Fuels, heterogeneous combustion of multicomponent; Combustion, of multicomponent fuels.*

F. A. Williams

V. Combustion Principles

Spalding, D. D. (Imperial College, London, England) "The Theory of Burning of Solid and Liquid Propellants," *Combustion and Flame* 4, 59–76 (1960)

The author examines the problem of determining the burning rates of condensed phases for a simple model of combustion. The theory is carried out in some detail for several types of condensed-gas phase interface reactions and general conclusions concerning burning rate dependence on pressure and nature of surface reaction are discussed.

In the model, the condensed phase is homogeneous and the process is assumed to be one-dimensional and laminar. The liquid or solid propellant first undergoes a phase change or reaction and then a chemical reaction in the gas phase. Thus, the reaction is of the form:

$$A \rightarrow B \rightarrow C$$
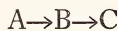
The step, A to B, may be a simple phase change or a surface reaction involving chemical reaction. The gas B, which is treated as a simple compound, undergoes a gas phase chemical reaction to form compound C. Gas phase mixing due to diffusion is considered with the assumption that the Lewis number is unity. This assumption leads to considerable simplification of the analysis because it implies that the enthalpy of the gas mixture is constant and hence that the local concentration depends in a simple manner on the temperature.

The equations for the gas phase reaction are the usual equations for a laminar

31

flame; however, the upstream boundary conditions are different due to the presence of the condensed phase-gas phase interface at which the temperature and product concentration must be specified. Solutions for the gas phase equations are obtained by means of an approximate method, introduced in previous works by the author, for several arbitrary forms of the reaction rate expressed as a function of the local degree of reaction. The final form of the gas phase solution is presented as a plot of burning rate as a function of the degree of reaction at the condensed-gas phase interface for various values of a parameter which characterizes the shape of the reaction rate vs. degree of reaction curves. In these plots, the burning rate is normalized by the burning rate which exists when the degree of reaction at the interface is zero. The pressure dependence of the gas phase reaction is included in the normalization factor and hence is not explicitly specified.

These numerical results do not fix the burning rate since the degree of reaction at the condensed-gas phase interface has not been determined. This determination is made by assuming (a) a pressure dependence for the reaction A→B and (b) a pressure dependence for the burning rate used to normalize the gas phase burning rate solutions. The correct degree of reaction is that for which the mass flow rates for reaction A→B is the same as that for the reaction B→C. The numerical solutions obtained in this manner are then used as a basis for considering the effect of pressure on the burning rate for several types of the A→B reaction.

The combustion of a liquid propellant is considered for the special assumptions that (a) the value of the degree of reaction at the liquid gas interface is proportional to pressure to a small positive exponent and (b) the gas phase reaction is second order. For these assumptions it is found numerically that the burning rate vs. pressure curve has a maximum and approaches zero at both high and low pressures.

The effect of pressure on the burning rate of a solid propellant, when the surface reaction is a decomposition, is examined numerically with similar assumptions: (a) the decomposition rate is proportional to a positive power of the degree of reaction at the solid-gas interface and (b) the gas phase reaction is second order. This model for the interface reaction leads to a plateau in the burning rate vs. pressure curve that is qualitatively similar to those observed for certain solid propellants. Surface decomposition by foam reactions are discussed qualitatively and are compared with simple decomposition reactions.

The remainder of the paper deals with the effect on the propagation rate of radiant heat loss from the condensed phase-gas phase interface. A qualitative analysis is carried out and the influence of heat loss is assessed for a variety of surface reactions. For certain of the assumed surface reactions, low pressure and high pressure burning limits are demonstrated.

In this paper, the author has attempted to explain many of the phenomena observed in the combustion of liquid and solid propellants by means of a model in which the chemistry has been greatly simplified. Unfortunately, the actual chemical phenomena appear to be complex and also important; consequently, the theory as it stands must be pushed beyond plausible limits to make it conform with the experimentally observed phenomena. For example, the theory predicts a plateau in the burning rate-pressure curves, but does so only when the propellant surface temperature approaches the adiabatic flame temperature. In fact, solid propellant surface temperatures are usually of the order of ¼ to ⅓ of the adiabatic flame tem-

perature and in addition, decomposition rate data indicate that in the plateau region no exceptionally high surface temperatures are encountered.

Although the solutions obtained by this analysis may be of use when the chemical phenomena are better understood, the present paper does little to elucidate the complex processes which fix solid and liquid propellant combustion rates.

Subject Headings: *Propellants, theory of burning.*

E. E. Zukoski

Wolfhard, H. G. (Thiokol Chemical Corporation, Denville, New Jersey) and **Bruszak, A. E.** (U.S. Bureau of Mines, Pittsburgh, Pennsylvania) "The Passage of Explosions through Narrow Cylindrical Channels," *Combustion and Flame* **4**, 149–159 (1960)

This paper is concerned with the mechanism by which explosions are transmitted through narrow cylinderical channels and it is aimed at obtaining a better understanding of flame traps and the flameproofing of electrical equipment in mines. It is closely associated with some earlier studies by one of the authors dealing with ignition of combustible mixtures by hot gases.[1]

The experimental arrangement consisted of two explosion chambers connected by a cylindrical channel whose length and diameter could be varied. Both chambers were filled with combustible mixtures and the conditions necessary for an explosion, initiated in the smaller chamber to be transmitted through the channel to initiate an explosion in the larger chamber, were studied. Stoichiometric methane-oxygen-nitrogen mixtures were used in the smaller chamber and were ignited by means of a spark. The strength of the explosion was measured in terms of the oxygen index (oxygen/oxygen plus nitrogen) of the mixture. Methane-, ethane-, or carbon monoxide-air mixtures were used in the larger chamber. Successful transmission of an explosion through the channel was indicated by an explosion in that chamber. Optical windows permitted schlieren photographs of the transmitted wave to be obtained. The effect of channel diameter, channel length, and mixture strength of the fuel-air mixture in the larger chamber was studied as a function of the oxygen index of the mixture in the smaller chamber.

Results were analyzed in terms of three possible mechanisms by which an explosion could be transmitted from one chamber to another.

A. A laminar or turbulent flame is carried through the channel and propagates without discontinuity into the larger chamber

B. The channel extinguishes the flame only gradually so that a certain channel length is necessary to quench the flame completely.

C. The flame front extinguishes virtually at the channel entry and ignition in the larger chamber is due to the hot jet of burnt gases issuing from the channel.

Mechanism A was found to be applicable only for large diameter channels where the channel diameter is larger than the quenching diameter of the flame. Mechanism B implies longer channels are more effective in inhibiting an explosion than are shorter ones. This was not supported by experimental evidence, which showed there is an optimum length for suppressing an explosion. Longer tubes permit transmission of the explosion. Mechanism C was found to be most favora-

33

ble for channels smaller than about 3 mm. in diameter. Under these conditions, ignition in the larger chamber was due to the hot jet of gas issuing from the channel. Schlieren photographs showed hot gases from the smaller chamber entered the large chamber as a turbulent jet and that eddies from this jet served primarily as the source of ignition in the larger chamber.

Reference

1. Wolfhard, H. G. "The Ignition of Combustible Mixtures by Hot Gases," *Jet Propulsion* 28, 798 (1958)

Subject Headings: *Explosions, passage through narrow channels.*

I. R. King

Knewstubb, P. F. and Sugden, T. M. (University of Cambridge, Cambridge, England) "Mass-Spectrometric Studies of Ionization in Flames. I. The Spectrometer and its Application to Ionization in Hydrogen Flames," *Proceedings of The Royal Society* A255, 520–537 (1960)

An apparatus is described for the extraction of ions from flames burning at atmospheric pressure, and for the subsequent mass analysis of the ions. The flame, at atmospheric pressure, impinges on a small hole in a thin foil separating a region where the pressure is maintained at 10^{-3} mm. Hg. In this way the greater part of the neutral molecules in the gas are pumped away, while the ions are focused by a series of electrodes in a train of chambers at successively lower pressures. They are analyzed in a fairly conventional type of mass spectrometer. A rather similar apparatus has been described by Deckers and van Tiggelen [1,2] which operates with a flame at reduced pressure. Broad agreement is obtained between the results of the two instruments.

It is important to know whether the ions which are detected reflect the ionic composition of the gas entering the sampling orifice. The authors have considered (1) secondary ionization, (2) charge transfer, (3) dissociation, and (4) ionic clustering, and conclude that the ions observed are representative of those emerging from the inlet. The effect of collision of the flame molecules with the wall in the orifice is not considered. This wall may be catalytically active in causing ionization. Ionic concentrations as low as $10^5/cm^3$ can be measured for ions ranging in mass from 10 to 400 atomic units.

A brief account is given of the ionization observed from premixed flames of hydrogen, oxygen, and nitrogen. The obvious feature of the data is the grouping of the pattern into subgroups which repeat at intervals of 18 mass units. This is a case of hydration or cluster formation by attachment of water molecules. The ion giving the largest peak is at mass 19, and appears to be hydroxonium (H_3O^+). The peaks at masses 20 and 21 stand in the correct relationship to that of mass 19 corresponding to the isotopic forms H_2DO^+ and $H_3{}^{17}O^+$ (mass 20), and $H_3{}^{18}O^+$ (mass 21), respectively. The peak at mass 18 was initially assigned to H_2O^+, but experiments in which argon was substituted for nitrogen as the diluent showed a decrease of the order of 10^3, and hence the peak at mass 18 appears to be due to NH_4^+. It is concluded that these hydrates occur to a large extent in the cooler parts of the flame and are considered to be a secondary phenomenon.

Experimental evidence is presented for the formation of H_3O^+ in the homo-

34

ABSTRACTS AND REVIEWS

geneous gas phase in a zone near the reaction rather than by catalytic interaction with the walls of the leak. The most likely reaction is

$$H + H + OH = H_3O^+ + e^-$$
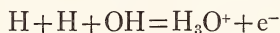
and the kinetics of this are considered. There is considerable doubt as to the heat of formation of this ion, its value being between 27 and 86 kcal.

Doubts about the heat of formation and kinetics of the NH_4^+ ion preclude quantitative results on many points. The ionization of nitric oxide is shown to be essentially a thermal phenomenon.

The rather high concentration of positive ions in hydrogen flames (of the order of 10^9 cm^{-3}) is in general agreement with previous values [3] reported for free electrons. This latter value was obtained by radio-frequency measurements of the conductivity of the burned gases of hydrogen flames.

No mention is made of the hydroxyl ion OH$^-$. Measurements of the OH$^-$ ion in the hydrogen flames indicate that there is only a very small amount present.

References

1. Deckers, J. and van Tiggelen, A. *Combustion and Flame* 1, 281 (1957)
2. Deckers, J. and van Tiggelen, A. *Seventh Symposium (International) on Combustion,* London: Butterworths Scientific Publications, 455 (1959)
3. Knewstubb, P. E. and Sugden, T. M. Transactions of the Faraday Society 54, 372 (1958)

Subject Headings: *Flame, ionization in; Ionization, in flames.*

W. C. Johnston

Gibbs, G. J. and Calcote, H. F.* (Experiment Incorporated, Richmond, Virginia) "Effect of Molecular Structure on Burning Velocity," *Journal of Chemical and Engineering Data* 4, 226–237 (1959)

The laminar burning velocities of a large number of fuels with air were measured and correlated. In order to facilitate the job, a simplified method, called the "apex-cone" method, was developed. The apex-cone method is a combination of the total area method and the frustum method, supposedly combining the simplicity of the former, and the accuracy of the latter. All experiments were performed with a range of burner diameters and fuel flow rates such that the burning velocity did not vary. The gas temperature, equivalence ratio, and moisture content were carefully controlled.

Data were recorded both by direct photographs of the flame and by shadowgraph images. The authors stressed the importance of choosing the proper flame outline in order to get consistent results. They concluded that the outer edge of the shadow cone is a true image of the reaction zone, and the image thus formed is relatively independent of the film-flame distance, because of the absence of refractive effects.

Using the flame area obtained from this flame outline, and assuming that the velocity profile could be calculated from the flowmeter reading, the authors obtained values of burning velocity as a function of equivalence ratio, which they compared with those of other workers. An evaluation was made of results obtained elsewhere, using other methods. When corrected for moisture content, initial temperature, burner diameter, and film-flame distance, the various measurements with

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35

cylindrical bunsen burners agree within about 5 per cent. These latter results nearly always give larger values of burning velocity than those taken with flame tubes, slot burners, spherical bombs, and soap bubbles, wherein the effects of flame curvature are minimized. The equivalence ratio at which maximum burning velocity occurs does not agree in all cases. The authors conclude from this analysis that the question still remains as to whether there exists an "absolute" burning velocity which is completely independent of the method of measurement.

The data was presented in groups, according to the number of carbon atoms and the type of molecular structure. The results were expressed as a function of equivalence ratio and at 25°C where possible. Compounds with insufficient vapor pressure at 25°C were studied at 100°C, along with a number of repeats for comparison. Although the title implies that there is a known effect of molecular structure on burning velocity, the authors state that not enough is known about the detailed structure of the various fuels involved to make it possible to predict the burning velocity of any specific substance.

Subject Headings: *Burning rates, effect of molecular structure on.*

J. K. Richmond

Brown, K. C. and Essenhigh, R. H. (Safety in Mines Research Establishment, Sheffield, England) "Dust Explosions in Factories: A New Vertical-Tube Apparatus," *Safety in Mines Research Establishment Report No. 165* (April 1959)

This paper describes the construction and operation of a vertical-tube apparatus for studying combustion properties of dusts falling through air under the influence of gravity. Mathematical relations were developed which relate dust concentration with the mass flow rate of dust, and the pressure drop along the tube caused by the falling dust particles. The basic assumption used to develop the theoretical relations was that the dust behaves as a porous plug. Agreement between theory and experiments with cork dust was obtained. Brief descriptions of some of the previously reported apparatus for studying combustion of dusts are given. This involves both horizontal and vertical tubes, open and closed end ignition, and the use of photography to follow the propagation rate of the flame.

The apparatus used consisted of a dust-feeding mechanism located at the top of a vertical tube of 3 inch diameter Pyrex glass pipe about 17 feet long. Cork dust contained in a closed hopper was continuously stirred with stirrers and fed out of the bottom of the hopper by a rotating spiral feeder. A 1 inch diameter side opening located near the top of the tube was connected to a micromanometer to allow measurement of the drop in pressure caused by the falling dust. For purposes of calibration of dust concentration, a butterfly valve located near the top of the tube and a gate valve at the bottom could be quickly closed to permit collection and subsequent weighing of the dust contained in the volume between the valves. In this manner the rate of rotation of the spiral feeder and the pressure drop recorded on the micromanometer were calibrated in terms of dust concentration in the test section. Dust concentrations varying from 0.03 g/l to 2 g/l were obtained. An igniter of the powder flash variety was located near the bottom of the tube. A rotating drum camera was provided to follow the movement of flame through the dust cloud.

The steady state equations of flow relating the dust concentration with pressure drop and mass flow rate were obtained by equating the frictional forces on the

36

dust (in the bulk of the cloud and also at the tube walls) to the gravitational force. The equations derived were:

$$P = \left(1 - \frac{2K_2}{ag}\right)ghD \tag{1}$$

where:

P = pressure drop
K_2 = a constant
a = radius of confining tube
g = gravitational constant
h = distance for which pressure drop pertains
D = dust concentration

and,

$$M = A\left(\frac{K_2}{K_1}\right)^{1/n} D^{(n+1)/n} \tag{2}$$

where:

M = mass flow rate of dust
K_1, n = constants
A = cross sectional area of confining tube

Experimentally it was found that P was proportional to both D and h when cork dust was used as predicted by equation (1). Also plots of log M versus log D were found to be linear in accordance with equation (2).

Subject Headings: *Explosions, by dust; Dust, explosions.*

C. P. Talley

Zehr, J. (Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, Germany) "Investigation of the Combustion Intensity of Wood Dust and Air Mixtures with Varying Oxygen Content," *Staub* **18**, 77–80 (1958)

This study is concerned with an experimental investigation of the ignition limits of wood dust in atmospheres containing varying amounts of oxygen, and with the peak pressures reached in a closed bomb. The measurements were carried out in a spherical vessel of 1½ liter volume. The wood dust particle size was in the neighborhood of 70–150 microns. No differences in results were observed between beech and fir wood.

The dispersion of dust in air was obtained by bleeding the oxidizer rapidly into a cup containing the wood dust. Ignition occurred from small thermite capsules. The results are summarized in Table I.

TABLE 1

Oxygen Content	Maximum Observed * Pressures (at)	Calculated Pressures *
21%	4.1–4.3	10.7
19%	3.9–4.1	—
17%	3.5–3.7	—
15%	2.9–3.1	8.3
13%	1.6–1.8	—
11%	No ignition	6.4

* The difference between observed and calculated pressures was attributed to slow and incomplete combustion of the large wood particles.

37

Carbon dioxide shows a somewhat improved inhibiting effect over nitrogen in view of its greater heat capacity.

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

W. G. Berl

Selle, H. and Zehr, J. (Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, Germany) "Experimental Investigation of Dust Combustion Processes from the Viewpoint of Thermodynamic Aspects of Reactions," *VDI-Berichte* **19,** 73–87 (1957)

The article represents an extensive survey of experimental methods available at the Material Testing Establishment, Berlin-Dahlem, for the investigation of dust combustion. The following techniques are described in detail:

1) Apparatus for the determination of self-heating and of ignition. Preheated air is passed through an insulated 5 cm. high dust column, maintained at the same temperature as the air. Onset of self-heating is defined as the temperature at which the dust temperature rises above the inlet gas temperature. A very sudden and rapid temperature rise indicates ignition. Self-ignition temperatures for a number of typical dusts are:

> Aluminum 190°C
> Carbonyl Iron 145°C
> Tobacco Dust 200°C
> Brown Coal 145°C
> Bituminous Coal 180°C

2) Apparatus for the determination of the onset of "glow" combustion of dust layer deposited on the top surface of a heated plate. Ignition temperatures are dependent on dust thickness and particle size. Impurities may have a pronounced effect in lowering the ignition temperatures. For example, the ignition temperature of carbon black (560°C) may be reduced to 440°C by 5% sodium chloride or 1% potassium hydroxide, and to 380°C by 5% lead chloride.

3) Apparatus for ignition temperature determination by a modified ASTM method in which dusts are injected into a preheated oxidizing gas inside an Erlenmayer flask.

4) Apparatus for ignition temperature measurements in which dust-air dispersions are blown against a heated surface.

In addition, a detailed description is given of an apparatus for the measurement of combustion pressure of dust dispersions in a closed vessel (as function of oxygen content) and of a method for determining the ignition limits of dusts. A table summarizes the "glow" ignition temperatures (apparatus 2) and dispersion ignition temperatures (apparatus 4) of 76 materials, including inorganic and organic dusts, plastics, plant materials, fibers, and solid fuels.

The survey is a useful compilation of a number of testing methods for investigating the combustion properties of dusts. No attempts are made to deal with the quantitative aspects of the problem.

Subject Headings: *Dusts, experimental techniques for investigating combustion of; Combustion, of dusts, techniques for.*

W. G. Berl

ABSTRACTS AND REVIEWS

Beer, J. M. and Essenhigh, R. H. (University of Sheffield, Sheffield, England) "Control of Reaction Rate in Dust Flames," *Nature* **187**, 1106–1107 (1960)

This paper is concerned with rate-limiting processes in dust-air flames. Calculations were made of the burning time of dust particles as a function of initial diameter on two bases, chemical reaction control and diffusion control. These showed that the rate of chemical reaction was slower than the rate of diffusion for sufficiently small particles (approximately 100 microns and smaller). Experimental data on the consumption of carbon as a function of time in a carbon dust flame in air were also presented. The chemical control theory was found to give a better fit to these data than the diffusion control theory. It was therefore suggested that more attention be given to chemical processes in dust flames.

Subject Headings: *Flame, reaction rates in dust; Dust flames, reaction rates in.*

C. P. Talley

Kaesche-Krischer, D. (Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, Germany) "Investigation of Premixed Laminar Dust and Air Flames," *Staub* **19**, 200–203 (1959)

A vertical dust cloud burner with which dust concentration can be varied by adjustment of gas flow rate or rate of dust supply (screw-feeder) is used to produce stationary laminar dust flames of lycopodium (particle size 30 micron) and of polyvinylalcohol (particle size not given) burning in air or 30 per cent N_2–70 per cent O_2. Burning velocities are measured on a Mache-Hebra nozzle (diameter not given) as function of dust concentration. Lean mixtures did not yield stable flames. Stoichiometric and richer mixtures gave practically constant burning velocities of 25 cm/sec up to 1.5 stoichiometric concentration for both fuels burning in air. With oxygen excess, lycopodium reaches 35 cm/sec and the polyvinylalcohol 25 cm/sec over the same concentration range. With further increase in concentration, the burning velocities decrease to a minimum at 2.5 stoichiometric of 16 cm/sec for lycopodium and 12 cm/sec for the polyvinyl. The pronounced maximum, characteristic of gas flames, is missing. The polyvinylalcohol dust flame differs from graphite or metal dust flames in that the fuel is subject to smoldering in the preheat zone so that, owing to rapid diffusion of volatile components, a premixed state might be assumed for the burning zone. This view is supported by the observation, at sufficiently high concentrations of polyvinyl alcohol, of polyhedral flames. A top view photograph of an octagonal, not quite symmetrical, flame is presented.

Subject Headings: *Dust flames; Flame, premixed dust.*

H. M. Cassel

Selle, H. (Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, Germany) "Principles of the Experimental Processes Used in the Evaluation of Combustible Dusts," *VDI-Berichte* **19**, 37–48 (1957)

This is a historical review of methods and equipment used to study the reactivity of pulverized combustible solids as dust layers and as air borne dust dispersions, with air or oxygen. Besides older methods, the ASTM apparatus for determining flash points and modifications by the Bundesanstalt für Materialprüfung are described. Different types of dust cloud generators are discussed. The development of procedures and apparatus to determine ignition temperatures from

39

Beyersdorfer (1925), over Wheeler, Godbert, and Greenwald (1935), to Hartmann (1954) is treated in detail. Time delays due to preheating and induction period are not considered.

Subject Headings: *Dust, evaluation of combustible.*

H. M. Cassel

Selle, H. (Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, Germany) "The Chemical and Physical Principles of the Combustion Processes of Dust," *VDI-Berichte* **19**, 25–36 (1957)

This article concerns safety limits in regard to ambient temperatures for combustible dust layers and dispersions in air. The elementary method of computing adiabatic flame temperatures, neglecting dissociation, is discussed. The significance of heat capacity, thermal conductivity, heat of reaction in the balance of rate of heat loss, and rate of heat generation under ignition conditions is qualitatively considered and amplified. On this basis, the author tries to explain the lower ignition temperature of dust layers as compared with that of dust dispersions.

Subject Headings: *Dust, combustion of.*

H. M. Cassel

VI. Radiation

Simms, D. L. and Hinkley, P. L. (Joint Fire Research Organization, Boreham Wood, England) "Protective Clothing against Flames and Heat," *Fire Research Special Report No. 3, Joint Fire Research Organization* (Department of Scientific and Industrial Research and Fire Offices' Committee, London, England)

This report analyzes the conditions in which protective clothing may be used and provides information relevant to the physical and physiological aspects of providing protection at high rates of heating. It is complementary to other surveys and does not claim to be exhaustive.

In the first section hazards likely to be encountered are reviewed. Conditions fall broadly into two categories: short exposures for a matter of minutes and long exposures which may last for hours. Tables are given to indicate the conditions of temperature and radiation to which the fireman is normally exposed. Occasionally, in rescue work, it is necessary to remain for short periods in an enclosed space which is very near to that stage of a fire known as "flash-over." More rarely the fireman is exposed to a flash of explosive violence of very short duration. It is pointed out that in normal practice, protective equipment is unusual as the present uniform seems to be adequate; the main dangers appear to be burns to the exposed skin, cuts, and bruises.

In rescue work from aircraft crash fires it has been estimated that the survival time after a fire has developed could not greatly exceed three minutes and this is a useful basis for estimating the amount of protection required. Present procedures require the firemen and rescuers to be kept "at the ready" and this raises the problem of ensuring that the perspiration of the body is evaporated during standby periods enabling the metabolic heat to be lost.

40

ABSTRACTS AND REVIEWS

Two operating procedures are possible; the rescuer is sent into the fire as quickly as possible while it is still being "knocked-down," or the rescuer waits until the fire is "knocked-down" and does not enter the flame zone (although the lower part of the body might be exposed to flames). In the case of a fuel tank explosion or a flashback the operator may be immersed in flames with a consequential large increase in radiated and convected heat.

In industry there are conditions where the operator is expected to work for comparatively long periods at ambient temperatures, normally below 50°C, although operators may have to withstand comparatively high radiation levels, for example, when a furnace is being tapped. Emergency conditions of short duration are also considered.

The report deals with physiological considerations and the limit of human endurance; the human body maintains its deep temperature nearly constant over a very limited range of ambient conditions (about 10°C). No degree of unbalance in the equilibrium between metabolic heat production in the body and dissipation by radiation, convection, and evaporation, can be tolerated for any length of time. A table and a figure provide information on heat balance. A worker may be incapacitated by one of several causes which are determined by the rate of heating, the humidity, and the time of exposure. This is illustrated diagrammatically.

If the temperature of the air and surroundings rises above that of the skin, heat can be lost only by evaporation. After a time, dependent on the rate of working, the rate of entry of heat into the skin, and the relative humidity, the body temperature rises which reduces capacity to work and leads ultimately to heat exhaustion and collapse if the condition persists for a long time. Work on the tolerance of men who are resting in hot environments is summarized in a figure. Results obtained by the National Coal Board Medical Service indicate that for men working in a saturated atmosphere while wearing breathing apparatus, the tolerance times are much shorter. The maximum safe periods are tabulated. Even slight unfitness greatly reduces the tolerance to heat.

The report continues with a consideration of burns; the relationship between the intensity of radiation falling on small areas and the time taken to feel pain is given in the form of a graph. The average pain threshold is about 45°C. It is pointed out that if the skin is initially cool, the time taken for the subject to feel pain is increased; thus, the rescue worker should keep as cool as possible beforehand. The relationship between the temperature of the skin surface and the time taken for a burn is also considered. Much higher air temperatures can be withstood if the boundary layer of cool air next to the skin is not disturbed by rapid movement.

The danger of damage to the lungs from breathing hot, but otherwise respirable air, is less than the danger of damage to exposed portions of the body, especially the face. Nevertheless, the interval between burns occurring on the skin and in the lungs may be short. When the whole body is protected by suitable clothing, inhaling hot air may be the limiting factor and breathing apparatus may then be required.

The highest ambient air temperature in which it is safe to remain is not known. A few experimental results are quoted. One of the most common causes of death in fires may be the rapid rise in concentration of carbon monoxide and a fall in oxygen concentration of the inspired air; the gases becoming toxic at about the same time as the air becomes too hot to breathe.

41

The second section of the report begins by considering the thermal properties of clothing materials; important properties are the thermal resistance (an inverse measure of the capability of the clothing to transmit heat), the thermal capacity, and the reflectivity.

The effect of heat and flames on garments is considered and it is pointed out that the ignition and continued burning of a garment may increase the amount of heat which reaches the body and will almost certainly increase the rate of disintegration of material. Rapid spread of flame over the cloth increases the supply of heat considerably and may increase the severity of burns. Most materials used in garments are flammable; asbestos and glass fiber are exceptions. Fire retardant treatments may prevent or more probably delay ignition. Most flammable materials burn faster in oxygen-enriched atmospheres or in compressed air.

A garment must retain its strength to remain in position and materials made from natural fibers char while most synthetic materials melt, often at low temperatures. Asbestos cloth often has a cotton base and tends to become brittle on heating and glass fiber cloth melts and becomes brittle below 600°C. Fire retardant treatments of textiles, although increasing the resistance to flaming, do not prevent disintegration.

Protection by clothing is considered and a curve illustrates the temperature rise of the skin with time if the front surface of a clothing assembly is exposed to a source of heat at a constant temperature. The factors determining the time taken to reach a critical level of heat flow and whether such a level is reached at all are the thermal resistance of the whole thickness of the assembly, the thermal capacity, the reflectivity of the outer surface, and the moisture content and moisture permeability of the assembly.

For long exposure times, thermal resistance is important, whereas, for short times where heating rates are high, thermal capacity is likely to be more important.

The thermal resistance of clothing is considered and it is pointed out that underwear may be of equal or greater importance than outer garments. Thermal resistance depends principally upon the still air contained within the fibers and yarns. Thermal resistance is proportional to thickness and for a given thickness the lower the density the greater the resistance (but there is a critical density below which convective transfer in the air spaces becomes important). The resistance decreases with increasing moisture content. At a high temperature the resistance is reduced. Increasing the air gap between the fabrics and the body improves the insulation and even small air gaps have prevented serious burns.

It is often desirable to provide extra protection to areas where the contact between skin and clothing is good and where the clothing may even be in slight compression, for instance the shoulders and upper arms and the front of the thighs.

A nomogram gives the relationship between the thickness of clothing, its thermal resistance at room temperature, the temperature of the outer surface and the heat flow (corrected for the change in thermal resistance with temperature). The maximum thickness of clothing that can be worn without undue loss of operative power is about 2.5 cm.; the maximum feasible resistance is about 25,000 cal^{-1}cm^{2}s°C and the corresponding maximum temperature at the clothing surface that can be tolerated is about 350°C. A graph gives the surface temperature of clothing exposed to radiation of varying intensity.

42

ABSTRACTS AND REVIEWS

The reduction in heat flow by thermal capacity is temporary but is important where the rate of heating is high or long term protection is not required. The temperature distribution through material during heating is indicated diagrammatically. Thermal capacity depends mainly on the density of the material and even where the main protection is due to thermal capacity, a high thermal resistance decreases the maximum possible temperature of the inner surface for a given heating rate and increases the time taken to reach a critical level. There is danger that heat stored in the clothing may only be given up slowly after the wearer has retreated from the source of heat and this effect is illustrated diagrammatically. The effect can be minimized by ensuring that the thermal capacity is concentrated in the outer layers of clothing (dense material) with the inner layers of very light open weave material.

Except for polished metallized surfaces the infrared reflectivities of all textiles are very low. It is possible to design clothing that reflects over 90 per cent of the incident radiation by having a reflective layer of aluminum on the outer surface but this is easily damaged by flames. A reflecting layer inside a garment is of limited value unless there is an air gap of about 1 cm. in front of it. A highly reflecting surface also reduces the rate of emission of radiation and so the rate of cooling of garments (when the wearer has retreated) is reduced. Dirt or soot on the surface greatly reduces the reflectivity.

The effect of water on clothing is considered and its effect on protection is discussed. Factors involved are the cooling effect of evaporation from the surface, heat transfer due to inward diffusion of hot vapor, and the change in thermal properties (thermal resistance will be reduced and thermal capacity increased).

Clothing with a high thermal resistance usually has a high resistance to the passage of moisture and this hinders evaporation of perspiration necessary for the wearer to remain comfortable. Reflecting aluminum deposited on the surface is impervious, leading to discomfort if garments are worn for long periods.

Protective clothing does not guarantee safety, for should mechanical failure occur, the operator will be exposed to great danger. Limits of protection are briefly considered.

Artificial cooling is considered; when the surface temperature of the clothing is not likely to approach 100°C, "wetting down" increases protection by increasing the thermal capacity and by evaporative cooling. At higher rates of heating, the onset of charring is delayed. Under these conditions protection is increased only if a moisture barrier is included in the clothing; without it, protection may be reduced.

Forced ventilation at a low rate could be applied to an impermeable suit while the operator is "at the ready" in hot conditions. A suit based on the principle of passing a stable liquid foam through a gap between two layers of material is also mentioned.

Other subjects considered in the report are the thermal testing of clothing. Special items considered are hand, foot, and head protection, and vizors. The results of tests on these items are tabulated.

Seventy-two references are quoted and appendices deal with the flammability and disintegration test, tests to determine protection, and tests for vizors.

Subject Headings: *Flame, protective clothing against; Clothing, protective, against flame.*

R. Long

43

Dixon-Lewis, G. (The University, Leeds, England) "Some Notes on Energy Transfer from Flames," *The Gas Council Research Communication GC58* London, England (1958)

J. K. Kilham has measured the energy transfer from flames to refractory tubes coated with various inorganic oxides and supported at different positions in the flame.[1,2] By measuring the radiation from the tube, the tube temperature, and the flame temperature, the energy transfer coefficient was determined. Comparison of these experimentally obtained values with theoretical ones obtained from the forced convection expression of McAdams,[3] reveals excellent agreement for carbon monoxide-air flames but rather poor agreement for hydrogen-air flames. Dixon-Lewis has attempted, in this paper, to arrive at a better agreement between the theoretical and experimental values of the energy transfer coefficient by consideration of the thermodynamic and kinetic aspects of combustion gas equilibrium. On the basis of these considerations, the author presents an approach for the evaluation of the energy transfer coefficient, utilizing the non-dissociative adiabatic flame temperature for all determinations, and re-evaluates the data of Kilham. This approach, however, leads to poor agreement for both carbon monoxide-air and hydrogen-air flames except for the case where the refractory tube is close to the tip of the hydrogen-air flame. The author concludes that the reaction rates in the surface film are too slow for the surface temperature equilibrium to be approached. For the hydrogen-air flame, the approach to equilibrium becomes less complete as the distance above the flame increases.

Possible explanations of the relatively high energy transfer from the hydrogen-air flames may be given in terms of catalytic recombination or combustion on the solid surface, transfer of excess energy by collision of gas molecules with the solid surface and exothermic displacement of equilibria.[1,2] In general, these explanations may be said to be due to the fact that the flame gases approaching the solid are not in equilibrium at the temperature of the solid. Even under the most favorable circumstances, the attempts of the gases to reach equilibrium at the lower solid surface temperature may lead to an exothermic reaction and hence to higher energy transfer than would be predicted by normal forced convection. The author is of the general opinion that too much prominence has been given to radical recombination on the surface as a possible major explanation of the apparently high energy rates from hydrogen-air flames.

Determination of the energy transfer coefficient is based on values of the physical constants for the undissociated combustion products at the film temperature. This implies, therefore, that no change in the gas composition should occur in the surface film. Practically, however, it is possible to have an exothermic reaction in the surface film.[2] This may be regarded as equivalent to increasing the effective values of the specific heat and thermal conductivity in the surface film and thereby increasing the effective energy transfer above that assuming no dissociation.

Consideration of the thermal conductivity cell [4,5] containing a chemically reacting gas leads to an effective average coefficient of thermal conductivity. This coefficient is found to be dependent on the ratio of the total heat liberated due to cooling the equilibrium combustion products plus reassociation reactions to the heat liberated due to the temperature drop assuming no dissociation. Determination of this ratio for hydrogen-air and carbon monoxide-air flames reveals that, for small temperature drops below the adiabatic flame temperature, the associa-

44

tion reactions may account for heat losses from the system which are of the same order of magnitude as the heat liberation due to the specific heat effects, assuming no dissociation.

Recent kinetic studies indicate that hydrocarbon oxidation in flames may be a two-stage process, viz., a fast reaction extending from the beginning of the reaction to the outer edge of the luminous zone and a more extended after-burning region beyond this zone. The first reaction is normally associated with flame propagation whereas the second stage involves primarily the oxidation of carbon monoxide to carbon dioxide. Although the thermodynamic approach indicates that the heat liberation due to the equilibrium shift between the adiabatic flame temperature and a given solid surface temperature is greater for the carbon monoxide-air flame than for the hydrogen-air flame, no effect on the energy transfer is observed for the carbon monoxide flame. This absence of an effect is attributed to the slow reaction rate under the conditions prevailing for the shift toward the surface temperature equilibrium. In the case of the hydrogen-air flame, an observable effect on the energy transfer is produced, but to a lesser extent as the distance from the reaction zone increases. The fall off in reaction rate may be partially due to the fall off in radical concentration.

It is concluded that for the stoichiometric flame studied by Kilham, forced convection is the primary mechanism of energy transfer. The limiting factor for the transfer of the chemical energy of the fuel to the solid surface appears to be the rate of conversion of the chemical energy to thermal energy in the later stages of the reaction.

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Subject Headings: *Flame, energy transfer from; Energy transfer, from flames.*

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L. A. Povinelli

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VII. Suppression of Combustion

Palmer, H. B. and Seery, D. J. (Pennsylvania State University, University Park, Pennsylvania) "Chlorine Inhibition of Carbon Monoxide Flames," *Combustion and Flame* 4, 213–221 (1960)

This paper is an attempt to elucidate the mechanism by which halogens inhibit flames of carbon monoxide with air, oxygen, and nitrous oxide. The choice of fuel was dictated by the desire for kinetic simplicity. Pure halogens were employed rather than organic or hydrogen halides. With the latter two, previous researchers concluded that the carrier of the halogen is ineffective as far as inhibition is concerned. This fact is confirmed indirectly in the present paper when a comparison of some previous carbon tetrachloride work and their own

chlorine results showed very good agreement in terms of chlorine atom concentration.

A bunsen-type flame was utilized and the burner was a one-meter tube of 1.28 centimeter I.D. For control of secondary air, a 3.0 centimeter I.D. tube was employed as a jacket. The burning velocity was used as a basis rather than the lean limit of flammability. The velocities were determined by the frustum cone method. Some flame spectra were observed during the qualitative studies.

Commercial "C.P." grades of all materials were employed without further purification, except for the removal of iron pentacarbonyl from the carbon monoxide. A wide range of fuel concentrations were used (25 to 55 per cent).

The qualitative observations were made with commercial CO (2.04% H_2) and C.P. CO (45 to 150 ppm H_2). Flames of both with air, O_2, and N_2O were observed spectroscopically. Most of these results were not too surprising, and for the most part, what the authors observed might very well have been expected from the outset. The most important observation in this qualitative "look-see" was the weakening or disappearing OH and CO+O continuum when large amounts of inhibitor were added to the flame. The reaction sequence is assumed to be a chain and molecular halogen is not thought to be the effective agent. It is believed that atomic halogen, or hydrogen halide, or both are really the effective chain breaker.

The major part of the paper concerns itself with the effect of chlorine on burning velocity. Better precision of data with commercial carbon monoxide than with the C.P. type was attributed to the thick reaction zone and low burning velocity of the latter. One per cent chlorine reduced the burning velocity by 30 to 40 per cent, and it was noted that other work had shown a 20 per cent reduction of methane-air by an equivalent amount of chlorine.

In the data analysis the authors present a plot of the square of relative burning velocity versus the square root of inhibitor concentration, and justify the graph by asserting the often used assumption of the correspondence of burning velocity with reaction rate. For additions of chlorine up to 1 mole per cent, equilibrium calculations of flame temperatures showed very slight changes. The authors conclude from this that halogen addition is, essentially, an isothermal effect as far as reaction kinetics are concerned.

In the quantitative analysis of the reaction, it is plainly stated that the assumption-filled kinetic arguments are presented in the hope of stimulating further research on the matter. However, their statements are sound and reasonable with the major assumption that HCl is the chain ending agent rather than the chlorine atom alone. The key agent in the propagation of the uninhibited flame is assumed to be the OH radical. Removal of this chain promoter is attributed to HCl, and the choice is based on the energetics and collision efficiency of several reactions involving the hydrogen halide. An inhibition equation is derived and a collision factor for the chain ending reaction is presented. For those who will continue to investigate halogen inhibited flame kinetics, this work should provide a somewhat firmer footing.

Subject Headings: *Carbon monoxide, flame, inhibition by chlorine; Inhibition, by chlorine; Flame, inhibition of carbon monoxide, by chlorine.*

C. O'Neal, Jr.

ABSTRACTS AND REVIEWS

Rasbash, D. J., Rogowski, A. W., and Stark, G. W. V. (Joint Fire Research Organization, Boreham Wood, England) "Mechanism of Extinction of Liquid Fires with Water Sprays," *Combustion and Flame* **4**, 223–234 (1960)

Since the factors which influence the action of water sprays on fires of flammable liquids are little understood, this investigation was carried out to find how the fire properties and water-spray properties influenced the ease of extinction, and to examine the extinction processes.

The tests were made using two fixed batteries of impinging jets mounted 175 cm. above the burning liquid contained in a 30 cm. diameter combustion vessel. The liquid level was kept 2.0 cm. below the top edge of the vessel, the liquid floating as a 6.0 cm. layer on water, except in the case of alcohol. Six liquids were used, alcohol (74 proof methylated spirit), petrol, benzole, kerosene, gas oil, and transformer oil, the latter three being primed for ignition by hexane addition. Some further tests with hand applied sprays at various angles were also conducted on a petrol fire. In all, five different sprays, produced by jets from $\frac{1}{32}$ to $\frac{7}{64}$ in. diameter were used giving mass median drop sizes from .28 to .49 mm. The mean flow rate of water spray to the combustion vessel and the entrained air current were measured.

Extinction times were measured when the following factors were varied; (1) the burning liquid, (2) the time between ignition and application of the spray (preburn time), (3) the spray properties, (4) the direction of application of the spray. Three of the sprays which differed mainly in drop size were tested on fires of all the liquids, with preburn times of 2, 5, and 8 minutes. The fires were found to behave in one of two ways when the sprays were applied. Either the flames were unstable, giving partial or complete clearance of the flame from the liquid surface followed by flashback or extinction, or a fairly stable flat flame was established near the surface, generally not accompanied by sudden clearances of flame. Alcohol fires nearly always formed type (b) flames, while the hydrocarbons formed type (a), sometimes changing to type (b) when the extinction time exceeded ten seconds, or where the preburn time was less than 30 seconds. With kerosene, gas oil, and alcohol following type (b) behavior, extinction occurred after a gradual clearance of flame from the surface and after extinction the liquid could not be ignited immediately by a taper. The conclusions drawn from these tests were:

1) Considerable differences in extinction times were obtained in many repeat tests. This was particularly so when fires changed from type (a) to type (b) burning.

2) With the conditions used, all the sprays extinguished reliably except the spray with mass median drop size .49 mm. on benzole and petrol.

3) The extinction time decreased with decrease in volatility.

4) With benzole, petrol, and alcohol the extinction time decreased as spray drop size decreased (mass flow rate remaining constant.)

With the preburn times of 2 minutes, used in the first series of tests, no effect was detected. A series of tests was carried out with short preburn times of 1 to 30 seconds using petrol and benzole fires and sprays with mass median drop sizes from 0.28 to 0.49 mm. The results showed that the fires were very difficult to extinguish under these conditions. With kerosene fires using a range of preburn

47

times from 30 seconds to 16 minutes and two sprays (mass median drop size .49 mm. and .29 mm.) rapid extinction was always obtained when the preburn time exceeded 5 minutes.

Tests were made on petrol and kerosene fires at preburn times of 5 and 8 minutes using sprays with a wider range of drop sizes than those in the first series. Mass median drop size were varied between .1 and .6 mm. and flow rates between 0.6 gcm^{-2}/min^{-1} and 9.0 gcm^{-2}/min^{-1}. As before the sprays were produced by batteries of impinging jets operated at pressures of 85 lb/in². The variation in spray pattern at the liquid surface affected the extinction time of the kerosene fires. With both fuels an increase in flow rate for a given drop size gave a marked reduction in extinction time. Since the entrained air velocity increased simultaneously, it was not clear which factor was responsible for the increased extinction efficiency. Regression analyses on the applicable results showed differences in the dependance of extinction time on drop size and mass flow rate for the two liquids. A table showing the effect of increasing the entrained air velocity on the extinction time is included. Some tests were also done using hand-applied impinging jet sprays on petrol fires, the angle of application varying from horizontal to 60°. Horizontal application and application at 30° failed to achieve extinction, while at 60° extinction was frequently obtained. The finer spray gave more rapid extinctions.

Broadly, extinction occurred differently according to whether the flame behavior followed type (a) or type (b). For type (a) flames with the spray on, extinction occurred after rapid clearance of a large part of the flame. The liquid could immediately be ignited again. For type (b) flames extinction was preceded by a gradual clearance of the flame from the surface; after extinction, the liquid could not immediately be ignited again. This type of extinction was for the hydrocarbons due to cooling of the liquid to the fire point and for the alcohol to dilution of the surface layers. Direct extinction of the flames seems to follow the expected trends if heat transfer from the flames to the spray drops is assumed to be the controlling factor. Thus, when flat flames, type (b), were formed the combustion intensity was about six times as great as that for the larger flames, while the heat transfer to the drops in such cases would not vary by more than twice. These arguments do not account for the variation in flame behavior under various conditions nor for the effect of entrained air current. The thickness of the vapor zone seemed to be very important. If the zone was thick, the spray application resulted in type (a) behavior; if thin, type (b) behavior occurred. Practically, the implications are that a wide range of water sprays can be relied on to extinguish liquid fires. Extinction efficiency is very sensitive to the manner of application of the sprays and to the preburn time. Water sprays with the properties described are not reliable for extinction of petrol and benzole fires, but they may be useful in checking and containing such fires until a better extinguishing agent can be brought into use. As far as explaining the mechanism of extinction is concerned, the reviewer feels that more work is required. Particularly, the effect of drop momentum (which increases as entrained air velocity increases) and the interaction of spray drops and the liquid surface ought to be investigated.

Subject Headings: *Fires, suppression of, with water sprays; Water, in suppression of fires.*

M. G. Perry

48

ABSTRACTS AND REVIEWS

Peterson, H. B., Jablonski, E. J., and Tuve, R. L. (U.S. Naval Research Laboratory, Washington, D.C.) "Studies on the Fuel-Ignition-Suppression Capability of Foam-Covered Runways for Aircraft," *NRL Report 5492* (July 1960)

Ignition of flammable vapors is a very complex phenomenon. Reproducible results are difficult to obtain even in a laboratory. Studies of ignition characteristics out-of-doors under highly variable weather conditions are even more complicated.

The authors investigated some of the basic properties of the ignition process as it might occur in fuel spillage from aircraft sliding on hard-surfaced runways. Attempts were made to correlate the following: (1) the ignition temperatures of sprays (containing vapors) of aircraft fuels under turbulent conditions, (2) the temperature of metallic fragments detached from aircraft structural metals under conditions of severe friction, (3) the size and apparent history of metal fragments ejected from metals in contact with abrasive surfaces under high loading conditions, and (4) the degree of frictional heating of the parent-metal mass.

Metal samples were dragged by a vehicle across concrete and asphalt runways with and without various types of foam. Eight metals were used, namely, 2024–T4 aluminum, TI–100A titanium, FS 1 magnesium, SAE 4130 and 4340 steel, AISI 347 and 420 stainless steels and cold-rolled steel.

Motor-grade gasoline, JP–4 and JP–5, were the fuels employed. Expansion −12, 30-minute drainage-time foam, expansion −8, 5-minute drainage-time foam, and expansion −8, chemical foam were the three distinct types utilized in the study.

Results show that there is little doubt that under the test conditions used, foam layers (preferably two inches thick) spread on the runway and aged for 10 to 15 minutes serve as an excellent method of suppressing metal-to-runway surface-friction spark ignition of aircraft fuels, except with titanium metals. It appears that foam suppresses ignition by cooling and dampening the incandescent fragments of metals (sparks) thrown out by abrasion. Water, settling out onto the runway surface from the foam layer, is the primary cooling agent.

Foam layers as thick as six inches did not suppress ignition when sparks were generated by titanium-alloy metals. The authors ascribe this failure to the high temperatures of the incandescent particles. They found that the important factor of aging time for the aqueous foams points to the desirable function of a water layer on the runway surface as the cooling agent in suppressing ignition of fuels. There seemed to be little difference in spark-suppression ability of the foams tested if a 10 to 15 minute aging period was allowed before commencing tests.

Results were not conclusive with respect to determining a critical threshold of foam thickness or water-volume distribution on the runway surface. Under certain restrictive conditions, a foam layer one-half inch thick can suppress fuel ignition, but under a much greater range of variables the use of a two-inch layer of foam is highly recommended.

It was found that much importance should be attached to the continuity of thickness of the foam layer on the runway. Intermittent gaps, holes, or pathways in the foam layer can cause immediate loss of ignition suppression.

The coefficient of friction was decreased a maximum of only five per cent on a foam-covered runway compared to a dry runway. Thus, the results do not sup-

49

port the theory that foam can cause a lubricating effect or can facilitate the sliding of an airframe or wheel structure coming into contact with it.

Test results regarding rainfall show that with two inches of expansion −12 good-quality foam on the runway, this cover will not be affected detrimentally in less than one hour unless the rain is very heavy. Foam layers are more effective when spread on smooth runways. Foam should not be employed if this action precludes the availability of fire-fighting equipment at the time and place of landing.

The report recommends, in general, the use of foam laid two inches deep on a smooth runway and aged for 15 minutes but not longer than 2½ hours. Much more study is required to determine the mechanism of metallic-fragment ignition of fuel vapors and sprays. Reaction kinetics, where catalysis is involved, probably has an important role in the ignition process.

Subject Headings: *Suppression, of ignition, on runways; Ignition, suppression on runways; Foam, use of, in ignition suppression on runways.*

L. E. Bollinger

Engibous, D. L. and Torkelson, T. R. (The Dow Chemical Company, Midland, Michigan) "A Study of Vaporizable Extinguishants," *Wright Air Development Division, Aeronautical Accessories Laboratory Contract AF 33(616)–5838. WADC Technical Report 59–463* (January 1960)

The authors review the general theory of fire extinguishment and discuss the uses of common extinguishing agents. It is apparent that the mechanism by which vaporizing agents extinguish fires is primarily chemical, i.e. halogen containing materials react with the chain propagating free radicals and cause chain breaking and quench the reaction. Physical processes, such as cooling the fuel by evaporation and inhibiting the diffusion of oxygen, are of secondary importance although this theory has not yet been conclusively proven. Vaporizing liquids are effective on fires involving liquid fuels, and also where the danger of electricity and subsequent arcing is present and must be minimized by the use of nonconducting agents.

This study was conducted to determine whether one of four agents, namely, dibromodifluoromethane (Halon 1201), bromochlorodifluoromethane (Halon 1211), bromotrifluoromethane (Halon 1301), and 1.2-dibromotetrafluoroethane (Halon 2402), was a better extinguishant than bromochloromethane (Halon 1011), which is said to present toxicity problems, although no fatalities or serious effects have been reported.

The physical properties of these five agents are reviewed. All of them meet the current U.S. Air Force requirements for vaporizing extinguishants, such as high extinguishing effectiveness, toxicity less than Halon 1011, stability on handling and storage for five years, capability of being used as a liquid, a freezing point less than −65°F, reasonable cost, and compatibility with foam extinguishants.

Effectiveness can be determined in many ways, ranging from inhibiting the explosion of fuel-air mixtures to tests on standard fires. Explosion studies were found not to correlate well with fire tests, and it was difficult to assess and compare fire tets. Fuel type, agent application rate, and the pattern and geometry of the fire are very important and seemed to be the main reasons for the different effectiveness values reported by different investigators.

From the results of pan fires, spill, and drip fuel fires, it appeared that no

50

marked benefits could be attributed to any of the materials. Halon 1011 required a longer time than any of the others and consequently more material.

With regard to toxicity, the effects of inhalation of concentrations of vapor from the agent during application were studied. Tests were carried out on small groups of guinea pigs and rats, and from the results it appeared that Halon 1301 was safer than all the others, including CCl_4, both as undecomposed vapor and pyrolysized ($800°C$) vapor. Due to its low boiling point ($-72°F$), Halon 1301 could cause skin burns from direct splashing.

On the problem of thermal decomposition, Halon 1301 followed by Halon 1211 were shown to be the most stable compounds tested. Since the extinguishing agent is required to be stable on handling and storage for five years, corrosion and penetration of metals tests were reported, and while Halon 1011 was highly corrosive towards aluminum, brass, and steel, all the other compounds were much less corrosive due to their containing fluorine, and were also far more stable. Again Halon 1301 proved the best agent tried, and Halon 1211 the next best.

Since a low pressure system is used by the Air Force to discharge the extinguishing agent, it is apparent from vapor pressure considerations that Halon 1301 is unsuitable, but that Halon 1211 can be used.

In conclusion, Halon 1211 is considered a better agent than Halon 1011 mainly because of its lower toxicity value, its ease of storage and handling and its slightly greater effectiveness. It is suggested that further extinguishing tests be carried out using Halon 1211 to determine the relation between fire geometry and agent application method.

Subject Headings: *Extinguishment agents, effectiveness of.*

P. L. Start

Campbell, J. A. and Busch, A. M. (National Aeronautics and Space Administration, Cleveland, Ohio) "A Combined Water-Bromotrifluoromethane Crash-Fire Protection System for a T–56 Turbopropeller Engine," *National Aeronautics and Space Administration Technical Note D–28* (August 1959)

A system for protection from a fire following a crash is intended to prevent a general crash-fire generated by ignition of spilled fuel by hot metal parts inside the engine. Achievement of this objective by quickly extinguishing the combustor flame, spraying the hot metal parts with water, and using the flight fire extinguisher agent (bromotrifluoromethane) to provide an inert atmosphere was investigated on an engine test stand.

A fuel shutoff and drain valve simultaneously stopped the flow of fuel into the engine fuel manifold and vented the manifold overboard, extinguishing the normal combustor flame in 0.07 second. Water, propelled by pressurized nitrogen, was immediately sprayed onto the hot internal engine parts. A high-flow, short-duration discharge of 34 lbs. of water suppressed ignition on thin metal parts such as combustor liners, turbine blades, and exhaust ducts. A slow-flow, long-duration discharge of 7 lbs. of water cooled the turbine rotor faces and the rear-bearing support struts. Ten pounds of bromotrifluoromethane was discharged during a period from 45 seconds to 10 minutes after fuel shutoff to inert the atmosphere around the turbine rotor, until the rotor had cooled sufficiently so that it was no longer an ignition source. The bromotrifluoromethane was stored as a liquid and discharged by its own vapor pressure.

By trial, engine operating conditions were established which corresponded to

51

those that exist in a crash on take-off. This is the most severe crash-fire hazard. At the time of the simulated crash the fuel flow to the engine combustors was stopped and the crash-fire protection system actuated. The engine was exposed to a JP–5 fuel mist sprayed into the engine inlet, 0.3 second after the normal fuel was stopped. A twice-stoichiometric fuel-air ratio was used to maximize ignitability. As the engine slowed, this spray was replaced by a 4 to 5 second pulsed atomized fuel spray directed into both the inlet and the exhaust. Later this interval was increased to 10 seconds, and then, after engine rotation stopped, the spray was actuated at 15 second intervals until 3 minutes after normal fuel shutoff.

Even under these rigorous test conditions the crash-fire protection system prevented ignition of ingested fuel. Although desirable improvements in this system can be visualized for a production situation, an effective prototype demonstration was accomplished. Principles of this system should be applicable to other aircraft turbine engines.

Subject Headings: *Fire protection, for turbojet engines; Turbojet engines, fire protection of.*

<div align="right">A. E. Noreen</div>

Drubel, R. B. and Rupprecht, W. E. F. (Dow Chemical Company, Midland Michigan) "Latex-Fire-Retardant Intumescent Coatings," *Forest Products Journal* **10**, 152–155 (1960)

Low cost, low density, fibrous materials which are in great demand as building products constitute potential fire hazards. The authors describe the development of fire-retarding coatings for low density wallboards and ceiling tiles of fibrous, combustible, wood or vegetable base composition. In undertaking their search for fire retardants for these combustible manufactured products, the authors examined three types of fire retardants; (1) intumescent compounds, (2) inorganic salts, and (3) non-resinous carbonaceous compounds. The intumescent compounds studied were coatings which puff up when subjected to heat or flame to provide an insulating layer between the heat source and the substrate.

The authors, by incorporating intumescent formulations in a latex binder, have developed an easily applied coating which is effective in retarding the flame spread rate through combustible wood fiber products. Comparing conventional low density wood fiber panels with those painted with latex intumescent coatings, the authors showed that whereas the conventional panel bursts into flame, the intumescent panel merely shows bubbling, charring, and searing without flame spreading, even after 25 minutes in a direct flame.

Two formulations were recommended, one with unplasticized and one with plasticized latex, both of which pass commercial and federal specifications for fire-retardant coatings. The basic ingredients of the two formulations on a dry weight basis are:

	Per Cent
Monoammonium phosphate	56
Dicyandiamide	10
Pentaerythritol	22
Titanium dioxide (rutile)	12
Added binder—Latex 744B (with or without plasticizer of dioctylphthalate and methocel)	25

ABSTRACTS AND REVIEWS

The results of this work should prove useful in preventing the spread of fires in buildings containing fiberboard and similar wood products.

Subject Headings: *Fires, retardation, by coatings.*

D. Dembrow

Seekamp, H. (Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, Germany) "The Future of Fire Retardants," *VFDB-Zeitschrift Forschung und Technik im Brandschutz* 6, 164–167 (1957) and 7, 11–15 (1958)

The attempts made in World War II to fireproof the wooden portions of buildings were not successful. The reasons are that unapproved techniques for the application of retardants were used, existing fire protection codes were not employed, the prescribed composition of the retardant materials varied and were of inferior grade, there were shortages of some of the ingredients and the effectiveness of retardants was overestimated. The general quality of the equipment was good.

Postwar developement has concentrated on flame retardant resistant coatings and heavy emphasis has been placed on textile protection due to the threat of the atomic bomb.

In these articles, the various stages of destructive burning are defined arbitrarily as ignition (up to one minute), surface flame spread (one to 15 minutes), major material consumption (15–60 minutes), after glow (60+ minutes). Testing methods to observe the fire at these stages are given. One important observation is the process of fire spread during the early or nascent stage of the burning and methods of testing this phenomenon are given for various-shaped specimens.

The results show the effectiveness of a series of retardants when applied to different woods. The principal ingredients of the older materials are: FM–1 (ammonium phosphate and ammonium sulphate), FM–2 (sodium silicate and pigment), and FM–3 (sodium phosphate). New materials discussed are designated as J1 and J2. These are artificial resins and phosphates designed to create protective foam layers. The phosphates proved to be superior in reducing the burning rate of various materials.

In his conclusions, the author questions the possibility of completely fireproofing a complicated system such as a home because of adverse factors such as lack of techniques, organization, and political economy.

The need for work on high intensity radiation exposure is cited. The incident energy is so great that conceivably even treated materials may give inadequate protection.

If the primary aim is to prevent flame from spreading rather than ignition, a plan may be worked out whereby areas of incombustible material would slow down or prevent further burning. If the aim is to prevent fire from spreading through wooden walls or floors, application of fire retardants can at least slow down the process. Strict adherence to building codes such as prescribed in "Normblatt" DIN 4102 would have to be followed after protective treatment has been given. An impregnation method would be superior to a coating technique since all building materials to be used could be treated prior to installation but there is little data on this method as yet.

Postwar progress in fire protection has been good. Governmental insistence

53

that most building and clothing materials be flameproofed to some extent prior to sale or use is necessary. As long as the unfavorable relation exists between the amounts of combustible and near incombustible materials, the effectiveness of treated materials is greatly diminished.

The principal aim of future work in fire protection should be a more comprehensive application of fire retardant material rather than the current attempts to improve their effectiveness.

Subject Headings: *Fire retardants.*

P. Breisacher

VIII. Model Studies and Scaling Laws

Fons, W. L., Bruce, H. D., Pong, W. Y., and Richards, S. S. (Pacific Southwest Forest and Range Experiment Station, Berkeley, California) "Project Fire Model," *Office of Civil and Defense Mobilization Contract No. DCM-SR-59-10 and U.S. Forest Service Contract No. 12-11-005-20170, Summary Progress Report, Period November 1, 1958 to April 30, 1960* (May 31, 1960)

This summary progress report on Project Fire Model covers the significant work accomplished to date at the Pacific Southwest Forest and Range Experiment Station. Project Fire Model involves basic and applied research on steady-state model fires, burned under controlled conditions. The project, as stated in the introduction to the report has as its purpose, "to develop and study a laboratory-scale fire which would provide a diagnostic model of a steady-state, free-burning fire in solid fuel."

In summary, the project has accomplished this goal through the development of a fire model using a crib constructed of wood sticks resting on a movable bed. A near heat balance has been attained, and additional data governing the fundamental laws of combustion has been collected.

National importance and over-all significance of the project is well stated in the introduction. At a time when emphasis has been directed toward broad areas of applied research, the basic approach taken by Project Fire Model toward a better understanding of fire fundamentals is refreshing. The fire model approach should provide a better understanding of the fire phenomena and in addition open the way to possible new techniques for controlling large-scale fires.

Early studies included research on liquid-fuel fires for determining model-scale techniques and the relation of burning rate to fuel surface area. However, most of the research effort has been directed toward burning homogeneous fuel beds of wood sticks having known dimensions and uniform structural characteristics.

The equipment used in the project and the laboratory facilities are described. It is well to point out that in a basic research project of this nature a great deal of ingenuity is needed to produce the modifications in existing instruments and develop the facilities needed to carry out the planned research program. Much of the equipment used in this project was developed or adapted for use by the project scientists themselves.

The results of this research to date are summarized by short write-ups of each

54

ABSTRACTS AND REVIEWS

phase of the study accompanied by necessary tables, charts, graphs, and photo-graphs.

Rate of spread in 27 test fires showed some variations. Maximum rate was 2.38 in/min and 11.9 ft/hr; and minimum rates were slightly over 1 in/min and 5 ft/hr. The spread of fire through these prepared cribs of fuel was linear after the initial build-up period. This linearity is characteristic of a steady-state fire and is well substantiated by photographs and graphs.

The effects of specific gravity of the wood fuels on rate of spread and rate of combustion is demonstrated. Both rate of fire spread and rate of combustion appear to decrease with an increase in wood density.

The thermo-structure of the test fire convection column was measured with a grid of 36 thermocouples. Maximum temperatures measured in the flames were in excess of 1600°F. As was expected, the temperatures measured at 1 inch above the crib in the region of incomplete combustion were lower than temperatures measured in the cleaner flame a short distance higher.

An approximate heat balance was attained on an experimental wood crib fire. Approximately 91 per cent of the heat energy released could be accounted for through actual measurement. Measurements indicated that 79.9 per cent of the total energy is released through convective and radiative heat while 11.4 per cent is lost through conduction into the concrete base, heat value of charcoal, and heat value of unburned combustion gases.

Research results summarized here are supplemented by additional information on (1) effects of fuel bed size and fuel particle size on rate of fire spread, (2) energy release through radiation, (3) heat residual of charcoal from test fires, (4) composition of stack gases from test fires, (5) height and width of flames, and (6) the period of time for each fire to develop steady-state conditions.

Conclusions of this research project on basic combustion phenomena are presented in the form of 21 concise statements concerning all phases of the experimental investigations.

Continuation of this fundamental fire research work had been insured through the approval of a recent proposal by the National Bureau of Standards. The proposal covers a 15-month period from March 1, 1960 to June 30, 1961. Three specific areas for investigation are included in this proposal. They are (1) effect of wood species and density on fire characteristics, (2) fuel moisture effects on fire characteristics, and (3) the formulation of theories concerning the effect of certain specified independent variables (i.e. fuel material, fuel temperature, particle arrangement, relative humidity, etc.) on the properties of free-burning fires.

A summary of the independent and the dependent variables considered in this experiment are included in the appendix.

Subject Headings: *Combustion, of solid fuels; Fuels, combustion of.*

J. H. Dieterich

Yokoi, S. (Building Research Institute, Ministry of Construction, Japan) "A Method of Determining the Size of Vents (To Prevent Smoke Blocking Passages in Burning Building)," *National Research Council of Canada Technical Translation 884* (1960)

The required venting for fire protection of a large closed area such as a theatre or auditorium is considered. If no venting is provided or if the venting is insuffi-

55

cient and a fire starts, then the smoke and heated gas produced must escape from the enclosed area through doors or other openings. With smoke gushing from the available exits, escape becomes difficult and fire fighting is hindered.

Adequate venting is defined as that amount necessary to provide an outlet for the products of combustion in a fire. For this reason the neutral zone in which the difference between pressures outside and inside the room becomes zero must be located not lower than the upper edge of the natural openings. In order to determine the amount of combustion gas that is produced it is assumed that all the air that enters through the natural openings is consumed in a combustion process, and that this available supply of oxygen determines the amount of combustion that takes place.

Utilizing conservation of mass while taking into account the amount of combustible material consumed, the author obtains the relation for a single natural opening

$$\frac{S''}{S'} = 0.050132 \sqrt{(T+273.2)\frac{h}{H}}$$

where S'' is the cross-sectional area of the vent in the ceiling, S' the area of the wall opening, T the room temperature, h the distance between the upper edge of the wall opening and the upper edge of the chimney, and H is the vertical length of the wall opening. The room temperature must be estimated independently and values from $300°$ to $1000°K$ are considered.

The author also treats the problem for a number of openings. A comparison of the present theory with experiments on an appropriate model seems necessary to justify some of the assumptions made. In any case the paper presents an interesting and useful approach to an important problem in fire research.

Subject Headings: *Vents, determination of size of; Smoke, elimination through vents.*

D. L. Turcotte

Ashton, L. A. and Smart, P. M. T. (Joint Fire Research Organization, Boreham Wood, England) "Sponsored Fire-Resistance Tests on Structural Elements," *Report of Joint Fire Research Organization* (Department of Scientific and Industrial Research and Fire Offices' Committee, London, England)

A compilation was made of the results of fire-resistance tests conducted in Great Britain on building elements of a proprietary nature or incorporating proprietary materials. The tests cover kinds of constructions available in the postwar years. Results of tests on 81 specimens are included.

As the statement is made that the publication of results was entirely at the discretion of the manufacturers of the materials, it follows that the omission of a material or structural element is not necessarily because it was not tested.

Fire resistance is defined as that property of a building element or structure which contributes to confining a fire in a building to the space of origin. Tests for fire resistance in Britain are conducted similarly to those in the United States which are governed by the requirements of ASTM E-119, Standard Methods of Fire Test of Building Construction and Materials.

Criteria for failure are also similar in the two countries, comprising collapse of the structure for any building element and for structural elements serving to bound spaces, and the requirement that there be no opening to flame or transmis-

ABSTRACTS AND REVIEWS

sion of sufficient heat to ignite flammable materials in contact with the surface not exposed to the fire. For the British tests, ratings are assigned as ½, 1, 2, 3, 4 or 6 hours, the grading period being that next below the time of failure in any relevant requirement.

The test specimens were classified by type of building element and function: loadbearing and non-loadbearing walls, simply supported and restrained floors, suspended ceilings, concrete columns, steel columns, and glazing. The number of specimens in a category varied from 2 to 22, the greater number representing steel columns and non-loadbearing walls. Simply supported floors were well represented with 15 different constructions, while loadbearing walls supplied 11 specimens. A variety of materials were employed in the structures. Walls were constructed of hollow dry block, asbestos boards, gypsum panels, aerated concrete block, cinder block, cavity plaster panels, laminated panels, glass block, and other materials in a number of combinations. Floors were of timber joists with vermiculite plaster on lath, prefabricated timber units, and concrete units, some prestressed. Steel columns were protected with block, board or panel encasements of a number of compositions, cements and plasters applied to lath, and several types of sprayed coatings.

As the materials or structural elements used are proprietary, it is not expected that identical elements will be available in the United States. The published results apply only to the construction described in the article. Any variation, even minor, may effect a considerable change in performance. Thus, it cannot be assumed that similar construction will achieve a comparable rating. However, some interpolation may be possible for homogeneous elements of different thickness from those described in the tests. An examination of results may be of value in indicating fire-resistance ratings which certain proposed constructions may attain, and in pointing the way to more effective use of materials in developing fire-resistant building elements.

Subject Headings: *Fire resistance, of building elements.*

H. Shoub

"Fire Effects of Bombing Attacks," *U.S. Office of Civil and Defense Mobilization* TM-9-2 (Technical Manual) (1955)

In any future war devastating fires in highly concentrated areas of vital industry and population will undoubtedly be a major menace unless appropriate counter-measures are carried into effect. In this technical manual a review is made of fire warfare on German and Japanese cities in World War II and of the incendiary affects of the Hiroshima and Nagasaki atomic blasts. Also an attempt is made to evaluate the susceptibility of American cities to crippling fires in warfare and to cite factors which must be considered in civil planning in order to avert such disaster.

Two types of major fires have been found to exist: fire storms and conflagrations. A fire storm is an extremely large bonfire with a tall vertical column of burning gases. The natural heat convective forces cause appreciable radial surface winds accelerating towards the center. A conflagration is an expansive fire in the presence of a surface wind. Its pillar of flame tips leeward, continually causing the flame to spread. The higher temperature of the pillar and its characteristic of spreading cause a conflagration to be generally more destructive than a fire storm.

There are several important factors which influence the ability of a city to avert wartime destruction by conflagrations or fire storms.

(a) The building density $\left(\dfrac{\text{total ground area of buildings}}{\text{total area of zone}} \right)$ should be small, apparently below 20 per cent. Hamburg which experienced a war-time fire storm had a building density of 30 per cent. The American dwelling areas in the older cities and commercial areas are comparable with those existing in Germany.

(b) The combustibility of structures should be low. In general the combustibility of American structures is higher than that of the German and lower than that of the Japanese. However the bulk mass of combustibles in the American dwellings is far greater than in the Japanese.

(c) There should be a system of fire breaks to limit fires. Properly planned streets, parks, water ways, and fire-resistive buildings can serve as fire breaks.

(d) The size of the target area should be small. Such size is obviously a function of the forementioned factors. The limited wartime observations suggest that the area under fire may have to exceed one square mile in order for a fire storm to form.

(e) Other factors which clearly affect the vulnerability of a city are: the continuity of combustible construction, such as fences, sheds, etc.; the combustibility of the contents of buildings such as household furnishings and mercantile storage; size of buildings, an important factor since conventional water sprinkler systems would generally be vulnerable in an attack; topography; and weather conditions (humidity, precipitation, and wind).

Subject Headings: *Fires, effect of bombing attacks on.*

G. A. Agoston

Fahnestock, G. R. (Intermountain Forest and Range Experiment Station, Ogden, Utah) "Logging Slash Flammability," *Intermountain Forest and Range Experiment Station, Forest Service, U.S. Department of Agriculture Research Paper No. 58* (May 1960)

Slash, the residue left in the woods after timber is harvested, is one of the most hazardous fuels in the Western States. It is a mixture of foliage, limbs, bark, and other unusable woody material.

This paper describes a study of slash flammability for nine conifer species. It involves three general types of investigations: (1) a study of the moisture in the various slash constituents; (2) development of methods for slash meaurement; and (3) experimental slash plot burns to study rate of fire spread and intensity.

The term "flammability" includes both rate of fire spread and fire intensity. The term "fire intensity" is not specifically defined but is measured in terms of intensity of radiation from the burning plots.

Tree crowns supply most of the slash. Conifer needles constitute that component of slash which dominates the initial spread and intensity of fire. If the nine conifer species are taken as a group, the needles comprise about ¼ of the total crown weight (ovendry basis). Twigs and branches less than ½ inch in diameter constitute a slightly smaller fraction of the total crown weight.

Flammability is strongly influenced by fuel moisture content. The moisture

58

content of the needles of freshly cut slash for most of the species studied ranged from about 100 to 150 per cent of their ovendry weight. Moisture content of branchwood of freshly cut slash was somewhat lower with a median value of about 80 per cent for the nine species.

The drying rate of a given slash component depends primarily on the initial slash treatment, the characteristics of the component and on the degree of shading. The rate of loss of moisture was greatest for needles and twigs on lopped branches (branches severed from the main trunk) in full sun and most of the initial moisture was lost in less than three weeks. The rate of loss was considerably less for similar fuel in the shade and less for needles on branches attached to the main trunk.

The drying of trunk wood appears to be a more complex process than the drying of needles and small twigs. For example, loss of moisture at the ¼-inch depth appeared to be considerably greater than at the ¾-inch depth even though the escape of moisture through the bark was probably negligible. Fahnestock attributes this to the possible diffusion of moisture from the outer sapwood to the heartwood. However, it may be more likely that, as a result of transpiration from the needles, water from the peripheral sapwood moved more rapidly into the branches than water at greater depths. Transpiration and the passage of moisture from the main stem to the needles is indicated by some of the other drying data such as that which shows higher drying rates for needles on lopped branches than for unlopped branches. Transpiration should also deplete the reservoir of trunk moisture more rapidly for unlopped tops in sunlight than in shade. The data in table 5 indicate this.

In the section on slash measurement, methods are presented for predicting the quantity of slash that a given timber harvest cut will produce. Since tree crowns compose most of the slash that will burn readily and rapidly, the estimating methods are based on procedures for determining basic tree crown weights. Following the work of Storey, Fons, and Sauer,[1] equations are developed which relate the ovendry crown weight to crown length and tree diameter for the different species studied.

A considerable part of the paper is devoted to the rate of spread and intensity of fires burning in slash spread over plots 21 feet square. Variables were quantity of slash, age or time since cutting, and species. Burns were made under as uniform weather conditions as possible, but because of its close relationship to fine fuel moisture, relative humidity was recorded. Plots were ignited at their centers and the radial rate of spread was measured as the fires burned toward the edges. A continuous radiometer record during the course of a fire was used as a measure of its intensity.

Some discussion is given to slash treatment to reduce flammability and the application in hazard reduction.

The basic work described in this paper on the composition and physical characteristics of slash, moisture behavior in slash, and the use of tree crown analysis methods in slash measurement contributes much to the knowledge of an important forest fuel. On the other hand, that part of the study using the small-scale test burns may have a considerably more limited significance. The fire behavior interpretation of these burns probably should be restricted to low-intensity fires in their initial stages.

Reference

1. Storey, T. G., Fons, W. L., and Sauer, F. M. "Crown Characteristics of Several Coniferous Tree Species," *U.S. Forest Service, Division of Forest Fire Research Interim Technical Report AFSWP–416* (1955)

Subject Headings: *Flammability, of logging slash.*

G. M. Byram

IX. Atomization of Liquids

Dodd, K. N. (Royal Aircraft Establishment, Farnborough, England) "On the Disintegration of Waterdrops in an Air Stream," *Journal of Fluid Mechanics* 9, 175–182 (1960)

A new theory is presented for the determination of secondary atomization criteria for waterdrops in an air stream. Although previous investigators had determined that secondary atomization occurred for a critical value of the Weber number as determined by the diameter (d), surface tension (T), and velocity (u) of the droplet and the density (ρ_a) and the velocity (V) of the air,

$$W_{cr} = \rho_a d (V-u)^2 / T \leqq k \tag{1}$$

Hinze[1] derived theoretically that the critical value is dependent upon the history of the relative velocity (V−u). The present author questions the applicability of Hinze's analysis to the experimental results of Lane and Edwards,[2] and proposes an alternate theory based on the bag-shaped bubble configuration observed experimentally. By assuming that the pressure differential across the "bubble" surface is proportional to the product of air density and the square of the relative velocity, the following equation is derived

$$r(V-u)^2 = 4T/\mu\rho_a \tag{2}$$

where r is the radius of the bubble, and μ is the constant of proportionality. The concept of minimum radius of the bubble r_m is then introduced and, by substituting in equation (2), the critical relative velocity is that which makes the radius a minimum

$$r_m (V-u)^2 = 4T/\mu\rho_a \tag{3}$$

Experimental observations indicate that r_m is about twice the radius of the original droplet.

The equation for the dynamics of the expanding bubble is derived by balancing the force on the bubble's shell and introducing previous hypotheses

$$\frac{d^2 r}{dt^2} = \frac{4\pi r^2}{f_m} \left[\mu\rho_a (V-u)^2 - \frac{4T}{r} \right] \tag{4}$$

where f is the total volume of the shell.

By using equation (4) and Stokes' equation for droplet trajectories, the growth and trajectory characteristics were determined by means of an electronic computer, and were found to be in reasonable agreement with Lane and Edwards' experimental data. It was found that μ mainly affected the rate of expansion of the bubble while C_D was a prime factor in the rectilinear acceleration of the drop.

60

ABSTRACTS AND REVIEWS

Some values of μ were found to be too small for expansion, while for a small critical range of μ a contraction followed the initial expansion, in a fashion similar to some phenomena observed by Lane and Edwards.

The theory was then applied to the behavior of drops in the path of moving spheres, for which the air velocity is determined by the equation

$$V(s) = v - v\left(\frac{a}{a-s}\right)^3 \tag{5}$$

where s is distance of fall, v is the (constant) air velocity in the tube, and a is the radius of the sphere. By assuming that $u = v$, and $r_m = 2r$ at the critical point, equations (3) and (5) yield

$$v\left(\frac{a}{a-s}\right)^3 = \left(\frac{2T}{r\mu\rho_a}\right)^{\frac{1}{2}} \tag{6}$$

which determines the critical value of s. Theoretical results which predicted either bursting or collision with the sphere compared favorably with experimental data.

Although the author has created an ingeneous theory for the explanation of some physical phenomena, the abundance of "adjustable constants" and arbitrary simplification indicates that the qualitative agreement with experimental data may have been fortuitous.

References

1. Hinze, J. L. *Applied Scientific Research* (a) 1, 273 (1948)
2. Lane, W. R. and Edwards, J. *Unpublished Ministry of Supply Report* (1948)

Subject Headings: *Water, disintegration of drops of; Drops, water, disintegration of.*
C. C. Miesse

Deo, A. V., Sanjana, N. R., Kulkarni, S. B., Gharpurey, M. K., and Biswas, A.B. (National Chemical Laboratory, Poona, India) "New Compounds for the Control of Water Evaporation," *Nature* 187, 870–871 (1960)

The effectiveness of various chemicals for the suppression of water evaporation from lakes and reservoirs was studied by spreading 0.32 ml. of 0.09 per cent solutions of various compounds in "Analar" (60–80) petroleum ether over a clean water surface in a 9 cm. diameter Petri dish. The desired properties of low melting point; large equilibrium film pressure; and stability, incompressibility, and compactness of the film are exhibited to a fair extent by cetyl alcohol. In order to evaluate the anticipated advantage of longer-chain compounds, compounds containing various numbers of ethylene oxide molecules attached to an alkyl chain were investigated. Results of the experiments indicated that reduction in water evaporation increases with the chain length and decreases in temperature, except for the C_{18} and C_{22} alcohols which exhibit a flattening and decrease, respectively, at lower temperatures.

Subject Headings: *Water, evaporation, control of; Evaporation, of water, control of.*
C. C. Miesse

61

X. Meteorological Interactions

Hay, J. S. and Pasquill, F. (Meteorological Office and Chemical Defence Establishment, Porton, England) "Diffusion from a Continuous Source in Relation to the Spectrum and Scale of Turbulence," *Advances in Geophysics* **6**, 345–365 (1960)

The aim of these experiments was to establish a relation between the spread of particles and the turbulent flow properties which are readily measureable. As a starting point Taylor's expression for the variance of particle displacement in the y direction is used. There are two quantities which must be specified, the variance in velocity $\overline{V^{12}}$ and the Lagrangian correlation coefficient. Difficulty is encountered evaluating $\overline{V^{12}}$ since, for short measuring time, the contribution from low frequency components are not included. If sampling time exceeds transit time, the velocity variance can be compensated. It is assumed that Lagrangian and Eulerian correlation functions have the same shape but different scales, i.e. $R_L(\beta t) = R_E(t)$. Values for β were determined experimentally.

The experiments involved measurement of wind speed, wind direction, and the dispersal of particles downstream of a continuous source. Additional analysis shows that the angular dispersion of particles σ_p^2 equals the angular variance of wind direction $\overline{\theta'^2}(T/\beta)$ when the averaging for variance is for a finite time equal to travel time divided by β. Both σ_p^2 and $\overline{\theta'^2}$ were measured so that it was possible to calculate β. Values of β from 1.1 to 8.5 were found with an average value of 4. This value of β indicates that the Lagrangian correlation persists for a long period compared to Eulerian correlation.

In order to obtain the variance for the angular dispersion of particles downstream of a continuous source in a turbulent flow, it is only necessary to measure the variance of the wind direction for a time period equal to travel time divided by β. This result appears to be valid for level terrain with no discontinuities in the flow (e.g. velocity or thermal discontinuities). Also the particles must be small so that flow velocity and particle velocity are identical.

Commonly, the change of cloud width with distance of travel is expressed as a simple power law. The exponent, b, as a function of sampling time, increases b whereas the more stable the air the smaller b.

Examination of other published data on diffusion reveals the important fact that β does not change with changing scale of turbulence over wide ranges. Other sets of data were interpreted in terms of the empirically developed theory. The values of cloud spread could be predicted with an accuracy of about ± 10 per cent.

Let X equal the distance of travel. Additional analysis based on Taylor's formula for $\overline{Y^2}$ indicates that $\overline{Y^2}/X^2$ is a function of X/λ and intensity of turbulence. Here λ is the geometrical scale of turbulence. The spread of a cloud will, of course, be similar for equivalent values of X/λ and u'. Values for b reported for widely different scales of turbulence have been nearly the same. The reported values for b apply to distances downstream such that the ranges of X/λ have been nearly identical.

Subject Headings: *Diffusion, continuous source of; Turbulence, effect on diffusion from continuous source.*

A. E. Fuhs

62

ABSTRACTS AND REVIEWS

Gifford, F. Jr. (U.S. Weather Bureau) "Atmospheric Dispersion," *Nuclear Safety* 1, 56–62 (1960)

The author discusses recent atmospheric dispersion observations and calls attention to the fact that they are of considerable interest in connection with the meteorology of nuclear safety problems. Instead of using Sutton's well-known mathematical dispersion model, which has certain limitations in regard to distance and atmospheric stability, the author discusses and shows the advantages of using the recently proposed method of moving averages in estimating atmospheric dispersion. Besides being less restrictive to boundary conditions the method of moving averages is well adapted to interpretation of continuously monitored atmospheric data.

By using an expression proposed by Hay and Pasquill [1] which corrects the turbulence-power spectrum for the effect of averaging raw data over time, the author by choosing the time for averaging raw data equal to the dispersion time or time of travel presents Taylor's dispersion equation in the following simple form:

$$\overline{y^2}(T) = <\overline{v^2(t)}>_{\mathrm{av}} T^2$$

were the symbol $<>_{\mathrm{av}}$ indicates that the original velocity signal, $v(t)$ is first subjected to a running mean (moving average) over an interval equal to the travel time, T.

The above equation states that to get a measure of the dispersion over a time T, it is only necessary to compute the mean-square deviation of the velocity signal (t), which has first been subjected to a moving average over the dispersion time T, and then multiplying the result by T^2.

The author points out that for application it would be very useful if the Lagrangian wind-fluctuation statistic in the above equation could be related to the Eulerian kind of wind fluctuation measurements made at a single point. Using Hay and Pasquill's [2] suggestion that the fluid-attached Lagrangian time scale, ξ, can be identified with the fixed-point Eulerian time scale, t, by a simple proportionality, $\xi = \beta t$, a dispersion equation of the following simple form results:

$$\sigma_\rho^2(T) = \overline{\theta'_s{}^2}$$

where $\sigma_\rho^2(T)$ is the variance, after a time of travel, T, of the particle spread, in angular measure from a continuous point source and $\overline{\theta'_s{}^2}$ is the variance of wind-direction fluctuation as measured at a fixed point and subjected to a moving average over time intervals $s = T/\beta$. The computed dispersion value is quite insensitive to variations in values β over a range of 1 to 10. Based on experimental data,[2] a value of $\beta = 4$ is suggested, which also agrees with results of another investigation.

Circuits are now available employing conventional electronic techniques by means of which the wind direction signal from a sensitive vane is continuously filtered in a form closely approximating the magnitude of $\overline{\theta'_s{}^2}$ in the above simple dispersion equation.

The author concludes that the method of moving averages has two distinct advantages: firstly, it relates the actual turbulent wind fluctuations directly to the dispersion without the necessity of introducing an intermediate hypothesis; secondly, the method is adaptable to the continuous monitoring of atmospheric dispersive capacity at a reactor site.

<center>63</center>

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

W. L. Fons

Schmidt, F. H. (Royal Netherlands Meteorological Institute, De Bilt, Netherlands) "On the Diffusion of Heated Jets," *Tellus* **9**, 378–383 (1959)

Turbulent diffusion and convective processes due to both buoyancy and imposed flow are assumed to govern the velocity and temperature field development in a heated jet which issues into an otherwise stagnant medium. In this paper, the author presents the consequences of a similarity theory of this problem. Since no assumptions are made as to the universal similarity functions describing both the velocity and temperature fields (other than their existence) the results contain and generalize the earlier findings of Tollmien[1] (1926), W. Schmidt[2] (1941) and Priestley and Ball[3] (1955).

In a subsequent discussion of the form of these similarity functions, the author departs from previous uses of the Gaussian distribution by suggesting a new, single parameter family of velocity profiles. This choice is shown to satisfy a necessary condition violated by the Gaussian distribution (it is not shown to be unique in this respect, however). Remarkably enough, the new profiles predict the existence of a counter-current (region of reverse flow) induced far from the jet axis. The new velocity law is then used to correlate the measurements of H. Rouse[4] *et al.* (1952); however, the resulting scatter, as well as the absence of data sufficiently far from the jet axis, preclude a decision as to its superiority over the usual Gaussian law.

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2. Schmidt, W. "Turbulente Ausbreitung eines Stromes erhitzter Luft," Z.A.M.M., *21,* 265 and 351 (1941)
3. Priestley, C. H. B., and Ball, F. K. "Continuous Convection from an Isolated Source of Heat," Qu. J. Roy. Met. Soc., *81,* 144 (1955)
4. Rouse, H., Yih, C. S., and Humphreys, H. W. "Gravitational Convection from a Boundary Source," Tellus *4,* 201 (1952)

Subject Headings: *Jets, diffusion of heated; Diffusion, of heated jets.*

D. E. Rosner

Bennett, W. D. (Pulp and Paper Research Institute, Montreal, Canada) "The Control of Lightning-Caused Forest Fires," *Pulp and Paper Research Institute of Canada Woodlands Research Index No. 106* (1958)

This publication reviews literature on forest fires caused by lightning, dating from 1912 through 1957. Consideration is given chiefly to the importance of lightning as a fire cause in Canada and the United States, the mechanics of thunder and lightning, general locations of areas susceptible to lightning fires, recognition

ABSTRACTS AND REVIEWS

of meteorological conditions preceding the occurrence of fire-starting thunder-storms, research in the control of forest fires caused by lightning, and possibilities of cloud modification. The treatment is brief and frequently superficial; thus the author, perhaps intentionally, emphasizes that the knowledge which actually promises major help in solving the lightning fire problem is yet to be obtained.

Twenty-nine references are cited; 132 more are listed in the appendix. The latter range from highly technical papers and comprehensive reports on major atmospheric research projects (e.g. the Project Cirrus and Thunderstorm reports) to extremely general articles that seem to have little bearing on the subject at hand. Omission of certain noteworthy publications makes one wonder how complete the bibliography is.

An interesting disclosure is that lightning is the second most important cause of forest fires in Canada, as judged by number at any rate, accounting for 20 per cent of the total fires from 1946 through 1955. British Columbia, Ontario, and the Northwest Territories are the areas most beset by lightning fires, and in some years fires in these areas comprise half the total number. The high occurrence in Ontario is especially noteworthy because in the United States lightning fires are few and severely localized east of the Great Plains.

Although the author does not in so many words recommend research in Canada on control of forest fires caused by lightning, he states that such study should (1) be preceded by investigation of the methods employed in Project Sky-fire, (2) as a first step determine what areas are most subject to forest fires, (3) give priority to high-value areas. General suggestions are made for the organization and administration of a national, research project on lightning fires.

Subject Headings: *Fires, control of lightning-caused; Forest fires, control of: Lightning, cause of forest fires.*

G. R. Fahnestock

Cramer, O. P. (Pacific Northwest Forest and Range Experiment Station, Portland, Oregon) "Using Fire-Weather Forecasts and Local Weather Observations in Predicting Burning Index for Individual Fire-Danger Stations," *Pacific Northwest Forest and Range Experiment Station Research Paper 28* (July 1958)

This paper presents results from an exploratory study which investigated the practicability of using several tabular and graphical aids for converting area forecasts and local observations of relative humidity and wind speeds into predicted values for individual fire-danger stations.

The study was conducted on five ranger districts in the national forests of Oregon and Washington during the summer of 1950 and 1951. It had three objectives: (1) to test the feasibility of field preparation and use of forecasting aids; (2) to determine the accuracy of the aids in comparison with the old system of assumed persistency; and (3) to determine what additional research was needed.

In general, field preparation of forecasting aids by regular personnel at ranger stations was found to be inadequate, due to the lack of uninterrupted time needed in the preparation, misunderstanding of the principles involved, and misinterpretation of the instructions. When correctly completed and arranged, however, the aids were found to be quite helpful and simple to use. Operational obstacles were also evident, the greatest being inaccurate fire-weather forecasts for both construction and application of the aids, and unsuitability of the aids because of inadequate exposure of many of the test stations.

The aids were specifically tested for ability to predict change from the previous day, abnormal conditions, and high burning-index situations. Results indicate that the accuracy of the aids varied greatly between stations and from year to year. None of the methods tested was considered reliable for all stations but the most promising procedures were found to be slightly superior in average accuracy to the old method of assuming persisting burning index at all stations.

The inadequacies and variations in predictive accuracy of the different forecast aids tested are discussed at great length in the paper. Though many of the aids exhibited improvements over the old method, the author states that further improvements are needed. A number of recommendations are advanced for improving the aids.

In conclusion the author emphasizes the need for additional research in weather forecasting, particularly in relation to the predictions of major weather changes. In addition, research in the development of techniques for accurate spot forecasts of fire weather is needed, further studies are needed in standardizing location and exposure of fire-danger stations, and better use of observations and predictions should be made.

Subject Headings: *Burning index, prediction of; Fire weather, forecasts; Weather, prediction of burning index by forecasts of.*

W. Y. Pong

XII. Instrumentation

Leslie, W. H. P., Hunter, J. J., and Robb. D. (National Engineering Laboratory, East Kilbride, Scotland) "Precision Temperature Measurement Outside the Laboratory," *Research* **13**, 250–256 (1960)

Temperature measurement between 0–100°C with millidegree accuracy, in pressurized flowing fluids, requires robust and compact precision equipment insensitive to field conditions of vibration and ambient temperature fluctuation.

Two years of testing with resistance thermometers wound with copper wire has led to development of a dual element probe which displays relatively long-term calibration stability. Within a stainless steel, low conductivity, watertight, tubular sheath are mounted the copper measurement element and a low temperature coefficient, *Minalpha,* reference resistor. Both are in contact with a high conductivity, finned, copper end-plug by means of a Dauphinee-type rigid mount free of thermal stress. The ratio of the two resistances at the same unknown immersion temperature is a unique indication of temperature. Self-heating of the measuring element can be compensated for by restricting current flow or calibrating in a proper environment.

Six different bridge measuring circuits are proposed, exploiting the use of new high permeability materials to produce a transformer ratio arm type of voltage supply. These bridges compensate for relatively long thermometer leads, typical of field measurements, by means of auxiliary transformers which compensate for the lead voltage drop. A multiple bridge circuit also is presented for averaging several temperatures. Three electrical characteristics required for the bridge designs are specified.

Subject Headings: *Temperature, precision measurement of.*

K. M. Foreman

66

INDEX OF AUTHORS

INDEX OF SUBJECTS

ABSTRACTS AND REVIEWS

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Fire Research
Abstracts and Reviews

Committee on Fire Research
and
Fire Research Conference

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

FOREWORD

A meeting of unusual interest and importance to fire research will be held at Woods Hole, Massachusetts, July 17 to August 11, by the Committee on Fire Research of the National Academy of Sciences—National Research Council, with financial support of the National Science Foundation. Dr. Howard W. Emmons of Harvard University is chairman. An eminent group of scientists and engineers, invited from the United States and some from abroad, will conduct an intensive four-week study and will present their conclusions, recommendations, and evaluation of the present status of the fire problem. This probably represents the first all-encompassing survey of activities in the fire field in the United States and should have an important bearing on its advancement. As shown by the tentative program, a very broad view is taken which includes the following topics:

City Fire Statistics
Forest Fire Statistics
Special Industrial Fire Statistics
Fire Statistics Collection and Organization
Chemistry of Combustion and Fire Inhibition
Fire Meteorology
Fire and Ecology
Fire Danger Rating, Principles and Practice
Underwriter Laboratories
Cost of Fire Protection
Fire Extinguishment in Different Materials
Fire Department Organization and Fire Attack Planning

Fire Attack Planning in Industrial Plants
Fire Extinguishment in Forests
Forest Fire Department Organization and Fire Attack Planning
The Training of Professionals
Meteorological Instrumentation
Control Burns
Equipment Development, including Detection Devices
Civil Defense Fire Problems
Department of Defense Fire Problems
National Bureau of Standards Fire Studies
Prefire Planning in Cities
Prefire Planning in Forests
Physiology of Burns and Asphyxiation
Survey of Present Fire Research

The Committee on Fire Research is co-sponsor of the Symposium on Fire Control Research (National Meeting, American Chemical Society, Chicago, Illinois, September 3–8, 1961) which promises to be of considerable interest. Four papers out of a total of approximately fifteen, have been received from abroad, i.e. "The Extinction of Fires by Water Sprays," D. J. Rasbash (Joint Fire Research Organization, Boreham Wood, England); "Iron Pentacarbonyl in CH_4-O_2 and Air Flames," U. Bonne, W. Jost, H. Gg. Wagner (University of Göttingen, Germany); "The Flammability of Methane-Air Mixtures in Water-Base Foams," J. H. Burgoyne, A. J. Steel (Imperial College, London); "Study of Various Influences on the Extinction of Methane-Oxygen Detonations by Fine Powders," P. Lafitte, R. Delbourgo, J. Combourieu, J. C. Dumont (Sorbonne, Paris, France).

The complete program of the Symposium will appear in the July 31, 1961 issue of *Chemical and Engineering News*. A preliminary program will be available on June 26 and can be obtained from Dr. R. Friedman, Atlantic Research Corporation, Alexandria, Virginia.

WALTER G. BERL, Editor

i

Table of Contents

Volume 3   Number 2

iii

Table of Contents—*Continued*

Table of Contents—*Continued*

REVIEW

Fire Research

S. H. Clarke

Director, Warren Spring Laboratory, D.S.I.R.

(The following article is an account of a Friday Evening Discourse before The Royal
Institution of Great Britain on October 21, 1960 and is reprinted with their kind per-
mission. The author was the first director of the Fire Research Station, Boreham Wood,
England, and his guidance contributed largely to the effectiveness and the endurance of
that organization.—EDITOR)

In his Presidential Address to the British Association, Sir George Thomson
described two aspects of science: it is useful in making possible the control of
natural processes, and it brings increased understanding of a pattern with an
intrinsic beauty as compelling as that of any art, and worthy of study in its own
right. Both aspects are apparent in fire research, an applied science in which all
the disciplines are marshalled to reduce the hazard to life and property by fire.

Like science, fire has two aspects: it is proverbially a good servant, but a
bad master. In the latter role it can be a social problem of some magnitude. Last
year fire brigades attended 240,000 fires in the United Kingdom and the damage
was estimated at £44,000,000. 445 people lost their lives. Figures for injuries
are not yet available, but in an average day some 500 patients are in hospitals as
a result of burns. These were only the direct effects; it has not been possible to
assess the many indirect ones which may be as great.

Many of the fires and much of the damage could have been prevented by
the application of existing knowledge. Nevertheless, the largest fire of modern
times—perhaps the largest single fire of all time—occurred a few years ago in
a modern building which had been assessed by experts as fire-resisting. One of
the main aims of fire research is to protect against the hazard of future fires
in a rapidly advancing industrial world which makes ever new and ever greater
demands.

While there is little point in speculating on the precise moment of history
at which research in fire protection began, it was at a very early stage that
experience taught the first lesson of fire protection—the necessity of controlling
what is still a major source of ignition, namely the domestic fire.

The continuous systematic study of fire started in Europe and the United
States in the closing years of the last century. Added impetus came with the war,
and modern fire research owes much to the vision of the late Sir Reginald Stradling,
then Chief Scientific Adviser to the Ministry of Home Security, the wartime
leadership of The Rt. Hon. The Viscount Falmouth, then Head of the Fire
Research Division, and to the knowledge and experience of Professors G. I. Finch
and D. T. A. Townend. Finch brought exceptional vigour and suggested many
critical experiments which were of great value in elucidating some of the more

important basic phenomena. He showed that although many of the problems of fire protection were extremely complicated, they were in fact the result of an intricate pattern built on relatively simple principles.

For a fire to occur there must be fuel, oxygen, and a source of ignition. This is a slight oversimplification, and there are exceptions, but they are of almost negligible practical importance.

It is helpful to approach the study of fire by examining a shallow dish of petrol—a volatile, flammable liquid. As the vapour escapes into the air, concentration is high near the surface of the liquid, and diminishes as the distance from the surface increases. If a small flame is gradually brought near to the surface, the vapour ignites when the flame is perhaps an inch from the liquid; the eye can just follow the rapid spread of flame. Incidentally, a cigarette can be extinguished by gently dipping the lighted end into a tray of petrol.

If the experiment is repeated with a tray of paraffin (kerosene) it will be found that quite a large flame must be played directly onto the surface for some little time before ignition takes place. Once ignition occurs, however, and the flames have warmed the liquid, if they are snuffed out by placing a board over the tray, immediate reignition occurs when the flame approaches the surface, exactly as with the petrol.

It is thus necessary to distinguish two temperatures: first the "flashpoint," which is the temperature at which vapour distills rapidly enough to support a flame; and secondly the "ignition temperature"—and this is usually a higher one—at which the flammable vapours can be ignited.

It should be noted that combustion occurs in the vapour phase, and in a region where there are convenient proportions of vapour and oxygen. The chemical reaction which takes place between the fuel vapour and the oxygen liberates heat which may itself be the igniting source which continues the fire. Fire research consists largely in tracing the pattern of this heat, measuring its temperature in a wide variety of conditions, and observing its effect on innumerable materials and on structures.

A great deal of research has been carried out to improve methods of measuring temperature, and scores of ingenious devices have been produced—not all directly for fire research but they have been used in its aid.

Ignition temperatures may vary. There are, for example, many substances which act as catalysts, and if small quantities are present, some chemical reactions take place at lower temperatures than normal. Again some substances, and ether is an example, can undergo a type of partial burning at a relatively low temperature, with what are known as "cool flames." Interesting pioneer work in this field was carried out by Professor D. T. A. Townend and his colleagues. Until these phenomena were elucidated certain mysterious outbreaks of fire were not understood: for instance, fires in hospitals which occurred when a blanket was pulled from a patient.

Although the chemical processes that are involved when wood is burned are much more complicated, in some ways wood and other similar materials may be thought of as behaving like liquids with a high flashpoint. When wood is heated it decomposes, and gases and vapours are formed which, in contact with air, behave just like those of petrol or paraffin, and burn with flame.

G. I. Finch summarised very neatly the behaviour of wood as a fuel. He found it convenient to classify combustible materials in three grades which he

68

called "tinder," "kindling," and "bulk fuel." Tinder can be ignited by an ordinary match and is then able to continue burning; it has a specific surface of not less than 20 cm²/g; paper or wood shavings are an example. Kindling cannot be ignited by a match but can by tinder, and if it is suitably arranged can continue to burn; it has a specific surface of not less than 2 cm²/g. Bulk fuel can only be ignited by a fire which already involves kindling, but under suitable conditions it can sustain self-combustion; its specific surface is less than 2 cm²/g.

It is simple to demonstrate that a sheet of paper can be ignited with a match, and will continue to burn, whereas a thick piece of wood will not do so. As Finch pointed out the reason is that heat from the burning wood is being dissipated by radiation from the flames, and by conduction with the interior of the wood, and if too much is lost destructive distillation ceases and the flames die out. If the wood is thin enough heat conducted from one side is counterbalanced by heat from the other, and burning continues; in practice wood of less than about ¼ or ⅜ inch (depending on density, and on dryness) will continue to burn when ignited.

Similarly, heat lost by radiation may be counterbalanced by supporting heat from a neighbouring fire. Large pieces of wood of any size will burn to destruction if they are near enough, say, ½ inch or less apart, and a fire is started between them.

D. I. Lawson, the present Director of Fire Research, and P. H. Thomas observed an interesting feature in the burning of wood. When small specimens are subjected to radiant heat of high intensity, vapours and gases are emitted which ignite spontaneously. The interesting thing is that ignition occurs not at the point of applied heat, but some distance above, and the flame jumps rapidly back to the wood.

The processes described form the background to the early stages of most fires. Once started, a fire spreads until all the exposed surface of combustible material is involved in flame. At that moment the maximum temperature is reached. The rate at which it is reached depends largely on the amount and arrangement of the combustible materials. When it is reached subsequent developments depend largely on the access of air to the fire. Approximately half the mass of the wood is lost in flame, and the other half glows as charcoal.

It has already been noted that the first practical fire precaution is the control of possible sources of ignition. The second is the control of the amount of combustible material that can be involved at one time. The problem of dealing efficiency with the large quantities of materials that have to be handled and stored in the modern world is extremely difficult, and a substantial proportion of the effort in fire research is aimed at its solution. Frequently it involves the division of large buildings into compartments each of which has a pre-determined degree of fire resistance.

Observations made at many large fires and in experiments have led to the almost universal acceptance of a standard time-temperature curve (Fig. 1) which is considered to represent the development of temperature in a severe fire. "Fire resistance" is defined as the length of time for which a unit of structure continues to perform its design function when it is heated in a furnace which is controlled according to the standard curve. By-laws in most countries now require buildings in towns to be constructed so that their walls, floors, structural columns, and certain doors and windows reach an appropriate degree of fire-resistance. Steel

69

columns have a fire resistance of about ten minutes and the problem is, therefore, to provide them with a heat-resisting coating which will stay in position.

It sometimes comes as a surprise to find that steel behaves so badly in fire; but it may be a greater one to learn that a number of fires have been caused by the combustion of fine steel wool, which is readily ignited by a match, or even by allowing a handful to fall across the terminals of a small battery; and there have been many fires in the steel tubes of boilers in which overheated tubes have burned in high pressure steam.

The variety of possibilities in constructing fire-resistant buildings is so great, and the present state of our knowledge so small, that full-scale tests are often necessary before approval can be given for the use of a new form of building construction. Furnaces were built by the Fire Offices Committee nearly thirty years ago to enable such tests to be carried out and they were made available to the Building Research Station of the Department of Scientific and Industrial Research for research purposes. When the Joint Fire Research Organisation was set up in 1947 they formed part of the contribution of the Fire Offices Committee to this Organisation.

Full-scale tests are costly and time-consuming, and much research has been designed to find means of eliminating them, or at least of conducting them on a smaller scale. The research involved the search for mathematical expressions for the variations in temperature in every part of a wall, floor, column, etc., when the temperature of the surface is raised at the rate demanded by the standard time-temperature curve. Bearing in mind that, to take a simple example, a steel girder may be protected by an air-gap between itself and a slab of building material which may range from chipboard to lightweight concrete using exfoliated vermiculite as an aggregate, with a coat of plaster, even when the thermal constants of the individual layers are known the calculation of temperature rise in the steel is a difficult and tedious operation. Lawson and McGuire devised and constructed an electrical analogue which has proved extremely valuable both as a research tool, and in reducing the number of full-scale tests. It exploits the close analogy which exists between the flow of heat in solids and the flow of a charge along a transmission line composed of series resistance and shunt capacitance elements.

The analogue deals with one scientific problem, namely the behaviour of units of building construction under closely defined conditions. There remain a wide range of problems resulting from the movement of hot gases and the transfer of heat, such as the provision of escape facilities in high buildings, the control of smoke in large basements or in ships, the "mushrooming" of hot gases in buildings of large area, the detection of fire, and many aspects of extinction. Before these can be studied on a small scale there is need of a reliable technique for the use of models. Considerable progress in this direction has been made by P. H. Thomas and C. T. Webster. Working with similar cubical models from 1 ft. to 10 ft. side, they have studied the burning of wooden cribs of various sizes, and have established relationships that have already enabled them to deal with some practical situations.

It has long been recognised that smoke is perhaps the fireman's greatest enemy. It offers particular difficulties in buildings with a large expanse of floor area with all kinds of obstructions which together make it impossible for the fireman to see or to find his way to the seat of the fire. The Covent Garden fire and several other recent large fires in this country have focused attention sharply

ABSTRACTS AND REVIEWS

on this problem. They have led to a revived interest in a method of fire protection that has been employed in theatres for many years, namely the provision of emergency venting in the roofs to release the smoke and hot gases at an early stage in the fire. P. H. Thomas has recently developed for the first time what appears to be a satisfactory solution with an adequate theoretical basis. Using models, he has explored the combined use of "curtains" to restrict the lateral spread of smoke in conjunction with roof vents of various sizes, and has established a relation between vent area and the proportion of heat released in experimental conditions.
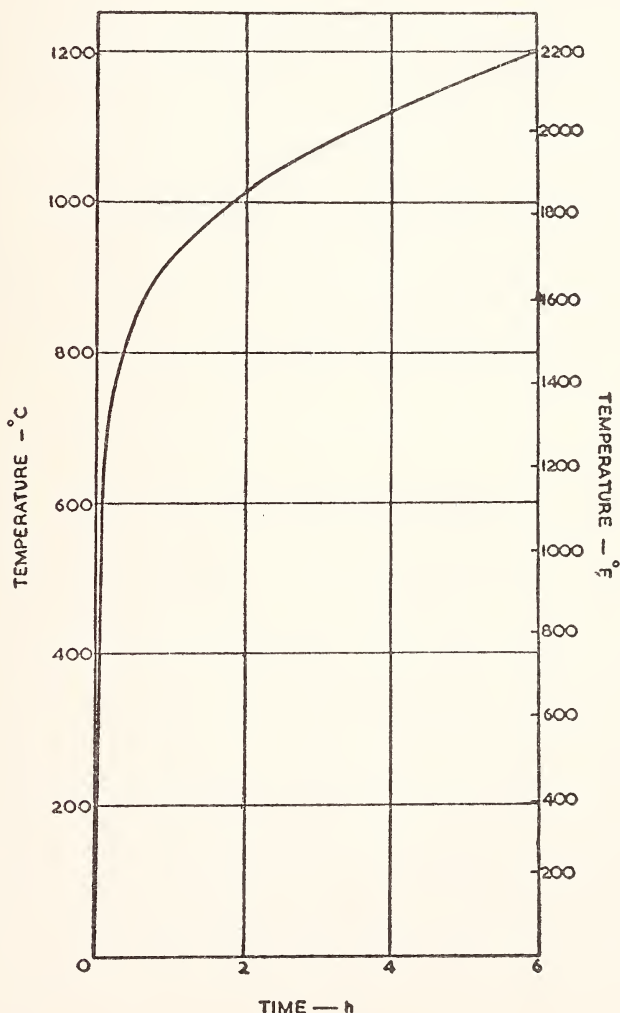

Figure 1. Standard Time-Temperature Curve.
(British Standard 476)

71

Detection

Experience of large fires soon convinces that when they get beyond a certain size, total destruction is inescapable. A surprisingly large proportion of the total damage is caused by a relatively small number of large fires; each year nearly half the damage is caused by some 200–300 out of some 50,000 fires in buildings attended by the fire brigades. Of the many factors that contribute to the development of large fires the most important is failure to detect and attack them while they are still small. P. Nash and R. Pickard have explored the rise in temperature and the movement of hot gases over fires of various sizes in enclosures of various heights and shapes, a task which called for entirely new instruments for measuring air-flow. Using the results of this work, together with information about the distance of travel of fire brigades and experience of the desirable balance between high sensitivity and the likelihood of false alarms, they have succeeded in developing a standard procedure which enables the merits of new designs of detector to be assessed.

Before leaving the subject of the occurrences of fires, reference should be made to the fact that effective statistics are collected by the Fire Brigades of the Local Authorities by arrangement with the Home Office. These have yielded a number of interesting results, including indications of significant differences in behaviour of pre-war and post-war houses and pre-fabs—the post-war housing having the best record. They have revealed a steady increase in fires associated with electrical equipment, and with the use of certain types of oil-burning apparatus.

Extinction

When attempts to control sources of ignition and accumulations of fuel have failed, there remains the task of fire extinction. The most common method is to cool the fuel to a temperature at which the flammable vapours cease to be emitted.

The commonest extinguishing agent is water, and the principles that govern its use have not changed fundamentally over hundreds of years. Whenever it can be used it is incomparably the best medium; it might have been designed for the purpose. There is plenty of it and it is cheap; it is easily transported (by pipes) and easily applied. It has a large thermal capacity and it boils at a convenient temperature absorbing a useful amount of heat in doing so. The only circumstances in which plain water is not the best medium are electrical fires, fires involving flammable liquids whose flashpoint is below atmospheric temperature, and circumstances in which water damage must be avoided at all costs.

The main lines of research in recent years have aimed at improvements in methods of applying water. Since the war improvements in equipment, training and technique have resulted in a marked and continued steady improvement in the effectiveness of Fire Brigades in this country (Figure 2).

It was appreciated during the last century that where possible it was more effective and economical to apply water as a spray. In the early post-war years the opinion was held in some quarters that high-pressure sprays, which were believed to have very fine drops, represented the ultimate in efficiency. A long and careful study by D. Hird, in which the fire brigades in London and Birmingham took part, demonstrated that there is no material advantage in increasing

operational pressure above about 100 lb. per square inch and any theoretical merit fine drops may have in extinction is offset by their limited trajectory.

D. J. Rasbash has shown that, where water is used, fires in liquids which cannot be cooled below their flashpoint must be extinguished in the vapour phase by the use of a very fine spray. Less volatile liquids such as fuel oil can be extinguished by cooling and larger drops which will pass through the flames and reach the surface of the liquid are more effective.

Another way of using water is as foam, which is made by dissolving a foaming agent (often a protein derivative) in water and aerating the solution mechanically or by producing bubbles of carbon dioxide chemically. The function of the foam is to cover the surface of the liquid and to shield it against radiant heat from the fire, thus cutting off the supply of flammable vapour.
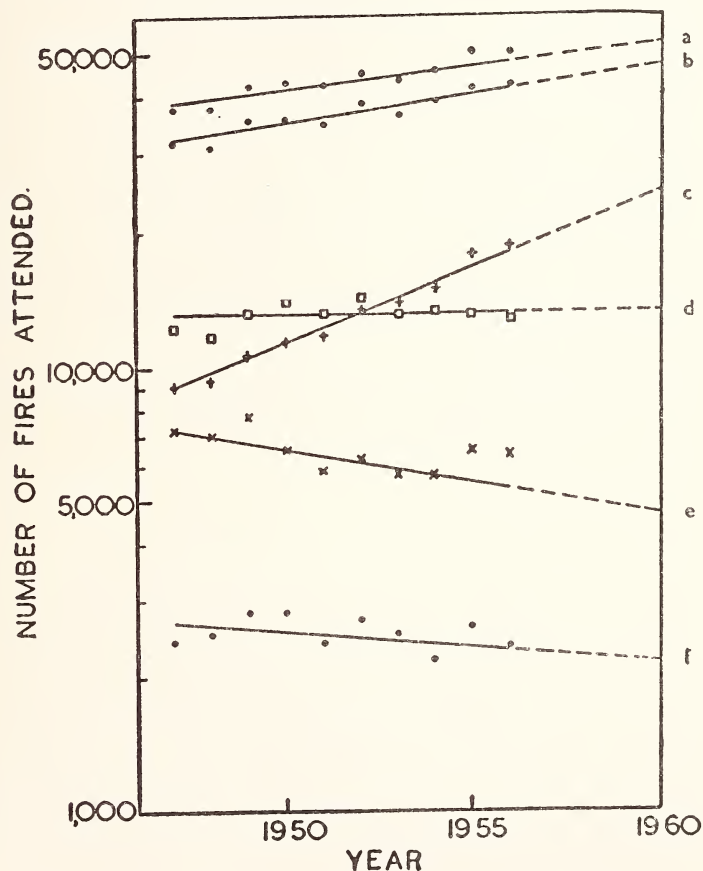
Figure 2. Methods of extinguishing fires in buildings.

(a) Total fires in buildings. (b) Total fires in buildings extinguished by Fire Brigades. (c) Fires extinguished by Fire Brigades using hose reel jets and water in tank. (d) Fires extinguished by Fire Brigades, methods not specified. (e) Fires extinguished by Fire Brigades using jets from Council hydrants. (f) Fires extinguished by Fire Brigades using hose reel jets and more water than that in tank.

73

One of the most interesting results of recent research has been the establishment of the best types of foam for certain special purposes. During the war it was found possible to introduce foam at the base of a tank of fuel oil and to let it rise by its low, relative density and spread over the surface of the oil. This was not possible with petrol, because in ascending through the bulk of the liquid the foam became impregnated with petrol which continued to burn and destroyed the foam. Studies in the Laboratory, which were confirmed on a large scale, revealed the surprising conclusion that very sloppy foams, with an expansion of about three times, could be used satisfactorily even with petrol.

There are two other types of media that can be used for special fires. The first are known as vapourizing liquids, the commonest being carbon tetrachloride. They operate in the vapour phase by absorbing heat, and possibly also by inhibiting the combustion reactions. Research has been devoted to seeking to understand the mechanism of the reactions, and to selecting the most effective of a wide range of reagents. In recent years chlorobromomethane has come to be regarded as the best of the available materials. When weighing the merits of various agents, the toxicity of the agent, or its decomposition products, has to be considered.

D. J. Rasbash recently made the bold suggestion that the principle of controlling the atmosphere might be used on the grand scale even for such fires as that at Covent Garden. A large jet engine was specially modified by the National Gas Turbine Establishment, and the exhaust gases from this engine are being used experimentally in a large building to see how far practical use can be made of the principle. The inert exhaust gases do not cool the fuel, but it is hoped that they will prevent the spread of combustion long enough for a fireman to be able to approach with his hose.

The other type of medium is known as "dry-powder," usually in the form of sodium bicarbonate. Research has not yet fully elucidated its mode of action, but experience has thrown considerable doubt on its superiority over other cheaper and better-known methods.

Fire as a Social Problem

It was said at the beginning that fire is a social problem. An example will illustrate some of the difficulties in applying the results of research. A few years ago D. I. Lawson and his colleagues studied the occurrence of casualties through the ignition of clothing. Fire brigades and a number of hospitals co-operated by sending reports on a large number of casualties, and in many instances they sent the garments which were involved, or samples of the ones which were first ignited. The researches involved studies of a large range of fabrics in the laboratory and a simple equipment was developed as a standard measure of their flammability. Statistics showed that nearly a quarter of the fatal casualties were children, and of those a large proportion were wearing nightdresses. Very few occurred between the ages of about 10 and 60, and the vast majority were elderly people, and often old ladies. It was clear that the practical solution was not to aim immediately at the prohibition of all but flame-resistant fabrics; special care of the young and old was called for, and increased attention to the control of sources of ignition such as electric fires, gas fires, and the domestic fire. It was considered important that the public should be informed about the hazards of certain fabrics

and that means should be provided for them to be able to recognise the ones which presented the least hazard.

Deliberations of this kind call for wide collaboration. Fire touches practically every aspect of life, and some fourteen Government Departments have special concern in fire protection: the Home Office is responsible for the safety of the public where they assemble in buildings and other places, and for ensuring that the efficiency of the Fire Brigades is maintained: the Ministry of Transport for ships: the Ministry of Aviation for aircraft, and so on. The Fire Research Board gives opportunity for members of industry and of the universities to consider their problems, and with assessors from the Government Departments, to ensure that the research programme is balanced and co-ordinated. The Joint Fire Research Organisation itself is believed to be the only example of an equal partnership of Government (through the Department of Scientific & Industrial Research) and industry (through the Fire Offices Committee) to deal at national level with a social problem.

ABSTRACTS

III. Heat and Material Transfer

Whitmore, D. H. and Moser, J. B. (Northwestern University, Evanston, Illinois) "Sublimation of Small Sodium Chloride Spheres into Argon," *Journal of Chemical Physics* **33**, 917–920 (1960)

A careful experimental technique was developed to measure the rate of sublimation of small (*ca.* 260μ) sodium chloride spheres into argon. The direct observational method utilizing a hot stage was found to be applicable in this study of the high-temperature kinetics of the sublimation of solids. Previous observations that the mass rate of vaporization of a spherical droplet into still air is directly proportional to its radius and not to its surface area were confirmed in these experiments. Langmuir's integrated rate expression for the isothermal vaporization rate of the spherical particle under constant ambient gas pressure was found applicable for the sphere sizes and argon pressures employed in this study. This expression, which was derived by Langmuir under the assumption that vaporization from a small sphere is controlled by diffusion of vapor away from the surface analogous to the loss of heat, may be written

$$r_0^2 - r^2 = kt$$

where r_0 is the initial radius and r is the radius at any time t. The constant k depends on the diffusion coefficient of the subliming vapor in the ambient gas atmosphere, the molecular weight and equilibrium partial pressure of the diffusing vapor species, the density of the solid particle as well as the absolute temperature, and the gas constant.

While the Langmuir treatment was applicable in these experiments, i.e. for particle sizes of the order of 260μ and ambient pressures from 0.2 to 2.0 atmospheres, the authors point out that it would predict an infinite vaporization rate per unit area in the limiting case where the size of the spheres or the inert gas pressure is reduced.

The technique employed enabled the authors to determine the diffusion coefficient of sodium chloride vapor in argon as a function of pressure. A change of temperature from the lowest to the highest employed (999° to 1043° K) would result in an increase of 6.7 per cent in the diffusion coefficient based on theory. This variation was too small to be confirmed by the present experimental technique.

Subject Headings: *Sublimation, of sodium chloride.*

A. Strasser

V. Combustion Principles

Berendsen, R. and van Tiggelen, A. (University of Louvain, Louvain, Belgium) "Ionization in Methane, Ethylene, Ammonia, and Vinyl Chloride Flames," *Bulletin Sociétés Chimiques Belges* **68**, 620–629 (1959)

By measuring the electrical resistance of flames stabilized on an annular slot burner (using the burner surfaces themselves as the electrodes [1]) as a function of

76

equivalence ratio φ and extent of nitrogen dilution, the authors have deduced values of an apparent activation energy E_f for ion formation in CH_4/O_2, C_2H_4/O_2, NH_3/O_2, and C_2H_3Cl/O_2 flames at atmospheric pressure. These activation energies are derived from Arrhenius type plots of $\ln n^+$ vs. $1/T_m$ at constant φ under the assumption that the ion formation process is a second order (bimolecular) process. Here T_m is the mean flame gas temperature (introduced in reference 2) and n^+ is the positive ion concentration deduced from the electrical resistivity measurements.

Interestingly enough, while the Arrhenius plots are indeed found to be linear, the inferred activation energy, E_f, is not found to be independent of mixture ratio. For the CH_4/O_2, C_2H_4/O_2, C_2H_3Cl/O_2, and C_2H_2/O_2 flames E_f generally decreases with increasing richness (φ increasing); however, this was not observed for the ammonia/oxygen flame. The apparent activation energies for ion formation are in each case considerably larger than the global activation energy E for the combustion of the respective fuel/oxygen mixtures (see Table); however, they are not so large as would be expected if the ion production mechanism were "thermal" in character. This is construed as support for the hypothesis that ion production in flames is the result of true "chemi-ionization processes." [3]

TABLE *

GLOBAL ACTIVATION ENERGIES (E) FOR COMBUSTION
AND APPARENT ACTIVATION ENERGIES (E_f) OF
ION FORMATION (in kcal) FOR STOICHIOMETRIC
MIXTURES AT ONE ATMOSPHERE

Flame	E	E_f
CH_4/O_2	38	77
C_2H_4/O_2	36	65.5
C_2H_2/O_2	31	50
C_2H_3Cl/O_2	50	142
NH_3/O_2	59	172

* Abstracted from Table V of Berendsen, R. and van Tiggelen, A.

The authors have included in the paper tabular values of the flame temperature (determined by sodium line reversal) and specific electrical resistivity for each mixture ratio, per cent dilution, and fuel/oxygen combination studied. These tables should be of interest to those who may wish to re-examine their data from other points of view.

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Subject Headings: *Ionization, in flames; Flame, ionization in.*

D. W. Rosner

Squire, W. and Foster, C. (Southwest Research Institute, San Antonio, Texas) "A Mathematical Study of the Mechanism of Wood Burning," *National Bureau of Standards Contract CST-362, Technical Progress Report No. 1* (February 3, 1961)

A method was sought for calculating theoretically the combustion of woody materials in which the solid decomposes slightly exothermically to form flammable vapor that burns by diffusion flame in surrounding air. A mathematical model amenable to numerical solution by high-speed computer was developed for the simplified case of variation in temperature and composition normal only to the burning surface, such as an infinite plane surface, a long cylinder, or a sphere heated or burning uniformly.

The development is based on partial differential equations proposed by Bamford, Crank, and Malan,[1] for the temperature gradient within the solid and for the first-order rate of formation of volatile material. The boundary conditions are a temperature gradient that is zero at a central point, that at a nonburning surface is proportional to the heat transfer coefficient multiplied by the temperature difference between surface and environment, and at a surface receiving "feed back" of heat from a flame is proportional to $fQ\left[\dfrac{\delta w}{\delta t}dx\right.$. Coefficient f represents the fraction of the heat liberated in the flame that is returned to the wood, Q is the heat of combustion, $\dfrac{\delta w}{\delta t}$ the rate of formation of volatile material, and x is the distance from the center of the specimen.

By introducing suitable dimensionless variables the basic differential equations become $\nabla^2\theta = \dfrac{\delta\theta}{\delta\tau} + a\dfrac{\delta W}{\delta\tau}$ and $\dfrac{\delta W}{\delta\tau} = W\,e^{\ln\beta - \theta^{-1}}$ in which there are the following dimensionless parameters: space X, temperature θ, time τ, heat release a, concentration W, and reaction rate β. The boundary condition at a nonburning surface becomes $-\dfrac{\delta\theta}{\delta X}_{\text{surface}} = Nu\,(\theta_\infty - \theta_s)$ where Nu is a dimensionless heat transfer coefficient. Calculations using physical and thermal data for woody materials from Akita[2] or from Gross and Robertson[3] show that a will be small, say 0.005 to 0.05, θ will range from 0.01 to 0.05, and β will usually exceed 10^{10} but for any problem $\ln\beta$ should be less than the initial value of $\theta_{\text{in.}}^{-1}$ or the initial state will not be well defined.

Problems of this type can be handled by replacing the partial differential equation by finite difference equations due to Crank and Nicolson.[4] For simplicity it is assumed that $\dfrac{\triangle\tau}{\triangle X} = 1$ so that $\triangle\tau = \dfrac{1}{M^2}$ where M is the number of spatial divisions and for the present only a slab for which $\nabla^2 = \dfrac{\delta^2}{\delta X^2}$ is considered. Basic equations are then set forth and programmed for a computing machine. The flow sheets for the machine program are given in an appendix. Solutions are obtained for boundary conditions corresponding to self-ignition (due to heat being generated by decomposition faster than it can be conducted away) and to forced ignition by an external source.

Self-ignition. The initial conditions are $\theta = \theta_{\text{in.}}$ and $W = 1$ at $\tau = 0$. Boundary conditions are $-\dfrac{\delta\theta}{\delta X} = Nu\,[\theta_{\text{in.}} - \theta(1)]$ at the surface and $\dfrac{\delta\theta}{\delta X} = 0$ at the center. The

78

behavior of the solution for W and θ as functions of X and τ depends on a, $\ln\beta$, $\theta_{initial}$, and Nu. There will be two types of solution for θ vs. τ, one showing a small temperature rise to a flat maximum and then decrease as the supply of volatile material is consumed and the other (called "thermal explosion") showing a rapid self-accelerating temperature rise. The explosive solution is favored by large values of a, β, and $\theta_{in.}$ and small values of Nu. For Nu=0, when the heat generated cannot escape, the solution must be the explosive type. The type of solution will depend on Nu and the combination $\delta = \dfrac{a}{\theta_{in.}^2} e^{\ln\beta - \theta_{in.}^{-1}}$ provided that $\dfrac{RT}{E}$ (gas constant, temperature, activation energy) is small so that $\theta_{in.}$ and a approach zero in such a way that δ remains finite. The solution will be explosive regardless of Nu when $\delta \geqq 0.88$ for a slab, $\delta \geqq 2.00$ for a cylinder, and $\delta \geqq 3.22$ for a sphere.

Numerical results are shown for two cases that differ only in the combination δ by reason of a difference in reaction rate. For both cases $a=0.05$, $\theta_{in.}=0.030$, Nu=10.0, but for case 1 $\ln\beta=30.0$ so that $\delta=2.0$ whereas for case 2 $\ln\beta=28.0$ so that $\delta=0.27$. For case 1 the graphs of temperature vs. time at various relative distances from the center are curves rising at a decelerating rate so that the system remains stable whereas for case 2 the corresponding curves rise at an accelerating rate that soon becomes rapid so that the system is unstable. An important property of the system is the ignition delay, which is the time at which rapid temperature rise begins. For wood at room temperature, even when no heat can escape, the ignition delay is extremely long because the reaction rate at such temperature is so slow. In the unstable case 2 the integrated rate of decomposition, $\dot{R} = -\displaystyle\int_0^1 \dfrac{\delta W}{\delta \tau}\, dX$, rises rapidly with time whereas for the stable case 1 it remains nearly constant. The method probably can be used to follow the "thermal explosion" through to the point where temperature begins to fall from exhaustion of fuel and hence to determine whether enough flammable vapor will be produced to sustain flame or whether there will be only charring.

Forced ignition. For wood the critical condition for the establishment of a self-sustaining flame has been taken as generation of more than 0.25×10^{-4} gm/cm²sec of flammable vapor. Numerical solutions were obtained for a 1 cm sheet exposed to 663°, 713°, and 763°K. Graphs show the temperature history and change in composition at different depths and the rate of generation of flammable vapor for those cases. The interesting features are (1) the rate of vapor generation goes past the estimated critical value very sharply, (2) the temperature has become fairly uniform throughout the wood, (3) appreciable decomposition has set in at the surface by the time the critical rate of vapor generation has been reached.

In a second part of the report the approximate analysis of the effect of reactant consumption on the initiation of a thermal explosion is considered. Reactant consumption is more important for materials like wood than it is for gas-phase reactions because the ratio of heat release/activation energy is relatively small for wood. A very simple approximate analysis of the critical condition is presented and methods for improving the analysis for the critical conditions and for obtaining the ignition delay are suggested.

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Subject Headings: *Wood, mechanism of burning.*

F. L. Browne

Harker, H. (Northern Coke Research Laboratories, King's College, Newcastle upon Tyne, England) "Catalysis by Alkali-Metal Salts in Carbon Gasification Reactions," *Proceedings of Fourth Carbon Conference,* 125–139 (1960)

An investigation was made of the mechanisms of catalysis by alkali-metal salts in $C + CO_2 \rightleftharpoons 2CO$ and $2C + O_2 \rightleftharpoons 2CO$ reactions in order to determine the rate-controlling step in the carbon gasification reaction. Since the catalysis strongly affects the gasification rate, the alkali-metal salts must affect the rate-controlling step. Therefore, information on the mechanism of catalysis could provide clues to the rate-controlling reaction. Numerous experiments are described which were performed to test the validity of various proposed catalytic reactions.

Carbon-Carbon Dioxide Reactions

Catalysis by alkali-metal salts in carbon-carbon dioxide reactions was investigated in the 700° to 900°C range in a constant volume apparatus. Purified charcoal in the chamber was first outgassed at 900°C and then pure carbon dioxide was introduced to an initial pressure of 27 cm Hg. The reaction was then observed by total pressure and gas analysis techniques. The pressure rise was measured as a function of time and the rate of rise indicated the gasification reaction rate. When 10^{-4} to 10^{-2} parts of sodium carbonate were added, the reaction rate markedly increased. During the experiments it was observed that Na_2SO_4 and Na_2CO_3, which are almost equally catalytic, disappeared and a deposition of free sodium vapor occurred. NaCl admixture (noncatalytic) evaporated without decomposition. Possible mechanisms are acetylide formation, liberation of free alkali-metal, sodium cycle, surface cleaning, and an electronic mechanism.

The hypothesis of an acetylide mechanism was negated when various analyses failed to show the presence of any acetylide or acetylene. The sodium cycle hypothesis, proposed by several investigators, described by the following reactions,

$$Na_2CO_3 + 2C \rightarrow 2Na + 3CO$$
$$2Na + CO_2 \rightarrow CO + Na_2O$$
$$Na_2O + CO_2 \rightarrow Na_2CO_3$$
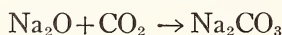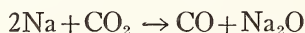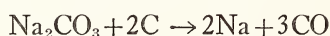
is doubtful, since the experiments show that after outgassing the carbon-salt mixture, a negligible portion of the original salt is present. The surface-cleaning hypothesis in which the salt decomposes the carbon surface oxide during outgassing and/or during the reaction and thereby increases the rate of formation of oxidation products from the surface oxide, has been adopted by several workers. The reaction rates measurements, as well as several experiments which indicate the occurrence of surface poisoning by an oxide, are all in agreement with the surface-cleaning theory.

The author points out that the surface-oxide theory, although in agreement with experiment, may be an incomplete explanation. He suggests the possible formation of alkali-metal-carbon complexes. The resulting catalytic effect would be due to its influence on the electronic structure of the carbon layer planes. Although a quantum mechanical explanation can be given, further investigation is needed for verification.

Carbon-Oxygen Reactions

Previous investigation by Riley [1] has shown that the ignition temperature for carbon in air in the 300°–700°C range is strongly affected by alkali-metal salt catalysis. The results seemed to conflict with the author's conclusion of the $C+CO_2$ mechanism because there is little possibility of liberation of sodium vapor in this temperature range. He therefore pursued a study of the catalysis of this reaction also.

An experimental study of the carbon ignition temperature was made by passing a stream of air over a sample of charcoal. The carbon was heated at a steady rate and the temperature of the sample was observed by a thermocouple. The ignition temperature was taken as that at which a sudden rise in temperature of the carbon occurred.

It was found that the ignition temperature of carbon is lowered (as much as 200°C) by the addition of certain alkali-metal salts. The decrease is proportional to the amount of salt added until a "saturation point" is reached after which the ignition temperature remains constant. A difference in the catalysis mechanisms in the $C+O_2$ and $C+CO_2$ reactions was indicated by tests which showed that some salts were effective in one reaction but had little or no effect in the other.

A correlation was found between the ionization potential of the alkali metal in a series of alkali carbonates and the catalysis of the ignition reaction. Further observations and arguments presented by the author lead to the conclusion that the catalysis mechanism is neutralization of a surface acid oxide by the salt. Saturation is explained as due to complete neutralization of the oxide.

The paper also discusses experiments on the structure, stability, and thermal decomposition of the acid oxide. The results seem to show that the separate effects on reactivity, of carbonization temperature, surface oxide, catalysts, and inhibitors, may have a common basis in the electronic structure of the carbon.

Reference

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Subject Headings: *Carbon, catalysis of gasification, by alkali-metal salts; Gasification, of carbon catalysis, by alkali-metal salts; Alkali-metal salts, as catalysts, in carbon gasification; Catalysis, of carbon gasification, by alkali-metals.*

R. W. Ziemer

Hering, H., Keraudy, S., Lang, F. M., and May, S. (Service de Chimie Physique, Commissariat a l'Energie Atomique, France) "Catalytic Effects in the Oxidation of Graphite by Air," *Proceedings of the Fourth Carbon Conference*, 115–122 (1960)

It has been observed that when certain industrial graphites oxidize, very distinct surface pitting, or etching, occurs. This suggests that local catalytic ac-

81

tion occurs, greatly increasing the oxidation rate, which may be caused by impurities in the graphite. A study of the cause and mechanism of this phenomena was conducted on laboratory samples of graphite. The results of an experimental study showed that the appearance of oxidation etching occurs mainly in the temperature range of 450° to 700°C with a net loss of about 2 per cent of mass. However, the etching was eliminated on samples purified with a scavenging gas at high temperature (3450°C).

To study the cause of surface etching, graphite samples were artificially impregnated with radioactive impurities of a variety of salts. It was found that the pattern of the locations of the impurities in the graphite as determined from autoradiographic photography, showed remarkable similarity to the surface etch pattern formed during subsequent oxidation in air.

The localization of the metal impurities was also shown by spectrographic analysis of material drilled from eroded areas and compared with material from other regions of the same graphite sample. In one sample of graphite, B, Ti and V became strongly localized and Cd, Mn and Zn not at all, while in a sample from another manufacturer, Zn was significantly localized and B, Cd were not. Coke shows these effects only after heating to 2000°C. Similar results by other investigators are referenced.

The catalytic effect of various metallic compounds was also shown by placing various powders of the salts in small drilled holes in purified graphite. Upon controlled oxidation at 650°C, the hole diameters increased manyfold indicating catalysis of the oxidation process by the salts. The order of catalytic effect ranging from the most effective to the least is: $CuCl_2$, $FeCl_3$, NaCl, Na_2CO_3, NaF, V_2O_5, TiO_2, and of no effect were SiO_2 and CaO. When two compounds were mixed together and applied to the graphite, the resulting effect was far greater than expected, assuming additive effects.

Quantitative measurements of catalytic effects were obtained by impregnating purified graphite with salt solutions. The oxidation rate, indicated by the per cent weight loss of a treated sample to that of an untreated control sample, was found to be linear over the test range up to 10 ppm. In order of decreasing effect were $CuCl_2$, $VOCl_3$, $FeCl_3$ and NaF. Ten ppm of $CuCl_2$ increased oxidation by a factor of 40, 10 ppm of NaF gave a sixfold increase.

The results of the several tests are inconsistent since V_2O_5 was almost ineffective in the "hole" test but $VOCl_3$ was very catalytic when impregnated by solution (the effect of O and Cl must also be considered) and hence the results are difficult to explain. The mechanism causing the catalytic effect is still unknown.

The authors have performed very interesting and valid experiments although the results do not lead to any definite conclusion on the mechanism of catalysis by metal salts. It does, however, provide valid experimental data which, in its seeming inconsistencies must be reconciled with any proposed theory. It definitely proves that in industrial and research applications in oxidizing atmospheres, the purity of the graphite may be a critical factor.

Subject Headings: *Graphite, catalytic oxidation; Oxidation, of graphite, catalytic effects; Catalysis, of graphite oxidation.*

R. W. Ziemer

ABSTRACTS AND REVIEWS

Bonnetain, L., Duval, X., and Letort, M. (Faculte des Sciences de Nancy et Centre d'Études et de Recherches des Charbonnages de France, France) "On the Role of Surface Oxides in the Graphite-Oxygen Reaction," *Proceedings of Fourth Carbon Conference,* 107–114 (1960)

Graphite samples of different origin and ash content (0.01, 0.02, and 1.25 per cent) crushed to grain diameters of 0.2, 0.7, and 0.13 mm, are exposed within a quartz reactor to a flow of oxygen at constant pressure between 10^{-4} and 10^{-1} mm Hg, at constant temperatures between 400° and 700° C. CO_2 is condensed and CO is catalyzed over Pt and then condensed as CO_2 in liquid nitrogen traps. After stopping O_2 supply the collected reaction products are separately measured by MacLeod at room temperature. Thus, amounts of CO_2 corresponding to $1 \pm 0.1 \mu g$, i.e. 1×10^{-5} the sample weight or 1×10^{-3} the total number of surface atoms (according to BET estimate) could be determined.

In consecutive experiments with samples first degassed at 950°C, the isothermal combustion rate begins sharply to decrease and gradually attains a steady-state value, up to 25 times smaller than the initial value. Degassing at temperatures below 950°C yields lower initial rates and decreases the quantity of carbon burned to reach the steady state. The quantity of carbon removed during degassing is approximately between 1/50 and 1/10 of the number of superficial carbon atoms. The volumes collected at constant temperature are linearly related: $V_{CO} = mV_{CO_2} + b$, where b, in some cases equal to zero, depends on the sample origin. Factor m increases from 1 to 2.5 exponentially with temperature, indicating an average activation energy of 7.5 kcal. In isothermal desorption without oxygen admission it increases slightly as degassing proceeds. There is a stage where the CO/CO_2 ratio equals that found in combustion. The sum of desorbed $CO + CO_2$ follows the exponential rule of Elovich [1] which describes also the rate of chemisorption by graphite at temperatures below 300°C.

A qualitative explanation is offered, based on two assumptions: (A) the formation and decomposition of adsorbed oxides $(CO)_x(CO_2)_yC_z$,[2] (B) desorption leaves on the graphite surface partially unsaturated carbon atoms, loosely bound to the substrate, which are consumed in the oxygen reaction without being sufficiently regenerated.

Topochemical and physical effects of adsorption,[3] like etching of surface layers, blocking of reaction sites by adsorbed CO molecules, decrease in oxygen adsorption with rising temperature, etc., usually considered in heterogeneous reactions, are not consistently discussed. Nor are observed CO/CO_2 ratios compared with expected equilibrium values.

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3. Meyer, L. and Gomer, R. "The Energy Exchange between Cold and Gas Molecules and Hot Graphite Surface," *Proceedings of Third Biennial Conference on Carbon* 425–431 (1959)

Subject Headings: *Graphite, surface oxides in oxidation.*

H. M. Cassel

VI. Radiation

Plyukin, B. I. (Chemical Physics Institute, Academy of Sciences, USSR) "The Laws of Thermal Emission of a Flame," *Academiia Nauk, SSSR Doklady* 131, 68–71 (1960)

In this brief communication it is shown that deviations from the Wien displacement law and the Stefan-Boltzman law in nonoptically dense combustion gases can introduce important corrections into the formulas used to determine the radiation, brightness, and color temperatures of a flame. These corrections are functions of experimental conditions through a nondimensional parameter of the form

$$\frac{\bar{a} \, P \, \bar{\mathcal{M}} \, s}{R \, \bar{T}}$$

where

$\bar{a}$ = mass coefficient of absorption
P = total pressure
$\bar{\mathcal{M}}$ = spatial average mean molecular weight
s = geometrical path (thickness) of radiating medium
R = universal gas constant
$\bar{T}$ = spatial average gas temperature

Analytical expressions for the deviations are given for flame gases of small and large optical density based on a model in which the flame gas is considered to be a nonscattering continuum in radiation and thermochemical equilibrium in the absence of solid inorganic particles. Averaging of the absorption coefficient and density over frequency and space, respectively, are considered to be physically valid. The results are then compared in structure to Schack's empirical formulae [1,2] for the dependence of the total radiation flux on pressure P, temperature T, and geometric thickness s. In the latter work power laws were given applicable to particular flame gases over small ranges of the parameters P, T, s. For the limiting case of an optically dense flame, the influence of pressure, structure (mean molecular weight and temperature) and the geometry disappear, and the Stefan-Boltzman law holds.

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Subject Headings: *Flame, thermal emission of; Emission, thermal, of flame.*

D. E. Rosner

Hase, R. (Hannover, Germany) "Problems of Extreme Thermal Radiation," *VFDB Zeitschrift Forschung und Technik im Brandschutz* 9, 104–106 (1960)

The ignition of solid combustible material, as well as the melting of metal or stone walls, is a possible consequence of the incidence of extremely intense radiation. The only likely source of such radiation is an atomic bomb. Wavelengths dealt with in this paper range from about 0.3 micron to 10 microns, covering the near ultraviolet, visible, and near infrared portions of the spectrum. Shorter wavelengths produce biological effects in addition to purely thermal effects.

84

ABSTRACTS AND REVIEWS

Laboratory experiments are described, using as sources chrome-nickel ribbons, hot flames, ordinary arcs, confined and water-stabilized arcs, a "self-confined" arc, and spark discharges. Temperatures of the latter reached 3×10^5°C. Radiation from electrically heated chrome-nickel ribbons was focused on the test region by means of ellipsoidal mirrors. In the test region a small blackened metal calorimeter was placed to calibrate the radiation intensity, in calories/cm², or samples of combustible material, 5 cm x 5 cm in area. A radiation shield was placed around the calorimeter, to protect it from stray radiation. With a thermo-element as an indicator, the temperature sensitivity was about 1/100°C, and the heat capacity determined to 1 per cent. A portable radiation detector was also constructed, consisting essentially of a thermopile with a built-in indicating meter. The measurement of radiation of very short duration, such as that which occurs in an atomic bomb explosion, was accomplished with bolometers and oscilloscopes, a system with very small thermal inertia. The total heat evolved in one of these explosions amounted to about 7×10^{12} calories, which gives an average radiation intensity of 400 watts/cm² at a distance of 1 km.

The measurement of the ignition of flammable materials by radiation is much more complicated, since additional factors, such as air currents, are involved. The ignition temperature for materials like wood, paper, and textiles is about 250° C; a rough figure for the corresponding value of radiation intensity for ignition is about 2.8 watts/cm² for wood, which is about 45 times the radiation intensity at the surface of the earth due to the summer sun.

An interesting discussion is offered, concerning the possibilities of protection against high heat radiation, although no more mention is made of ignition of combustible materials. The most important factor in radiation protection is reflectivity or absorptivity of the surface of the materials. Unfortunately, most substances offer high absorptivity to radiation, the exceptions being limited to highly specular metals. For heat flow in an exposed wall, the other significant physical parameters are heat capacity (density times specific heat), thermal conductivity, temperature conductivity (the quotient of the two previous parameters), melting point, and heat of fusion. The importance of temperature conductivity is pointed out, because, even though the heat capacities of most substances are about the same, metal walls are able to conduct the heat away from the surface faster than do nonmetals. In this way, metals may be able to resist the high, short-time radiation better than nonmetals, in spite of the higher melting points of the latter.

An ideal radiation protection wall might be composed of several layers of different materials, with a highly reflecting surface, a highly conducting interior, combined with high heat of fusion. An aluminum wall placed 1 kilometer away from the Nagasaki bomb would have experienced only 10°C rise. The possibility of further development of techniques for the protection against intense thermal radiation is suggested.

Subject Headings: *Radiation, intense thermal; Ignition, by intense thermal radiation.*

J. K. Richmond

Libby, W. F. (University of California, Los Angeles, California) "Optical Transparency and Resistance to Flash Heating," *Journal of Chemical Physics* **33**, 1588–1589 (1960)

A combination of low thermal conductivity and optical transparency, as found in silica or certain clear plastics, allows very high-temperature gradients to be maintained. The surfaces of such solids can be very hot while the bulk solid a short distance away is unperturbed. In this way high-temperature evaporation, which consumes more energy by breaking chemical bonds to form smaller molecules, radicals, and even atoms, becomes possible, so that heats of vaporization rivaling those of the highest-boiling solids can be achieved.

With optical transparency goes low emission efficiency, so the radiation heat sink is reduced in importance for these materials. This reduction in cooling power can be compensated by the evaporative cooling. One would expect that the vapor generated at the surface of such a solid would have a composition corresponding to its temperature. Thus, close to the surface of an organic plastic, the monomer probably would predominate, while farther out the monomer would be broken into radicals and atoms, some of which might be carried away in the air and thus serve as a heat sink.

It seems likely that applications of these principles can be made in the ballistic-missile nose-cone problem and in the use of plastic paints to resist flash-heating.

Subject Headings: *Heating, transparency to flash.*

E. C. Woodward

VII. Suppression of Combustion

van Tiggelen, A. and Grognard, M. (University of Louvain, Louvain, Belgium) "Theoretical Considerations of the Action of Flame Inhibitors," *Bulletin de la Société chimique de France,* **11–12**, 1818–1822 (1959)

Our lack of understanding of the detailed reaction kinetics prevalent during combustion renders speculative any attempt of explaining quantitatively the mechanism of flame quenching by chemical inhibitors. A phenomenological approach to this problem is presented by the authors of this paper based on the essential hypothesis that flame propagation is governed by the rate of chain propagation relative to that of chain termination. Consequently, flame inhibition may be interpreted in terms of the effect of an inhibitor on the chain termination reactions. Denoting by δ the probability of chain propagation, and by β that of chain rupture, the authors derive an equation for the flame speed of the form:

$$V_o = \frac{4T_o}{\pi}\left(\frac{2R}{3M_r}\right)^{1/2}\left(\frac{\delta-\beta}{T_m}\right)^{1/2}$$

where T_o is the initial gas temperature, R, the gas constant, M_r, the average molecular weight of the active species, and T_m, the mean temperature of the flame $[T_m = T_i + 0.74(T_f - T_i)]$. As δ becomes equal to β, V_o approaches zero. It is apparent that the authors do not take into consideration energy and mass transport; they merely wish to examine the rate expression applicable to a system

86

reacting at T_m by simple second-order kinetic processes including chain propagation and chain branching. Great emphasis is placed on the magnitude of the activation energies for the various reactions. Actually at the temperatures prevalent in the combustion zone the reaction rates are of formidable size even in the presence of considerable energy barriers. Finally, it is shown that the equations derived are applicable also to those cases where the additive acts as a promoter rather than an inhibitor, such as in H_2—O_2—Cl_2.

Subject Headings: *Flame, action of inhibitors; Inhibitors, action in flame.*

H. Wise

Guise, A. B. (Ansul Chemical Company, Marinette, Wisconsin) "The Chemical Aspects of Fire Extinguishment," *Quarterly of the National Fire Protection Association* **53,** 330–336 (1960)

The action of fire-extinguishing agents is explained in nontechnical language. Four primary types of extinguishing agents are recognized. (1) Water in its various forms and with additives acts by cooling and smothering. Liquid sprays, steam, and foams, with or without wetting agents, and viscosity-increasing additives are examples. (2) Carbon dioxide acts to dilute the reactants and smother the flame. (3) Halogenated hydrocarbons combine these actions and add chemical chain-breaking capability. Carbon tetrachloride, chlorobromomethane, methyl bromide, and bromotrifluoromethane are mentioned. Water solutions of Group I metallic salts are also included in this category. (4) Dry chemical extinguishers act strictly as chain-breakers. Sodium and potassium bicarbonate are discussed.

The old fire-fighting formula of remove the fuel, remove the heat, or remove the oxygen must be modified by adding, "interrupt the flame chain-reaction." The hydrogen-oxygen flame is used to illustrate the production of free radicals and their importance in flame propagation. Removal of free radicals from the flame zone by interaction with the extinguishing agent causes nearly instantaneous flame suppression.

The effectiveness of the various types of extinguishing actions (chemical, physical, or a combination of both) is compared by examining the relative quantity required for extinguishment of a given fire. Rate of application and particle size are considered to be important parameters.

Subject Headings: *Fire extinguishment, chemical aspects; Extinguishment, chemical aspects.*

B. Greifer

Extinguishing Agent Developments Eight articles in the *Quarterly of the National Fire Protection Association,* Volume 54 (October 1960)

Ratzer, A. F. (Chemical Concentrates, Division of Baker Industries, Inc.) "Chemical and Physical Properties of Foam," p. 135
Rivkind, L. E. (Foam Products Division, Mearl Corporation) "Testing of Fire-Fighting Foams," p. 139
Manning, G. E. (Underwriters' Laboratories, Inc.) "A, B, C Dry Chemical Extinguishers," p. 151
Zeratsky, E. D. (Ansul Chemical Company) "Special Dry Powder Extinguishing Agents," p. 154

Tuve, R. L. (U. S. Naval Research Laboratory) "Recent Navy Research on Dry Chemicals," p. 158

Cousins, E. W. (Factory Mutual Engineering Division) "Carbon Dioxide Extinguishment Tests," p. 164

Palmer, F. S. ("Freon" Product Division, E. I. duPont de Nemours & Company) "New Compressed Gas Extinguisher," p. 173

Neill, R. R. (U. S. Naval Research Laboratory) "Trimethoxyboroxine for Magnesium Fires," p. 178

These eight papers, which are relatively short in length, are reviewed as a group since they constitute contributions to the development of extinguishing agents for fires.

Ratzer begins his discussion by defining a foam to be a concentrated, aqueous solution of chemicals which, when diluted in water and aerated, will produce a foam suitable for the extinguishment of fire. The term employed by the NFPA Foam Committee to describe this material is "foam liquid concentrate."

Low-expansion, high-expansion, and an alcohol-resistant type are the three basic kinds of foam liquid concentrates. The low-expansion type consists of a protein hydrolysate together with organic solvents and metal salts as the foam stabilizer. These protein-base foams are employed to fight oil, gasoline, and other hydrocarbon fires. Foams of the protein type are used to protect refineries and tank farms and aircraft crash fires can be fought with this type of foam.

Low-expansion foams have expansion ratios between 6:1 and 10:1 depending upon the type of equipment utilized. Performance of the foam from a chemical standpoint depends upon the type of protein employed and the extent of hydrolysis, the type of alkaline metal salt of the protein hydrolysate, the nature and quantity of the iron salt, and the type and quantity of solvent used.

High-expansion foams are employed where water supplies are limited, where rapid coverage of the surface is of maximum importance in spill fires, and where exposure protection is needed. Expansion ratios vary from 16:1 to 20:1. A very fluid foam is produced so as to obtain the maximum rate of coverage and flow.

The alcohol-resistant type of foam withstands breakdown by the solvent action of alcohols and other polar agents while other foams collapse. Alcohol stability can be achieved during dilution and aeration by using a substance which will precipitate out in the bubble wall to form an insoluble barrier between the alcohol and the body of the foam.

Protein-base and high-expansion types of concentrate come in four different compositions, namely 6 per cent regular, 6 per cent minus 20 low-freeze, 3 per cent regular, and 3 per cent minus 20 low-freeze. The percentage value designates the concentration at which the liquids are to be used when diluted with water.

Stainless steel is the best material for storage tanks of the concentrates. Conventional pumps can be used if there are no air leaks in the suction side, and if there is no contamination by oil.

Rivkind points out that the stability of foam is a function of the resistance to spontaneous collapse, thermal radiation, chemical attack, and mechanical disruption. He discusses methods of measuring the amount of expansion, the amount of foam drainage, the viscosity, the thermal and chemical resistance, and the mechanical stability.

88

Tests with protein-base foams to find the relationship between foam viscosity and quarter drainage time show these results.

1) At any given expansion, drainage time increases with foam viscosity.
2) For a given viscosity, drainage time increases with increasing expansion.
3) At low expansions (6-7), the relative increase in drainage time is much less than foam viscosity.
4) At intermediate expansions (8–12), either drainage time or viscosity measurements can be used to characterize foams.
5) At still higher expansions (12–16), drainage would be the method of choice.

Results of actual fire tests are discussed in relation to the various foam properties.

Manning presents information on the so-called "all-purpose" dry chemical extinguishing agent that can be used ideally on fires of Class A, B, and C types. Current dry chemical extinguishers are useful on Class B and Class C fires. A new dry chemical, called an "intumescent powder" by the manufacturer, has been found useful on all three classes of fire and on magnesium fires.

G-1 and Met-L-X dry powder agents are discussed by Zeratsky for use with fires involving combustible metals and highly reactive flammable liquids. Both powders are noncombustible, and no known health hazard results from their use. He reports their relative effectiveness with magnesium, uranium, titanium, zirconium, sodium, potassium, sodium-potassium alloy, and lithium fires. Other special dry powders were used effectively on triethylaluminum fires.

Tuve reviews the development of "foam-compatible" dry chemicals and tests on potassium bicarbonate which is called "Purple-K-Powder" by the Navy. He states that the fundamental efficiency of an extinguishing agent can be judged only at critical rates of application to a flame front. The critical rate is the rate of agent application below which extinguishment is not possible.

Cousins reports on an investigation of factors pertinent to the extinguishment of fires by carbon dioxide. Using this agent, it is necessary to exclude oxygen from the fire for a sufficient period to allow the flames to go out and to allow cooling. After describing the problems, Cousins outlines the test equipment employed.

Results showed that extinguishment depended upon only three factors if a given nozzle design is used at a fixed height above the hazard. These factors are the area covered per nozzle, the weight-rate of carbon dioxide application and the velocity of the carbon dioxide through the face of the nozzle horn. The proportion of carbon dioxide in the liquid phase in the piping or in the solid phase in the discharge was found not to affect the extinguishing ability.

Palmer discusses bromotrifluoromethane ($CBrF_3$) or Halon 1301 which is a numbering system to specify, in succession, the number of atoms of carbon, fluorine, chlorine, bromine, and iodine. Halon 1301 is a liquefied compressed gas as stored and handled. It boils at minus 72°F and has a vapor pressure of about 200 pounds per square inch at room temperatures.

This compound is considered less toxic and more effective than Halon 1202, 1211, or 2402. The natural vapor of Halon 1301 has a relative hazard rating of unity compared to 56 for chlorobromomethane (1011), and 140 for carbon tetrachloride (104). According to the tests reported by Palmer, Halon 1301 is at least

equivalent in fire-extinguishing effectiveness to dry chemicals. Halon 1301 has been adopted by the major aircraft manufacturers for use as an aircraft engine fire-extinguishing medium.

Neill discusses the use of trimethoxyboroxine on magnesium fires. They are particularly important because of their expanding use in airframes. Magnesium-alloy fires occur most frequently in crashes after fuel fires ignite thin sections of the alloy.

Magnesium ignites at a temperature close to its melting point which is 1204°F; alloys ignite at a somewhat lower temperature. Magnesium burns as a result of vaporization; a brilliant white flame results with the liberation of a cloud of white magnesium oxide smoke. Flame temperatures are over 5000°F. Trimethoxyboroxine, or TMB, is effective in extinguishing this brilliant fire.

Another type of burning takes place at a much reduced rate and without visual external evidence of flame or smoke. Water can be applied at this later "red glowing" stage without causing vigorous reaction such as one obtains in the "white fire" stage.

TMB is not a panacea to the magnesium fire problem, but it offers considerable help.

Subject Headings: *Magnesium fires, use of trimethoxyboroxine; Extinguishment, use of foam; Trimethoxyboroxine, in magnesium fires; Foam, use of, in fire extinguishment; Dry chemicals, use as extinguishing agents; Foam, stability; Carbon dioxide, use as extinguishment agent.*
L. E. Bollinger

Nash, P. (Joint Fire Research Organization, Boreham Wood, England) "Recent Research on Foam in the United Kingdom," *The Institution of Fire Engineers Quarterly* XXI, No. 41, 14–33 (1961)

The use of foam in fire fighting has been studied to ensure the most effective method of application, the optimum rate of application and concentration of foaming agent so that control of the fire can be achieved at the earliest possible moment. Different types of applications considered are (1) surface application to large spill fires or fires in storage tanks of flammable liquid, (2) base injection or subsurface application of foam to fires in petroleum storage tanks, (3) aircraft crash fires.

Three properties of foams are discussed; expansion, critical shear stress, and drainage time. Methods of measurement and correlation with other standards are described. All of the foams used are of the protein-based type, manufactured to a specification prepared by the Ministry of Works. The change of critical shear stress of the foam with concentration of the foaming agent and with the total energy available for foam production and projection is studied.

An apparatus is described to measure the time to control a liquid fire by surface application. A critical rate of application is found below which the fire cannot be controlled, and an optimum rate which is about three times the critical rate. The extinction time is increased by using a stiffer foam but the amount of foam used may be decreased by increasing the concentration. Loss of liquid from the foam occurs by evaporation and by drainage; this factor must be considered in determining optimum conditions. A very interesting comparison of all these influences is presented.

ABSTRACTS AND REVIEWS

The main problem connected with base injection of foam into burning fuel tanks is that as the foam rises to the surface it becomes contaminated with petrol which collects as globules in the foam layer. If the volume of the petrol exceeds about 10 per cent of the volume of the foam liquid, it can be ignited and it will ultimately destroy the foam layer, although the original fire has been controlled. The correlation between petrol pickup and foam expansion is discussed. A low expansion of 3½ is required and also a 25 per cent drainage time of not less than 3 minutes. A solution strength of 3 per cent and a critical shear stress of 150–200 dyn/cm² mean that only certain protein-based compounds are suitable to fulfill those requirements. Tests on a 9 ft diameter tank 27 ft deep were successful but "cold" tests on a 45 ft diameter tank showed that both petrol pickup and distribution of the foam were markedly dependent upon the positioning of the foam inlets below the surface, only a central inlet seeming to be satisfactory. Other inlets gave rise to petrol pickup above the limit and to rafts of foam.

The most difficult type of spillage fire occurs in aircraft crashes where the quickest possible control is essential. Opinions differ as to whether it is better to protect the fuselage from heat radiation or to concentrate from the outset on controlling the fire. The physical properties of the foam may have to be altered to suit the different applications. Two series of tests have been made using a 10 ft x 10 ft and a 30 ft x 30 ft fire area with simulated fuselage. Analysis of results for the smaller area show the rate of application and shear stress to be significant factors while expansion is not. Application by spray and jet are shown to have a different control time due to different evaporation losses as the foam passes through the flame. Results from the larger fire area suggest the rate of application and expansion to be the most important factors.

Subject Headings: *Foam, research on, as fire extinguishing agent.*

G. L. Isles

Aidun, A. R. and Grove, C. S., Jr. (Syracuse University Research Institute) "Additives to Improve the Fire-Fighting Characteristics of Water," *Bureau of Yards and Docks, Department of the Navy Contract NBy 13027, Quarterly Progress Reports Nos. 7 and 8* (July 1959) *and No. 9* (October 1959)

During the period covered by these Quarterly Reports, two of which, Nos. 7 and 8, are combined into one report, work was continued both in the laboratory and in the field on the study of the influence of viscosity additives, opacifiers, and detergents on the fire-fighting effectiveness of water.

Further viscosity additives were screened and the two new compounds, Monsanto Inspissator DX-840–91 and bentonite Clay, selected because of their dispersion rate in water, were tested along with the previously selected American Cyanamid Reagent S-3251 on the run-off simulator Apparatus (ROSA)* to determine the run-off properties of their aqueous solutions. For this test, one liter of the solution is poured on the inclined heated plate at a constant rate of 2.4 liters per minute and the length of time for the film to evaporate is measured. Results show that the film time is affected by the viscosity of the solution only in the presence of a small quantity of detergent (Alkanol WXN). While the American Cyanamid Reagent solution indicated under these conditions a decrease in film time as the viscosity was increased, a gradual increase in the film evapora-

* *Fire Research Abstracts and Reviews* 1, 18 (1958)

91

tion time was obtained with the Monsanto Inspissator up to a viscosity of 15 centipoises from which value on, the film time adopted a constant value. The use of bentonite Clay, on the other hand, produced a sharp maximum film time value at a viscosity of about 5 centipoises. Only the two compounds which showed an increase in film time were selected for the small-scale fire tests.

For these fire tests, the new pump system described in a previous report * was used. The test fire, contained in an enclosure (4' x 4' x 5' high) made of sheet steel, consisted of eight one-foot lengths of 1" x 3" clear white pine predipped in kerosene and disposed edgewise in two tiers at right angles to each other. In preliminary tests aimed at determining the relationship between preburn time and the amount of wood burned, a carbon dioxide extinguisher was used to put out the fire and the loss in fuel weight was noted. These tests indicate that the burning rate is fairly constant during the first three minutes of the test and then slowly tapers off as the quantity of unburnt fuel decreases. In actual tests, the fire was allowed to reach a constant burning rate and the extinguishing solution was ejected through a nozzle fixed at the top and in line with the axis of the fire box. The use of Alkanol WXN alone as additive does not modify the extinguishing effectiveness of water, but increasing the viscosity of the solution either up to 10 centipoises by addition of the Monsanto Inspissator or up to 6 centipoises by addition of bentonite Clay results in a gradual increase in effectiveness. However, no improvement can be obtained in either case by increasing the viscosity. This is in conformity with the results obtained with ROSA on the Monsanto compound and on another viscosity additive previously tested, Acrysol ASE-60.

When aluminum powder is added in a 0.1 per cent by weight concentration together with a small quantity of detergent to improve its dispersion properties, the extinguishing time is cut down by a factor of 10, but a similar result can be obtained with only 0.02 per cent aluminum powder if the viscosity of the solution is first increased to 10 centipoises by the addition of Monsanto Inspissator. Substituting bronze powder to the aluminum as the opacifier and using a solution viscosity of 6.5 centipoises, best results are obtained at a 0.3 per cent by weight concentration of the powder. At this concentration, the extinguishing time passes through a minimum corresponding to an increase by a factor of 5 in extinguishing effectiveness.

In order to determine whether the above findings would remain valid in full-scale experiments, a large-scale fire apparatus was constructed which consisted of a fire box (8' x 8' x 12' high) made of an asbestos-based material and provided with a 12-in. square window for visual observations and a chromel-alumel thermocouple, inserted 3 feet from the ground in one side of the enclosure, for radiant heat measurements. During the tests, water was applied through a single nozzle fixed at the top of the enclosure, except in a few tests where a system of 4 nozzles equally spaced at a distance of 1.4' from the fire centerline was used. The solution to be tested was mixed prior to the start of the fire in a 55-gallon drum and fed to the nozzle by means of a 60 GPM Oberdorfer centrifugal pump at a predetermined rate.

Optimum operating conditions for the large-scale fire tests were determined in preliminary tests in which water alone was used as the extinguishing agent.

* *Fire Research Abstracts and Reviews* 2, 71 (1960)

ABSTRACTS AND REVIEWS

It was found that the best fire for the purpose of this study consists of 37 pieces of 2″ x 4″ California clear pine predipped in kerosene and arranged in three tiers at right angle. Thirteen wood pieces 36″ long are placed in the bottom tier, 12 pieces 36″ long in the second tier and 12 pieces 32″ long in the top tier. A preburn time of between 8 to 10 minutes and a water application rate of about 3.5 gal/min seem to provide a sufficiently long extinguishing time to allow good contrast in water-extinguishing properties when containing various additives.

Results of a series of tests on different formulations indicate that in general additive-modified water is more effective as extinguishing agent than water alone, and that the viscosity additive is the agent that contributes the most to the rapid extinguishment of the fire. The influence of opacifiers is still not too clear and further tests will be necessary.

Subject Headings: *Water, fire-fighting characteristics of; Fires, use of water in.*

J. R. Jutras

Aidun, A. R. (Syracuse University Research Institute) "Additives to Improve the Fire-Fighting Characteristics of Water," *Bureau of Yards and Docks, Department of the Navy Contract NBy 13027, Quarterly Progress Report No. 10* (January 1960)

Run-off properties of two additional viscosity-additives, the E. I. duPont polyelectrolyte B-5546 and the Dow Chemical polyelectrolyte ET-435 have been studied with the runoff simulator apparatus using the same procedure as previously described. Though the two additives both increase the viscosity of their solution, they exhibit different run-off properties. The duPont thickener does not improve liquid film time as viscosity is increased, irrespective of the presence or absence of a surface active agent (Alkanol WXN). On the other hand, increasing the solution viscosity by the addition of the Dow product results in a definite increase in film time and the increase is more pronounced when a small quantity (0.2 per cent) of Alkanol WXN is also added. Larger concentrations of Alkanol have, however, an adverse effect on run-off time.

Only one small-scale fire test is reported. It showed that extinguishing time is shortened when the viscosity of water is gradually increased to 10 centipoises by the addition of the duPont polyelectrolyte. No further improvement is, however, observed at higher viscosities. This is in agreement with previous results obtained with other viscosity additives, Acrysol ASE-60, Monsanto DX-840–91, and bentonite clay.

New large-scale fire test facilities have been installed which consist of a galvanized sheet-metal fire box (13′ x 12′ x 12′ high) provided with a 30″ sq glass window for visual observations and a 16 in diameter stack with a variable speed exhaust fan for the removal of smoke. The test fire will consist of 2″ x 4″ California clear pine pieces mounted in three tiers with thirteen 36″ long pieces on the first tier; twelve 35″ long pieces on the second tier; and twelve 34″ long pieces on the top tier. The extinguishing solution will be ejected from a height of 12′ through a system of four Full jet ¼ GG nozzles equally spaced at a distance of 1.4′ from the fire center line. A 36″ sq pan, 6″ deep, will be placed under the fuel to collect drainage from the wood during extinguishment. Temperature at various points in and around the fire will be measured by means of a number of

93

thermocouples and the radiometer will measure and record radiation temperatures. The test procedure will be as described previously.

Subject Headings: *Water, fire-fighting characteristics of; Fires, use of water in.*

J. R. Jutras

Alumbaugh, R. L. (U. S. Naval Civil Engineering Laboratory, Port Hueneme, California) "Fire-Retardant Coatings," *U. S. Naval Civil Engineering Laboratory Technical Report 087* (20 October 1960)

This report is a review of three phases of work being undertaken by the Naval Civil Engineering Laboratory covering fire-retardant coatings for protecting wooden structures, namely, (1) weathering and fire retardation, (2) comparison of test methods for evaluating retardation, and (3) fire-retardant chemical impregnates.

A total of 39 fire-retardant impregnates and coatings were tested in various combinations. Fifteen samples of fire retardants were applied to wooden test panels and exposed to a coastal atmosphere of from 4 to 18 months of weathering. In general, the fire-retardant properties decreased as a result of weathering with the exception of a gray, oil-base, exterior, intumescent-type coating which withstood full weathering conditions for 18 months without coating failure and an improvement in fire-retardation quality.

Nine samples were compared for the purpose of evaluating three fire-retardation test methods: (1) Fire Test Cabinet (ASTM), (2) Stick and Wick (ASTM), and (3) Radiant Panel (NBS). While the radiant-panel method differentiated between coating systems most effectively, the Stick and Wick method was recommended for quick screening purposes.

Of the chemical impregnates tested, deterioration generally occurred from weather exposure. Although the sodium silicate-talc systems showed slightly superior fire retardation to the phosphates and poorer weathering qualities, a 40 per cent diammonium phosphate impregnate with an exterior type topcoating was recommended as being compatible with the surface coating. For interior paints where weathering is not of concern, an intumescent chlorinated alkyd base fire-retardant paint was found to be superior.

Although this report does not provide full details of coating compositions and the data presented therefore are of limited application, it does point to possible paints and impregnates that will afford considerable fire retardancy for wooden structures, capable of withstanding severe weathering conditions, and probably costing no more than standard maintenance paints.

Subject Headings: *Coatings, fire-retardant; Fires, retardation, by coatings.*

D. Dembrow

VIII. Model Studies and Scaling Laws

Stern, M. E. (Woods Hole Oceanographic Institution, Woods Hole, Massachusetts) "The Moving Flame Experiment," *Tellus* 11, 175–179 (1959)

The author considers the problem of the fluid motion induced in a cylindrical annulus when a flame is rotated around the bottom of the annulus. In an unpublished report, Fultz (1956) described an experiment in which a flame was rotated

94

ABSTRACTS AND REVIEWS

around the bottom outside rim of a cylindrical vessel filled with water. He observed that a net angular velocity was induced in the fluid in a direction opposite to the rotation of the heat source. The author repeated the experiment in a cylindrical annulus with a radial width which was large compared to the vertical depth, and yet small enough to be completely covered by a bunsen flame. This was done in order to reduce the radial convection and to establish the fact that the same results were obtained in an approximately two-dimensional flow. Qualitative experiments indicated that the same phenomena occurred.

The theoretical model considered was a two-dimensional rectangular channel flow with height corresponding to the vertical depth of the annular section. The x axis was assumed to correspond to the circumferential distance so that the motion was required to be periodic in x. The rotating flame was replaced by a distribution of heat sources and sinks, moving along the bottom of the channel with a constant velocity, forcing a sinusoidal density variation depending only on x and time. The density variation was employed only to calculate the buoyant forces, being neglected in all other terms. Also, it was assumed that the correlation between the velocity components is changed very little by the induced mean flow so that it may be calculated from the linearized hydrodynamic equations. Evidently, this approximation is good as long as the mean-induced velocity and velocity perturbations are small compared to the rotational velocity of the heat sources and sinks.

The solution indicates that the total x momentum of the fluid at equilibrium, which corresponds to the vertical component of angular momentum in the cylindrical case, depends primarily on a characteristic Reynolds number, changing sign as the Reynolds number varies from zero to values large compared to unity. Further, in the equilibrium state, no net stress is exerted on the upper or lower surfaces of the channel. Within the fluid, momentum transported toward the center from both upper and lower regions, is balanced by the viscous stress of the mean motion. It is shown that while no mean motion could exist in an ideal inviscid fluid, in a real fluid with small viscosity, the mean motion could be relatively large, being inversely proportional to the square root of the viscosity. In addition, a plausible explanation of the transient process is given although this problem is not considered in the mathematical solution. Finally, an example calculation of the velocity induced in the atmosphere by the motion of the sun relative to the earth is presented.

As the author points out, although the theoretical model bears a superficial resemblance to the experiment performed, it represents a simple problem with which the phenomena may be studied.

Subject Headings: *Flame, fluid mechanics of rotating.*

<div align="right">T. C. Adamson</div>

Fons, W. L., Pong, W. Y., Bruce, H. D., and Richard, S. S. (Pacific Southwest Forest and Range Experiment Station, Berkeley, California) "Project Fire Model," *National Bureau of Standards Order No. S–35372–60, Fifth Progress Report, Period May 1, 1960 to August 1, 1960*

This fifth progress report on Project Fire Model summarizes work accomplished during a three-month period May 1, 1960 to August 1, 1960. Originally research was carried out in cooperation with the Office of Civil and Defense

95

Mobilization. Since April 1960, the work has been continued under contract with the National Bureau of Standards.

Project Fire Model emphasis has recently been directed toward continued study of the effect of wood species and specific gravity on the characteristics of test fires. Basswood, sugar maple, and southern magnolia have been tested in addition to the standard white fir fuel beds, prepared in previous experiments. Cribs having precisely the same measurements were constructed using each of the three species. The wood for each crib was selected to provide material within a narrow density range. The cribs were conditioned to approximately 10.5 per cent moisture content and the test fires were then conducted under specified conditions used in other experimental fires. As in the past, heat value of the wood was determined; rate of spread, rate of combustion, and radiation were measured; the amount of charcoal remaining after each fire was determined; and combustion gasses were analyzed by gas chromatography.

Four tables are used to summarize the results of these experiments. A quick inspection indicated the following:

1) Heat values for the four species tested (white fir, basswood, magnolia, and sugar maple) differ from each other only slightly.
2) Rate of spread in crib test fires increases with a decrease in wood density.
3) The heat of combustion for each species increases with increase in specific gravity.
4) One test fire was burned with a fuel moisture content of 8.28 per cent. This crib sustained the highest rate of spread and the highest rate of combustion of any of the other cribs tested.

Plans for the next quarter are stated and include the continued development of gas chromatograph apparatus and the testing of other wood species in test fires.

Subject Headings: *Combustion, of solid fuels; Fuels, combustion of.*

J. H. Dieterich

Fons, W. L., Pong, W. Y., Bruce, H. D., and Richard, S. S. (Pacific Southwest Forest and Range Experiment Station, Berkeley, California) "Project Fire Model," *National Bureau of Standards Order No. S–35372–60, Sixth Progress Report, Period August 1, 1960 to November 1, 1960*

Project Fire Model Progress Report No. 6 summarizes project accomplishments and plans for the period August 1, 1960 to November 1, 1960. The project continues under contract with the National Bureau of Standards and is under the supervision of Carl C. Wilson, Chief, Division of Forest Fire Research at the Pacific Southwest Forest and Range Experiment Station.

The entire project has been moved from Berkeley, California to the Southern Forest Fire Laboratory at Macon, Georgia. This move was prompted by the need to continue the burning of test fires under more strictly controlled environmental conditions. Care was taken to insure the use of uniform techniques and conditions at the two project sites. Eight identical cribs were constructed at Berkeley; four of these were burned at Berkeley and four at Macon, using the usual testing procedures. These tests will give a basis for comparison of results at both laboratory sites.

During the three-month period covered by this progress report, five cribs of longleaf pine stock were constructed and tested. Each crib was constructed of

stock having different specific gravities. Once again rate of spread and rate of combustion increased with the decrease in wood density. The heat of combustion in longleaf pine cribs increased with the increase in specific gravity.

Thermal diffusivity was calculated for 28 cribs. When plotted on a curve of rate of spread over thermal diffusivity, the data for sugar maple, magnolia, white fir, and longleaf pine appear to fall along the same line and indicate a close relationship between measured rate of spread and calculated thermal diffusivity.

Measured heat values for longleaf pine were slightly higher than any of the other species tested. The average high heat value for all densities was 8,771 Btu. per pound.

An attempt was made to determine the resin content of each wood species. Two methods were used to extract the resin from the various wood samples.

Additional measurements were made on radiation and convection heat, charcoal residue, combustion gases, and temperature distribution in the convection column.

Four figures and three tables summarize many of the findings common to the five species of wood used in the experimental wood crib fires.

Subject Headings: *Combustion, of solid fuels; Fuels, combustion of.*

J. H. Dieterich

IX. Atomization of Liquids

Taylor, G. I. (University of Cambridge, Cambridge, England) "The Dynamics of Thin Sheets of Fluid," *Proceedings of The Royal Society* A253, "I. Water Bells," 289–295, "II. Waves on Fluid Sheets," 296–312, "III. Disintegration of Fluid Sheets," 313–321 (1959) and "Formation of Thin Flat Sheets of Water," *Proceedings of The Royal Society* A259, 1–17 (1960)

This series of papers describes some very pretty theoretical and experimental studies of the dynamics of thin sheets of water. Consideration is restricted to systems in which gravity is negligible and the air pressure is the same on each side of the liquid sheet; these conditions are valid in the atomization region of most atomizers of practical importance. Thus the behavior of the sheets investigated is governed by a balance between the dynamic and pressure forces of the liquid and the surface tension forces. The effect of the viscous air-friction forces acting on the sheet (which may be of importance in practical atomizers) is accounted for in a few instances. Although the scientific aspects of the subject are emphasized, a number of results which appear to be of direct practical importance are also given.

The Dynamics of Thin Sheets of Fluid

I. Water Bells

The first experiments deal with "water bells," i.e. liquid sheets in the shape of surfaces of revolution, formed by the impingement of a turbulence-free water jet on a small coaxial conical impacter. A theory implying that the velocity of the water in the sheet remains constant but that the radius of the bell and the thickness of the sheet (which are related by the continuity equation) vary in a manner determined by the balance of dynamic forces and surface tension (the

momentum equation), is shown to predict bell shapes which agree reasonably well with experiment. The only region of substantial disagreement between theory and experiment is in the downstream portion of the bell; the extent of this discrepancy increases as the angle of the cone producing the bell increases. These last effects are explained qualitatively in terms of air friction, and a theory predicting the velocity change of the sheet due to air friction is developed (by L. Howarth) and applied to the case in which the sheet is a flat disk.

II. Waves on Fluid Sheets

A theoretical analysis of the nature of small amplitude disturbances on thin sheets reveals the existence of two kinds of waves; antisymmetrical waves (opposite surfaces displaced in the same direction) which are nondispersive, traveling with a constant velocity corresponding to a Weber number of unity, and symmetrical waves (opposite surfaces displaced in opposite directions) for which the propagation velocity depends upon the wave length. An analogy between the antisymmetrical waves and Mach lines was developed and used to predict wave shapes in uniform sheets and in radially expanding disks (for which the thickness is inversely proportional to the radius). These shapes, which are straight lines in the uniform sheet and cardioids in the case of the disk, were shown to be in excellent agreement with the shapes of antisymmetrical waves experimentally produced by point disturbances in the sheets and recorded by reflection photography. An analogy between the antisymmetrical waves and waves in a stretched string was exploited for the purpose of predicting the variation in wave amplitude along a cardioid in a radially expanding sheet. A theoretical prediction that the flow direction can change discontinuously along a cardioid in a disk was verified experimentally by suitably obstructing the flow. From a similarity analysis for one-dimensional time-dependent symmetrical waves it was inferred that the wave pattern for two-dimensional steady symmetrical waves in a uniform sheet should be parabolic at large distances downstream from a point disturbance. The agreement of this prediction with experiment was demonstrated by measurements on schlieren photographs which reveal the symmetrical waves in uniform sheets and in expanding disks.

III. Disintegration of Fluid Sheets

Equations determining the shape of the edge of a sheet of fluid were derived from a balance between dynamic forces and surface tension, accounting for the accumulation of mass of fluid at the edge. For sheets of uniform thickness both theory and experiment show that the edge is inclined to the flow direction at the same angle as the antisymmetrical waves (i.e. it propagates at a Weber number of unity). The radius of a radially expanding sheet and the shape of an edge formed by placing a wire obstruction in a radially expanding sheet were measured photographically and shown to be in agreement with theory in a number of respects. The shape of a sheet produced by a swirl atomizer was shown to resemble closely a truncated water bell; the observation that the sheet disintegrates at a downstream position where the Weber number is less than unity was explained in terms of observed variations in the thickness of the sheet, probably caused by circular air oscillations inside the orifice of the atomizer. On the basis of this

model, a rough prediction of the diameter of water droplets produced by swirl atomizers is given as

$$D/d \approx (d/y)^{1/2},$$

where D is the drop diameter, d is the orifice diameter, and y is the radius of the sheet at the position of disintegration.

Formation of Thin Flat Sheets of Water

It is shown both theoretically and experimentally that a water sheet leaving an orifice with a flat elliptical cross-section transforms itself first into a stream of circular cross-section, in which the pressure on the axis exceeds the initial pressure in the water, and then back into an identical sheet of flat elliptical cross-section, oriented at right angles to the initial sheet. Two turbulence-free water jets were directed toward each other at angles of 60°, 90° and 120°, in order to form thin flat fluid sheets. The thickness of each sheet was determined as a function of the azimuthal angle in the sheet by measuring the amount of water collected in a known time by a box with an opening formed by two razor blades placed with their edges normal to the sheet and a known distance apart. Assuming that the flow in the sheets was radial and at constant velocity, the measured azimuthal thickness distribution was used to predict the shape of the edge of the sheet (corresponding to the locus of points at which the flow velocity equals the velocity of the antisymmetrical waves). This shape was in good agreement with the experimentally observed sheet shape. As the water velocity was increased ripples developed in the downstream portions of the sheets, and eventually the sheets disintegrated. This phenomenon was attributed to an instability caused by air friction, the theory of which was previously developed by Squire to explain why flags wave.

Subject Headings: *Water, dynamics of thin sheets; Disintegration, of fluid sheets.*
F. A. Williams

Dobbins, R. A. (Princeton University, Princeton, New Jersey) "Further Studies on the Light Scattering Technique for Determination of Size Distributions in Burning Sprays II. Wide Range Photographic Photometry," *Aeronautical Engineering Laboratory Report No. 498. Air Research and Development Command, United States Air Force Contract AF 18(600)–1527 AFOSR TN 60–353 (1960)*

This report deals with the development and feasibility of a photographic technique for the measurement of droplet-size distribution in burning or evaporating fuel streams with an accuracy equal to, or greater than any presently known electronic measurement techniques.

The technique is based upon the relationship between angular distribution of scattered light and size distribution of the scattering particles. The measurement of this angular variation of scattered luminous intensity by electronic instrumentation means under actual conditions in the rocket motor test cell presents many problems. The use of photographic recording of the scattered light pattern with later analysis under ideal conditions would greatly simplify the test procedure and eliminate all the mechanical and electrical components needed for the present electronic method.

The first consideration of photographic photometry immediately raised questions of obtainable accuracy and range. This report covers the work done to

establish the range and accuracy that might be expected in the photometry of the diffraction image.

The response of the photosensitive emulsions and the various problems and effects encountered in photographic photometry are thoroughly explained and discussed. A Jarrell Ash Model 2310 microphotometer was used for transmittance measurements and a densitometer (Weston Electric Instrument Corporation Model 877) was used for preliminary investigations.

Adjacency, border, and edge effects as well as the Eberhard, Kotinsky and directional effects are thoroughly covered. An interesting circumstance is noted from the spectroscopic image which is of the type which would give rise to the adverse adjacency effects. The integrated defraction pattern, on the other hand, creates a developed image which has smooth gradations of density. This would lead one to believe that adjacency effects would be very mild or nonexistent. In the present case this was very favorable in the selection of photosensitive material.

It was found that there were no stringent requirements for high resolving power or spectral response. Hence, the selection of film was made on the basis of speed or suitability of the characteristic curve. Three commercial films manufactured by Eastman Kodak Company were used in the investigations Panatomic X, Royal Pan, and Royal X Pan.

Extensive work was done on uniformity of development and this is thoroughly documented. This development, of course, is the most difficult to achieve. A review of previous methods is presented, such as the use of bubbling air or inert gas, high pressure jet, brush agitation. Many others are discussed. It was found that a variation of hydraulic brush technique gave the most uniform development without edge effects. Attenuating filter and emulsion calibration techniques and reproducibility of shutter speeds are well covered and specific data are presented.

Several characteristic transmission curves are presented from data taken on a recording microphotometer, thereby giving a highly specular measurement that was then converted to specular density. Conspicuous features of the curves are the wide range of exposures and the specular density and also the wide variation of contrast controlled by duration of developing time. These curves point out the great flexibility of the photographic process.

The work concludes with an accuracy comparison between electronic and photographic photometry that indicates that a microphotometric procedure applicable to high density films was devised which permitted measurements to be made to a high accuracy. This accuracy compares favorably with the electronic photometry method in the measurement of diffracted light intensities in the optical determination of droplet size distributions in fuel jet streams. The method can be used also for a radiation measurement in connection with pyrometric and spectroscopic investigations, with comparable accuracy.

Subject Headings: *Sprays, drop size distribution, measurements in.*

C. C. Miesse

Lowell, H. H. (National Aeronautics and Space Administration, Cleveland, Ohio) "Dispersion of Jettisoned JP-4 Fuel by Atmospheric Turbulence, Evaporation, and Varying Rates of Fall of Fuel Droplets," *National Aeronautics and Space Administration Technical D-84* (October 1959)

Since it is occasionally necessary to jettison some or all of the fuel load of an aircraft, it is desirable to be able to estimate the fuel concentration as a function of position and time after the jettisoning has been begun. With this information the degree of ground contamination and combustible-mixture hazard can be predicted quantitatively. In this report the dispersing effects of atmospheric turbulence and of vertical separation associated with the various falling velocities of different size droplets are treated in an approximate manner. For a small number of cases the combined effects of mechanical dispersion and droplet evaporation are considered. No attempt is made to treat the details of "early" dispersal phenomena, i.e. the fuel history within a second or two of jettisoning. In this way down-wash and aircraft-generated turbulence are ignored.

It is assumed that immediately after the fuel is released a wake, or plume, of fuel droplets of varying size is present behind the aircraft at the original aircraft altitude. The plume, once formed, sinks to the ground while spreading both horizontally and vertically. Equations are developed to describe the spreading due to these forces. In the application of these equations to a "quiet day," account is taken of the anisotropic nature of the diffusion coefficients for typical inversion situations. For a "gusty" meteorological situation this anisotropy is considered to be negligible.

Since the dispersion calculations were carried out by hand it was necessary to limit the calculation to that original droplet size which, it was felt, would make the maximum contribution to fuel concentration. For that reason the volume mean was chosen and a value of 500 microns was assumed. Although this approximation was used, it is emphasized that under conditions of significant evaporation this procedure weights the contribution of the larger droplets too lightly. Calculations were carried out for a warm (21°C), windy day; a warm, quiet day; a cold (−39°C), windy day; and a cold, quiet day. Results were based on a fuel release rate of 0.24 pounds per foot of flight, a value typical of the maximum rate expected for existing aircraft at fairly low airspeeds.

For all cases calculated it is shown that with JP-4 fuel jettisoned at the 1000-foot level the resultant fuel-air ratio at sea level is significantly below 0.0001. In fact, after falling only 300 feet the ratio for the cold quiet day (the most extreme case) is less than 0.0008 while the other conditions result in values of about 0.0001 or less, even for this short distance. Additional data are shown to demonstrate the jettisoning rate at various altitudes which would result in a fuel air ratio of 0.035 (considered the flammability limit) at ground level. Even under least favorable conditions ground clearances of only 200 to 300 feet would be satisfactory.

Although "early" dispersal phenomena and random air motion near the ground have been disregarded, it appears safe to conclude that jettisoning at current rates will be permissible at altitudes above 500 feet under virtually all atmospheric conditions. This is true if ground contamination and possible evaporation from the ground accumulation of fuel can also be shown to be non-hazardous.

Subject Headings: *Fuels, dispersion, evaporation, and fall of droplets; Evaporation, of fuel droplets; Dispersion, of fuel droplets; Droplets, dispersion, evaporation, and fall.*

F. Falk

X. Meteorological Interactions

Murgai, M. P.* and **Emmons, H. W.** (Harvard University, Cambridge, Massachusetts) "Natural Convection Above Fires," *Journal of Fluid Mechanics* **8,** 611–624 (1960)

A fire produces hot gases which experience an upward buoyant force and thus form a rising column or plume. It is assumed that the mixing of the ascending hot gases with the surrounding air is essentially a turbulent process. The analysis is developed in such a manner that the convection column properties at any height above the surface can be computed for an atmosphere with a lapse rate which varies with height. This is done step by step by graphical and numerical procedure. No assumption of virtual source is made.

Fires are assumed to be circular in shape. The convection column is taken to be cylindrically symmetrical with the $\bar{x}$-axis vertically upwards and r radial. The corresponding velocity components u and v, as well as the density ρ, the pressure p, and all other fluid properties are assumed to be local mean values. It is assumed that the vertical pressure distribution is given by the approximation

$$p = p_0 - \gamma_\infty \bar{x}$$

in which p_0 is the pressure at the earth's surface and γ_∞ is the specific weight of the air outside the plume at infinity. The equations expressing conservation of mass, momentum and energy are

$$\frac{\delta \gamma r u}{\delta \bar{x}} + \frac{\delta \gamma r v}{\delta r} = 0$$

$$r u \frac{\delta u}{\delta \bar{x}} + r v \frac{\delta u}{\delta r} = r \frac{(\gamma_\infty - \gamma)}{\rho} + \frac{1}{\rho} \frac{\delta r \tau}{\delta r}$$

$$r \left(u \frac{\delta h}{\delta \bar{x}} + v \frac{\delta h}{\delta r} + ug \right) = -\frac{1}{\rho} \frac{\delta rq}{\delta r}$$

in which γ is the specific weight of the air in the plume, h is the enthalpy per unit volume, g is the acceleration due to gravity, τ the vertical shear stress and q the radial component of heat flux. If u', v', and T' are the fluctuating components of u, v, and T, then for linear turbulence τ and q are given by $r\tau = -\rho u'v'$ and $rq = \rho c_p v'T'$ respectively; c_p is the specific heat of air at constant pressure.

By introducing the concept of potential properties (the values that the properties of a parcel of air at some given level in the plume at pressure p would have if brought adiabatically to pressure p_0) the conservation equations are rewritten in a form from which it is possible to define mean values of these properties. This is done by integrating each of the three equations from r=o to r=∞. The resulting values of mean velocity $\bar{u}$, mean width $\bar{b}$, and the mean specific gravity differences $\left(\frac{\Delta \gamma_0}{\gamma_0} \right)$ may be regarded as the equivalent "top hat" distributions. A shape factor I is also defined which is equal to unity if the distributions of velocity and specific gravity difference across the convection column are given by the same function as some investigators have assumed. Murgai and Emmons do not make this assumption but they do assume that I is independent of height. The conservation equations are then written in terms of the mean values previously defined.

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ABSTRACTS AND REVIEWS

To write the final form of the conservation equations, the variables are first expressed in dimensionless form. The final conservation equations are

$$\frac{d}{dx}\, ub^2 = ub$$

$$\frac{d}{dx}\, u^2b^2 = \lambda b^2$$

$$\frac{d}{dx}\, \lambda ub^2 = -\Gamma ub^2$$

in which x, u, b, λ and Γ are vertical distance, vertical velocity, column width, buoyancy and lapse rate, respectively. All of these variables are now dimensionless. From this last set of equations, values of u, b, and λ can be determined for an atmosphere in which stability varies with height. The atmosphere is divided into layers, ordinarily of varying depth, such that the lapse rate is approximately constant within each layer. The boundary conditions at the bottom of the nth layer are simply related to the solution at the top of the $(n-1)$ layer just below. Solutions of the equations were drawn by a Pace computer for values of u_0 (the dimensionless upward velocity just over the combustion zone) ranging from 0.2 to 5.0 and for values of Γ ranging from -10 to $+10$. Methods are presented for interpolating for values of u_0 and Γ not appearing on the charts.

The step by step details of the solution are presented for the specific case of a fire ten meters in diameter with a heat output rate of 10^8 calories per second. Stability conditions were taken as those which existed in the stratified atmosphere over Seattle, Washington, on August 1, 1957. A maximum upward velocity of about 13 meters per second occurs at a height of approximately 50 meters above the ground. The convection column shows a constriction or minimum diameter (6.1 meters) at this same height. However, throughout a zone more than 1,300 meters deep above the level of the constriction the column is conical in shape with an apex about 40 meters below the earth's surface. The lapse rate in the first 1,400 meter layer is near the dry adiabatic. Above this layer where the atmosphere is stable, the column has a slightly greater tendency to spread than in the neutrally stable layer. Although the buoyancy becomes negative at about 1,400 meters, the column reaches a height of nearly 2,200 meters.

From the standpoint of obtaining quantitative calculations of the properties of a convection column over a fire or heated surface, the treatment in this paper goes considerably beyond the work of previous investigators. Perhaps the most important features of the analysis are the elimination of the assumption of a virtual source and the development of the step-by-step method for dealing with a stratified atmosphere.

Subject Headings: *Fires, natural convection above; Convection, natural, above fires.*
G. M. Byram

Schroeder, M. J. (U. S. Weather Bureau, Berkeley, California) and **Country-man**, C. M. (Pacific Southwest Forest and Range Experiment Station, Berkeley, California) "Exploratory Fireclimate Surveys on Prescribed Burns," *Monthly Weather Review* 88, 123–129 (1960)

Local wind patterns greatly affect the behavior of wild fire, and the fire in turn often appears to affect the local wind pattern. Precise knowledge of both these

103

effects is lacking for fires burning in mountainous terrain. Yet it is this knowledge that will permit safer and more effective prescribed burning as well as suppression of wild fires. The prescribed burning in California of more than 100,000 acres of brush land annually in the process of converting it to useable range or forest presented an opportunity to study both of these effects.

Following a preliminary survey on a prescribed burn in Lassen National Forest in 1956, four areas scheduled for burning were selected for study in 1957, two in the Sierra Nevada and two in the Coast Range. The procedure was in three steps:

1) A detailed study of local variation of wind, humidity, and temperature was made in each area using 5 or 6 stations equipped with continuous recording instruments. These were located to sample weather in exposed places around the periphery of the burn as well as in the bottoms and draws. They were operated for 3 to 8 days before a scheduled burn. One station was located in a well-exposed place far enough from the burn so that the fire would not be expected to influence its readings. Supplementary manual observations were made at several sites. Observations were analysed and local weather patterns were correlated with general weather patterns.

2) Using the knowledge of local weather gained from this survey and the general fire-weather forecast, the authors prepared a detailed forecast for the burn area. The forecast included diurnal trends in temperature, humidity, wind speed and direction, and even indicated the height of the expected convection column.

3) Winds occurring during the actual burning were observed and wind patterns analysed to detect any differences that might be attributed to the fire.

The authors found that the preburn survey made it possible for local wind patterns to be predicted in considerable detail. On each prescribed burn the winds dominated fire behavior. There were no obvious effects of the fires on local wind patterns except on one fire where there was an increase in speed of winds blowing out of the lee side of the fire. Unexpected afternoon down-canyon winds were observed in east-facing canyons of the Coast Range.

Success of this procedure for determining local wind characteristics a few days prior to burning depends on continuation of the same general weather conditions the day of the burn. For example, conditions are most favorable for burning logging slash in the fall when weather patterns are usually quite changeable.

The authors use two specialized terms not in the Weather Glossary. *Fire-climate* apparently means the local weather characteristics that might be expected to affect a fire. *Firewhirl* is apparently the same phenomenon referred to as *fire whirlwind* by other fire-weather meteorologists (Graham 1955).

Subject Headings: *Fire climate; Wind, effect on fires.*

O. P. Cramer

Schroeder, M. J. (U. S. Weather Bureau, Berkeley, California) "Humidity Patterns at Middle Elevations in the Coastal Mountains of Southern California," *Pacific Southwest Forest and Range Experiment Station Research Note*, No. 165 (September 1960)

Humidity, by influencing the moisture content and thereby the flammability of forest fuels, is of considerable importance in forest fire control operations. Usually showing a diurnal curve just the opposite of temperature, summer humidity in the mountains of the Pacific coastal states is often dominated by

the depth of the maritime layer. A change in height of the top of this moist, cool layer may cause abrupt humidity changes as great as 70 per cent. The author reports on this important fire-climate phenomenon as studied in the coastal mountains of San Diego County.

Normally in a layer 1,500 feet deep, the maritime layer ranges in thickness from 0 to 4,000 feet. Overlying air is usually much warmer, sometimes by more than 20 degrees, and distinctly drier. Striking contrast in humidity behavior is shown in hygrographs typical of (1) stations near the top of the maritime layer, (2) stations remaining entirely above it, and (3) stations remaining within the maritime layer. A sharp drop in humidity near the top of the maritime layer in late afternoon was found to coincide with the onset of downslope and down-canyon winds.

This field-study type of fire-weather research is producing information essential for accurate, detailed fire-weather and fire-behavior forecasting.

Subject Headings: *Humidity patterns; Fire climate.*

<div align="right">O. P. Cramer</div>

Beers, F. D. (U. S. Weather Bureau, Portland, Oregon) and Colson, D. (U. S. Weather Bureau, Washington, D. C.) "Use of Extended-Range Prognoses for Fire-Weather Forecasting," *Monthly Weather Review* 88, 131–136 (1960)

Low humidity and lightning are of great importance to those responsible for protecting wild lands from fire. In many forest areas lightning is the primary cause of fires. Except for precipitation effects, humidity controls the moisture content and thereby the flammability of forest fuels. Extended period forecasts of lightning and low humidity are, therefore, of great concern in fire-weather forecasting and to forest fire-control agencies.

This article reports the first attempts to use data from the routine Weather Bureau 5-day forecast for making 5-day predictions of (1) periods of low humidity, and (2) periods of widespread thunderstorms. Objective procedures are described (1) for predicting low humidity east winds over northwest Oregon, and (2) for predicting thunderstorms over the northern Rocky Mountains, each for 5-day periods.

The measure of humidity was the 5-day mean of 4 p.m. humidity at Salem, Portland, and Eugene Weather Bureau Stations. Over a 10-year period, departure of humidity from the 5-day normal in northwest Oregon was found to be related to departures from 5-day normal 700 mb heights in the Gulf of Alaska. The system was limited to September, a month in which low humidities often occur, and when they do, nearly always as the result of easterly winds. These dry east winds accompany a typical weather-map pattern.

The forecasting procedure separates 5-day periods into high and low humidity groups using 40 per cent as the dividing line. Parameters used were (1) the 5-day mean 700 mb height at a point immediately off the coast, (2) the 700 mb height difference between this point and another point in the interior, and (3) the observed 5-day temperature anomaly, i.e. above normal, normal, or below normal. Using coincident data (not prognostic), separation of 5-day mean humidities proved 70 per cent correct on the original data with a skill score based on chance of .53. Using actual 5-day forecast data for the same period, accuracy was 67 per cent with a skill score of .32. Applied to September 1959, the objective system

was correct for 12 of the 13 5-day periods compared to 10 correct for the fore-caster. No east winds occurred in that month, however.

For the other forecasting problem, thunderstorm occurrence over northern Rocky Mountain national forests was separated into three classes—none, scattered, and widespread thunderstorms. Procedure for predicting the class of occurrence was based on five years of July, August, and early September data. Parameters used included measures of east-west and north-south height gradients over the forecast area measured from 5-day mean 700 mb maps, and four classes of 5-day precipitation anomaly. Using coincident data the system was 59 per cent correct with a skill score of .38. With actual prognostic data for the same period, the procedure was 50 per cent correct with a skill score of .24.

The degree of success enjoyed by this initial study is encouraging and indicates the practicability of additional applications of 5-day prognostic material to specific local forecasting problems.

Subject Headings: *Fire weather, forecasts.*

O. P. Cramer

Robb, J. D., Hill, E. L., Newman, M. M., and Stahmann, J. R. (National Advisory Committee for Aeronautics, Cleveland, Ohio) "Lightning Hazards to Aircraft Fuel Tanks," *National Advisory Committee for Aeronautics Technical Note 4326* (September 1958)

A program was undertaken to evaluate the hazard of lightning strokes to aircraft fuel tanks by studying the basic mechanism of fuel tank ignition from such strokes under simulated flight conditions. Natural lightning discharges to aircraft were simulated in artificial-lightning-generation facilities constructed for this purpose.

Among the methods of ignition previously proposed is the heating of a spot on the fuel tank to a temperature which causes initiation of combustion within the tank. By both mathematical and experimental techniques this is shown to be quite unlikely. Analytically, it is demonstrated that for reasonable strokes a temperature not much above 480°F will be maintained for less than 60 milli-seconds. Although this is approximately the slow spontaneous-ignition tempera-ture for JP-4 or kerosene, such short times could hardly suffice to cause ignition. Even unusual strokes which might cause higher temperatures could not maintain these temperatures long enough to make ignition likely.

To verify the above, 53 discharges, at approximately the puncture level for the tanks involved, were fired at tanks containing JP-4. In the sixteen cases when a puncture occurred, explosion invariably followed. From only one of the 37 strokes which failed to puncture did an explosion result. This one explosion is explained by the proximity of the stroke to a vent hole permitting a spark to fly in or near the opening.

With both JP-4 and 100/130-grade aviation gasoline it was shown that practi-cally whenever puncturing of the tank occurred explosions resulted. This was true over the range of 0 to 160 parts per thousand of fuel in the air above the liquid in the tank. At extremely overrich conditions, e.g. a tank of gasoline held at 80°F for five minutes, explosion did not result even when the tank was punctured. However, fire did start outside of the tank at the puncture hole for this overrich case. It is indicated that for moderate to rich mixtures explosion is initiated by the penetration of the discharge into the tank, producing the equivalent

of spark ignition. For those mixtures below the normal lean limit it is suggested that ignition is caused by incandescent metal particles entering the richer fuel-air interface near the liquid surface.

It is obvious from the above that the relation of flammability ranges of various fuels to the temperatures at which most lightning strokes occur to aircraft is the most significant bit of information reflecting on the degree of hazard. Data are brought to prove that over 90 per cent of lightning strokes to planes occur at temperatures between 14°F and 50°F. Since these temperatures include the extreme overrich range for gasoline, are below the lean limit of JP-1, JP-5, and kerosene, and include the flammability range of JP-4, it follows that with respect to lightning induced explosion aviation gasoline is the safest fuel and JP-4 is the most dangerous. Recent strokes to aircraft fuel tanks in flight are sighted as confirming this conclusion.

A series of tests were carried out to determine the thickness of fuel tank wall required to eliminate punctures. Aluminum tanks with wall thicknesses between 0.020 and 0.081 inches were used. In all cases below 0.064 inches thick, punctures invariably occurred, but with a thickness of 0.081 inches punctures never resulted. Since the energy of natural strokes could exceed the laboratory simulation it is unlikely that 0.081 inches would always prove to be puncture proof. Nonetheless, it follows that thickening of fuel tanks in those locations especially susceptible to puncture would increase safety considerably.

Subject Headings: *Fuels, lightning hazards to tanks; Lightning, hazard to fuel tanks.*
F. Falk

XI. Operational Research Principles Applied to Fire Research

Broido, A. and McMasters, A. W. (Pacific Southwest Forest and Range Experiment Station, Berkeley, California) "Effects of Mass Fires on Personnel in Shelters," *Pacific Southwest Forest and Range Experiment Station Technical Paper 50* (August 1960)

Measurements of temperature, oxygen concentration, and carbon monoxide concentration were made continuously on gas streams taken through vent pipes at various locations in large fires. The fires were (1) two different school classrooms loaded with wood scrap, (2) a four-apartment, two-storied building and two single-story wood houses, (3) windrowed brush and fallen trees, (4) an old municipal building of composite construction, and (5) 500 tons of scrap lumber simulating fuel density piled about a shelter in a densely populated area. The continuous measurements were supplemented by gas bottle samples, and in the case of fire (5), radiation and pressure measurements were made. Meteorological observations also were made prior to fire (5), and the results are reported.

Gas temperatures were measured with chromel-alumel thermocouples, and the readings were corrected to true gas temperature. Oxygen concentrations were followed by a device utilizing the paramagnetic properties of the oxygen molecule. Carbon monoxide was monitored by recording the temperature rise in a catalyst bed that oxidized the carbon monoxide to carbon dioxide. The gas bottle samples were analyzed by an infrared method. Not unexpectedly, malfunction of the measuring devices was a problem under the extreme conditions in the fires.

Nonetheless, a considerable amount of detailed data was obtained. Of particular interest are the high levels of carbon monoxide recorded. These are judged

107

more hazardous than the oxygen depletion and high carbon dioxide concentrations also observed. In general, high gas temperatures occurred soon after ignition, and fell fairly rapidly, except when the vent was covered with rubble. Smoldering rubble maintains high temperatures and toxic gas concentrations for relatively long periods of time. The authors point out that the largest areas burned in these tests (9 acres) is much smaller than a mass fire (640 acres).

The principal conclusions are:

1) Extreme carbon monoxide concentrations occur in large-scale fires burning in the open.

2) Air temperatures will exceed 2000°F in the fire, and vents must be closed during this time.

3) If the vents are not covered by rubble, they will need to be closed only an hour or two; if covered by rubble, they will have to be closed for days.

4) A home shelter vent placed just outside a residence may be of little value because high concentrations of toxic gases may be found in such locations.

The data presented in this report should be of value to those designing shelters. In particular, the recommendations currently given for home shelters require review.

Subject Headings: *Fires, effect on personnel in shelters; Shelters, effect of fires in.*

P. R. Ryason

XII. Instrumentation

Martin, S. B. (U. S. Naval Radiological Defense Laboratory, San Francisco, California) "Simple Radiant Heating Method for Determining the Thermal Diffusivity of Cellulosic Materials," *Journal of Applied Physics* 31, 1101–1104 (1960)

The author determines the thermal diffusivity of poorly conducting materials with a dynamic, radiometric method which is based on the "long time" solution of the heat conduction equation for the infinite slab with constant heat input rate. He has used a relatively thin specimen geometrically designed to represent the opaque infinite slab of finite thickness.

For the model, H is a constant net flow of heat across the surface x, which equals 0 at the face and L at the back, a is the thermal diffusivity, K is thermal conductivity, T is temperature, t is time, and q is sensible heat per unit area. The heat-flow model is described by

$$\delta T/\delta t = a(\delta^2 T/\delta x^2) \tag{1}$$

$$\text{at } t=0 \text{ and } 0<x<L; \quad T=T_o \tag{2}$$

$$\text{at } t>0 \text{ and } x=0; \quad -K(\delta T/\delta x)=\delta q/\delta t=H \tag{3}$$

$$\text{at } t>0 \text{ and } x=L; \quad \delta T/\delta x=0 \tag{4}$$

The author presents an approximate solution to this heat conduction boundary value problem since in the strict solution the series summation rapidly approaches zero for long times, i.e. as the Fourier modulus, at/L^2, increases. The "long time" solution is

$$T(x,t)=T_o+\triangle T=T_o+(HL/K)[F_o+\tfrac{1}{2}(1-x/L)^2-\tfrac{1}{6}] \tag{5}$$

ABSTRACTS AND REVIEWS

By solving for $\triangle T_1$ and $\triangle T_2$ at points x_1 and x_2 and then equating $\triangle T_1$ and $\triangle T_2$ (i.e. at times t_1 and t_2) one obtains the expression for thermal diffusivity

$$a = [(L-x_1)^2 - (L-x_2)^2]/2(t_2-t_1) \qquad (6)$$

This equation has been used for determining the thermal diffusivity of metals but it required *in vacuo* measurements to minimize losses. The advantages of applying this method to poorly conducting materials include the elimination of the need to electrically insulate imbedded thermocouples, steep temperature profile resulting from low input rates, minimum losses from the edges, and one-dimensional treatment of the conduction when the material is heated uniformly over an area whose dimensions are large compared to the thickness.

The first attempts to obtain consistent data failed because of the violation of boundary conditions, especially (4). It was concluded that if the conditions of (4) could be met rigorously, the method would work since deviations from (3) could be minimized by not allowing the surface temperature to rise excessively. To attain zero back-surface losses, two specimens were arranged back to back and their front surfaces were irradiated identically. Symmetry of the system was assured by spacing two thermocouples equally within each specimen and adjusting the photoflood bulbs until the difference in temperature between the two shallow and the two deep thermocouples was minimized (generally less than 1½ °C during a rise to 200°C).

The cooling curve was used to correct the measured interval (t_2-t_1) for losses which are primarily through the exposed surface. The correction assumes equal losses during heating and cooling, which is reasonable for low irradiance levels. A table presents data obtained over 20° intervals from 40° to 160°C, at various lamp voltages and lamp to sample distances. The resulting estimates of thermal diffusivity give a mean value of $1.06 \pm 0.06 \times 10^{-3} cm^2/sec$ while the value $0.95 \times 10^{-3} cm^2/sec$ has been published for calculations from conductivity, density, and specific heat. No significant trend of differences appeared for changing lamp position so errors due to nonuniform heating and uncompensated surface losses must be small. However, diffusivity apparently reaches a maximum in the 60° to 100°C range which is probably due to desorption of moisture. This phenomenon warrants further investigation.

Subject Headings: *Cellulose, thermal diffusivity; Thermal diffusivity, of cellulose.*
G. M. Steffan

Walker, I. K. and Harrison, W. J. (Dominion Laboratory, D.S.I.R., Wellington, New Zealand) "Spontaneous Ignition of Wool. III. Calorimetry of Slow Oxidation Reactions in Materials of Low Thermal Conductivity," *Journal of Applied Chemistry* 10, 266–276 (1960)

This communication is about the design considerations and test results of a new simple calorimeter to measure very low rates of heat output (10^{-5} cal/sec/gr) from relatively large (10 liter) samples. The technique is considered particularly suited to an investigation of the spontaneous ignition of bulk porous combustibles of low thermal conductivity; a process typified by the slow reaction of wool by air at near ambient storage temperature.

In theory, this device measures the temperature gradient of a ventilated

spherical sample between its center and perimeter. This gradient results from the thermal resistance of the sample material itself.

The temperature difference, t, between the center of the sample and the outer radius, r, is $t = r^2 \rho Z_c / 6k$ where ρ is the sample density, Z_c, the rate of heat production per unit mass for the temperature at the center, and k, the specific thermal conductivity.

If the temperature gradient under stabilized conditions is less than 4°C, then the effect of reaction rate variation with temperature can be neglected. The total rate of heat generated within the sphere of radius, r, is $P = 8\pi t k r$.

The calorimeter vessel is a round-bottomed glass flask. A ½ to 20 liter capacity reaction vessel is mounted in a frame and submerged in a 20-inch cube water bath whose temperature is regulated by a 100 ohm platinum-resistance heater up to 98°C with a $\pm .02°$ accuracy. For a temperature rise greater than 0.5°C a single differential thermocouple is sufficient. The bare copper-constantan junction is drawn into the center by a steel needle. The cold junction is soldered to a copper block immersed in the water, but electrically insulated from it.

To insure an unchanging reaction rate, it is necessary to maintain the oxygen partial pressure at near constant values. By maintaining a slow flow rate of reactant gas within calculated limits, proper ventilation of the spherical charge can be provided to keep the oxygen level within a 1 per cent variation and yet not carry away too much heat from the reaction.

The two major heat measurement errors are due to ventilation gas and thermocouple wire leads. For a ventilation gas of density, D, and specific heat, C, the error can be kept within a design tolerance of 3 per cent by not exceeding a flow rate, F_1, given by $F_1 = .6\pi k r / DC$ (ml/sec).

The minimum flow rate, F_2, to maintain the oxygen concentration within 1 per cent of the initial value, or within the design limits, is determined as

$$F_2 = .8\pi k r t / D' \quad \text{(ml/sec)}$$

where D' is the oxygen density.

For air at 20°C the optimum flow rate is

$$F = 950 k r (t + 3.4) \quad \text{(ml/sec)}$$

The copper lead wires from the thermocouple conduct heat away from the calorimeter. The error introduced can be kept less than 5 per cent if the ratio d^2 / r^2 is less than .18k, where d is the copper wire diameter in centimeters. A chromel alumel couple would eliminate this source of heat leakage.

Practical consideration of the surface cooling of samples exposed to the air indicate this effect to be negligible for spheres of radius greater than 10 cms.

Experiments were conducted with typical New Zealand pie wool taken from 2½ years storage. A one-liter specimen was kept in 98.10°C water bath and a ten liter sample in 44.39°C water bath. Two and five liter quantities were kept at intermediate temperatures. Samples were dried with a CO^2 stream and upon establishment of a set temperature, the ventilating gas was changed to N_2 and then to dry air. Air flows were set between 2.4 and 5.0 ml/sec to keep ventilation errors less than 5 per cent. Temperature rises ranging from 3.13°C for the smaller sample to .26°C for the larger amount (standardized to a time of 40 hrs at a bath temperature of 70°C) were recorded by means of a Diesselhorst potentiometer.

Within the first 2 to 5 hours there was a rapid rise in temperature at the

center of the sample which was attributed to an accumulation of reactive materials. Thereafter, the measurements decreased asymptotically to less than 1°C for times longer than 100 hrs. Heat loss by the copper lead wires was less than 5 per cent.

With calculated values of thermal conductivity, the rate of heat generated by the reaction was found to double for each rise of 9.2°C between 45° and 100°C. The mass rate of heat produced ranged between 8×10^{-6} and 5×10^{-4} cal/sec/gm and the reaction rate, Z, relation to wool temperature, τ, can be given by

$$Z = .211 \times 10^{-6} e^{0.07535\tau} \quad (\text{cal/sec/gm})$$

Subject Headings: *Wool, spontaneous ignition; Ignition, of wool; Calorimeter, for wool oxidation.*

K. M. Foreman

Christiansen, W. H. (California Institute of Technology, Pasadena, California) "Use of Fine Unheated Wires in Shock Tubes," *The Physics of Fluids* 3, 1027–1028 (1960)

This letter summarizes the development of a very high response calorimeter for accurate heat measurements of very short duration, high temperature flow, such as detonation waves. The device makes use of the resistive changes of fine wires with temperature, but unlike hot-wire anemometers, the initial excitation current is sufficiently small so that Joulean heating and the effect on the surrounding still gas temperature is negligible.

As the hot wave passes over the wire, heat is convected to the wire and stored. The wire temperature increases until it reaches equilibrium or the flow ceases. The heat transfer per unit area is proportional to the time rate of change of voltage across the length of wire which, in practice, is recorded by an oscillograph.

Response of the instrument is better than 3 microseconds and is limited by the time for flow establishment over the wire and the heating of the wire. Tests with platinum wire of diameter, d, between .0005 and .0025 cm, and gas pressure, p, between 5.0 and 500 mm Hg., at flow Mach numbers ranging from 1.2 to 4.8, have given consistent and repeatable data, and indicated the heat transfer rate to be proportional to $(p/d)^{\frac{1}{2}}$ and to decrease exponentially with time.

Subject Headings: *Temperature, measurement with fine wires.*

K. M. Foreman

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INDEX OF SUBJECTS

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Fire Research
Abstracts and Reviews

Committee on Fire Research
and
Fire Research Conference

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

FOREWORD

A summer fire study, with Professor H. W. Emmons as chairman, was held at Woods Hole, Massachusetts from July 17 to August 11, 1961, under the auspices of the Committee on Fire Research of the National Academy of Sciences—National Research Council and with support from the National Science Foundation. The final report and recommendations from panels on economic aspects, operational and organizational aspects, and fundamentals of fire phenomena will be published by the National Academy of Sciences—National Research Council later this year.

The Proceedings of the Symposium on "Fire Control Research" (jointly sponsored by the Committee on Fire Research, NAS-NRC, and the Division of Fuel Chemistry, American Chemical Society, as a part of the National Meeting of the American Chemical Society in Chicago, Illinois, September 3–8, 1961) will appear in this and the following issue of *Fire Research Abstracts and Reviews*. The organizers of the Symposium believe that publication in this journal will enhance the value of the papers. The Editor of *Fire Research Abstracts and Reviews* is happy to welcome these contributions.

Additional copies of this issue of *Fire Research Abstracts and Reviews* are available at cost from the Printing and Publishing Office, National Academy of Sciences—National Research Council, 2101 Constitution Avenue, Washington, D.C.

WALTER G. BERL,
Editor

Contents

Volume 3   Number 3

Contents—*Continued*

Contents—*Continued*

PROCEEDINGS OF SYMPOSIUM ON

FIRE CONTROL RESEARCH

Survey of Current Fire Research Activities

W. G. Berl

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Introduction

This review addresses itself to the following topics: What is fire research? What is the motivation behind it? Where is it done and how are the findings reported? A few high points in several areas of current research will be discussed in detail.

What is fire research? It is an important branch of combustion research and is concerned, in particular, with the reaction of solid and liquid fuels with gaseous oxidizers. It differs from the more conventional and better explored combustion problems (such as those of premixed flames, engine and furnace combustion and detonations) in that the availability of the reactants and their rates of consumption are not normally independent variables, but are set by the structure and heat generation rate of the reaction zone. The buoyancy of the gaseous products provides the dominant driving force by which the circulation into and out of the fire is maintained. As in most combustion research, interest includes the problems of initiation, steady-state burning and burning limts. The nature of the fuel, its geometry and structure may vary widely while the oxidizer is frequently, though not exclusively, air. Of particular interest are the aerodynamics of fires, radiation of flames, inhibition and extinguishment, the thermal decomposition and combustion of solids and the heat and mass transfers in the presence of flames. Fire research, in this narrow definition, is not directly concerned with the important operational problems of fire detection, prevention and extinguishment nor with the promulgation of fire codes and fire-resistant designs or the testing of structures or devices under typical fire situations. Rather, it seeks to understand the physical principles involved in fires. What is desired is to think with the concepts of pure science about fires, and to draw conclusions which can assist others with their immediate practical problems.

What is the motivation behind fire research? The annual losses from fires (which in the United States result in an economic cost to the country of $5,000,-000,000, and 11,000 deaths annually) are sufficient in themselves to demand that the advanced weapons of scientific research are mobilized. The very complexity of the interactions and the bewildering multiplicity of situations in which fires occur, make it imperative that the important general principles be understood. By thus supplementing inventive efforts, improved fire-fighting organizations and more effective preventative measures, these appalling losses could be scaled down to more acceptable levels.

113

Where is fire research done? The organization of fire research in the countries that have accepted the research challenge varies with the prevailing attitude toward research and industrial development and with the severity of the fire damage to the particular national economy.

In the United States the Committee on Fire Research of the National Academy of Sciences—National Research Council has interests which extend over the broad area of all fire problems.[1] It has as its main objective the stimulation of a broad research effort on fire growth, spread and extinguishment. The Forest Service of the Department of Agriculture has assumed, in large measure, the responsibility for carrying out the forest fire research and is proceeding to attack it in several in-house laboratories, and through contracts with university and commercial research organizations. In terms of breadth of interest and effort in this particular area, it is probably unmatched anywhere in the world. The research problems of fires in enclosures are the concern, on a more modest scale, of the Bureau of Standards as part of its Division of Building Research while the Bureau of Mines is concerned largely with propellant fires and problems of explosions in mines. The Armed Services and the Atomic Energy Commission support modest efforts relating to their particular spheres of interest. Universities, research institutes, and commercial research laboratories also participate in the effort with varying degrees of effectiveness and with support from diverse sources. A useful summary of current projects is available in the recently published "Directory of Fire Research" (NAS-NRC #904). Considering the magnitude of the losses, the expenditure on basic research which is considerably less than one per cent seems inadequate.

In Britain, the senior research establishment is the Joint Fire Research Organization of the Department of Scientific and Industrial Research and Fire Offices' Committee at Boreham Wood, operated and funded jointly by the British government, and insurance companies. Its technical effort is broadly conceived, dealing almost exclusively with urban and industrial fire problems. From its five Divisions (Chemistry and Chemical Engineering, Extinguishing Materials and Equipment, Operational Research and Intelligence, Ignition and Growth of Fire, Building Materials and Structures) originate research findings of consistently high standards and laudable continuity. Through university grants, some academic interest is focused on specific fire problems.

The Japanese effort, spurred on by many man- or nature-made disasters, is vigorous. Research is carried out in the Fire Research Institute of the National Fire Defense Board, in the Fire Research Division of the Building Research Institute and in universities. The intensive Japanese work and enthusiasm is probably too little appreciated outside their country and is of high standard.

In the U. S. S. R., the principal responsibility for fire research appears to be delegated to the Central Scientific Research Institute of Fire Protection. While very little of its program and interests is known to us, a recent monograph on "Diffusive Burning of Liquids" indicates a very intensive effort in the Soviet Union, with a number of laboratories of related interests cooperating in the solution of research problems. It would be a serious mistake to minimize or underestimate their effort.

On a more limited scale, work is proceeding in Australia, Canada, Germany, France, Italy, and elsewhere.

How is the work reported? Exchange of information in the fire research field

is severely handicapped, since the pertinent scientific papers are badly scattered throughout numerous technical journals and laboratory reports. While FIRE RESEARCH ABSTRACTS AND REVIEWS attempts to counteract this fragmentation, it remains a serious barrier to progress. No satisfactory textbooks on this subject exist, nor are surveys and summaries written at reasonably regular intervals. This poses an obstacle to new investigators who wish to acquaint themselves with the background in this field. As the research effort becomes more intense, the need for scientific meetings becomes more and more apparent. Indeed, in the past several years, a modest beginning in this direction has been made. Much more needs to be done, however, to bring about a satisfactory state of affairs.

Reviewing current research activities, combustion inhibition and extinguishment will be discussed first because there it is easier to understand the more fundamental problems of chemistry and fluid flow. Fires involving liquid fuel surfaces and fires in "three-dimensional" structures, the status of convection column research, and some ignition and thermal decomposition problems of direct interest to fire research will then be discussed, emphasizing recent findings which have contributed new and useful information. This review has been aided by including information from a recent symposium on "The Use of Models in Fire Research," [2] and the American Chemical Society symposium on "Fire Control Research." [3]

In view of the intricate complexity of the physical situations in which fires occur and the very considerable number of combinations that can lead to fires in the first place, an exhaustive survey of all these possibilities will not be attempted. Let us consider, instead, what is known about the simplest situations and what conclusions can be drawn from them.

Homogeneous Inhibition of Premixed Flames

At present encouraging progress is being made in the study of inhibition of homogeneous premixed flames. Although such flames include only a very small fraction of the typical fire situations, they represent the one case in which it is possible to investigate the basic phenomena with the advanced techniques available to physical chemists and fluid dynamicists. The question one asks is: What is the action of a typical inhibitor on a relatively simple flame produced, for example, by the combustion of methane and oxygen? The objective of such research is to obtain a thorough understanding of the mechanism of chemical inhibition. It has been known for a long time [4] that halogen-containing compounds have a pronounced flame-inhibiting effect on the hydrocarbon-oxygen flame. Experimental evidence suggests that the effectiveness of these materials is due to specific interaction with some chemical reactions in such flames. It has now been established that the inhibition is a function of the concentration of the halogen and that the order of effectiveness of the halogens is inversely proportional to the reactivity of the free atoms (i.e., fluorine is less effective than chlorine, bromine and iodine). While it appears reasonable from evidence that the mechanism for such flame inhibition is the exchange reaction between the inhibitor and the free radicals that are responsible for the primary propagation reaction in the reaction zone, and that these reactions lead to the formation of stable molecules and free halogen atoms less reactive than the flame radicals, the available data are too fragmentary to allow direct insights into the radical reactions at the high temperature encountered in flames.

115

The most effective procedure to settle these problems is to establish the microstructure of a flame with and without added inhibitor, together with such other chemical and physical studies as are necessary to explain the details of the chemical inhibition of flames.[5] While from a more practical point of view it may be adequate to screen compounds, one after the other, over a variety of conditions of pressure, composition of reactants, inlet temperatures, etc., it remains an unsatisfactory procedure since for every system the same wide net has to be spread, unsupported by generalizations of what functions an effective inhibitor could play and how effective it can be expected to be in a variety of circumstances.

Flames are chemical systems in which the processes of diffusion and heat transfer are so significant that they play an important part in the interpretation of the data and cannot be neglected. By offering a steady state system without walls, and since no mixing problems are involved, they are very desirable for kinetic studies of fast reactions. However, the data analysis is complex because even the simplest reaction can proceed by a number of paths and considerable experimental precision is required to obtain satisfactory kinetic information. From the chemical standpoint the most important pieces of information are the concentration profiles of the stable species which disappear and appear in the flame, and the atom and free radical concentrations. While the methods for microsampling and quantitative identification of stable species are reasonably well advanced,[6] the principal current problem has to do with quantitative determination of free radicals. The approach is to fix free radicals with chemical scavengers which react with a radical to produce a characteristic stable product. The method must meet the stringent requirement of one-to-one correspondence between the stable reaction product and the precursor radical, since it is notoriously difficult to obtain absolute radical concentrations with the space resolution required in flame profile work by any other way. This technique is now in process of development and, when successful will fill the last major missing link in the flame structure puzzle. Temperature profiles of flames can be obtained with adequate precision with either very small thermocouples or, when solids are absent, with pneumatic probes where gas flows through two sonic orifices in series. Aerodynamic profiles are obtained by the introduction of fine particles and photographing their path through the flame.

In addition to these primary experimental data, it is necessary to have enthalpy and heat capacity data for all species present in the temperature range of interest. These are generally available with sufficient accuracy. In addition, it is important to know transport coefficients of the major flame components for quantitative interpretation of flame structure data.[7] Such data are now being acquired for typical halogen inhibitors.

The data analysis is based on the flame equations, consisting of the conservation laws and the differential equations of transport and chemical kinetics. Flux profiles of mass and energy can then be established, making allowances for the effect of molecular diffusion and thermal conductivity. This step is essential to avoid false impressions of the rate processes involved, since in many flames the effects of diffusion and thermal conduction are large. For flame inhibition work, what is desired is the simplest possible interpretation of the dominant reaction consistent with a quantitative description of the events.

At present, the work of Fristrom and colleagues [5] is concerned with investigating the effect of HBr on a methane-oxygen flame. A partial flame structure

116

ABSTRACTS AND REVIEWS

determination in the presence of HBr has been made. A quantitative interpretation of the observed changes will have to await the completion of measurements of temperature profiles and diffusion coefficients. The following significant differences in the profiles of the inhibited and uninhibited flames have been observed: the rates of reactions of all the major species (methane, carbon monoxide, oxygen) are decreased in the presence of HBr; the peak concentration of the intermediate species has changed and shifted slightly in relative position; the apparent hydrogen atom concentration, deduced from the hydrochloric acid concentration produced by the scavenger, decreased about five fold; no molecular bromine was detected in the flame. This study represents the initial attack on the detailed effect of a single inhibitor. When successfully completed, it should represent a landmark in the understanding of the phenomenon.

While the work of Fristrom promises to give a deeper insight into the processes of flame propagation and inhibition, rather remarkable findings on a less detailed level have been reported recently.[8] It was found that iron pentacarbonyl and lead tetraethyl have a very pronounced effect in decreasing over-all reaction rates of methane-oxygen flames although they are incapable by themselves to produce complete extinguishment. This effect, which is noticeable at much lower concentrations than the inhibition of halogens and halogenated hydrocarbons, may be of some practical usefulness in the future although it is premature to more than speculate on the mechanisms by which it functions. Preliminary information would suggest that the iron acts either as iron oxide in the condensed phase, or, at low concentrations, acts in the gas phase affecting the recombination reaction of hydroxyl radicals in the flame. This discovery of the effects of non-halogen-containing compounds on hydrocarbon flames is indeed unexpected and was missed in previous investigations. A too large concentration of these inhibitors reverses the trend since the compounds are combustible by themselves, and cannot, therefore, be used in high concentrations. This example shows very clearly how important it is to understand the mode of action of inhibitors and the particular reaction steps one wishes to inhibit in order to use them effectively.

While hydrocarbon-air fires are of considerable practical significance, combustible systems involving oxidizers other than oxygen and fuels other than hydrocarbons have now become prominent in rocket propulsion. The fire hazard when oxidizer and fuel are stored in close proximity and mixed accidentally with generally disastrous results, has increased our interest for finding ways and means to decrease the hazard potential. This incursion into a new regime of oxidizer and fuel combinations has uncovered an embarrassing lack of understanding in this field. The only published information on the use of conventional halogen-containing extinguishing agents on the system methane-NO_2 showed that they exhibit no significant inhibiting effect at all.[9] In fact, the addition of nitrogen or carbon monoxide had a more pronounced effect than similar addition of, say, trifluorobromomethane. One must conclude that bromine compounds do not inhibit hydrocarbon-NO_2 flames, and that the flame propagation mechanism of this system is entirely different from, and based on, different steps than the methane-oxygen reaction which is now being investigated in such detail. A few quenching measurements with ammonia-NO mixtures indicate that these flames, too, are not greatly affected by halogen inhibitors. These examples suffice to show that there is a very large unexplored area yet to be studied and that the techniques and methods developed for the methane-oxygen flames should be used and adapted to the other cases.

117

Inhibition of Homogeneous Diffusion Flames

The extinction of diffusion flames is intimately tied to the problem encountered in fires. While much useful kinetic information can be obtained from low-pressure diffusion reactions [10] typical combustion reactions have not yet been investigated under conditions which permit quantitative deductions of kinetic parameters. Nevertheless, a considerable body of information has been built up on diffusive burning, mainly due to the interest in the laminar combustion of single droplets of fuel surrounded by a gaseous oxidizer. On burning, a steady state is established in which fuel vaporizes from the liquid surface and flows toward the flame zone while oxidizer diffuses against the flow of products into the flame front. The exothermic chemical reaction is limited to a region in which both reagents are present. The transport of matter and enthalpy in such a system is given again by equations of conservation of mass and energy from which estimates of the structure of the flame zones surrounding the droplet can be obtained. Of particular interest for inhibition is the effect of the activation energy of the reaction on the thickness of the reaction zone and the effects of inhibitors on this zone. The mass burning rate of the liquid fuel is independent of the kinetics of the reaction as long as they are fast enough, but depends on the energy transport rate from the flame, and the mass transport rate of fuel and oxidizer to the flame zone. The extinction limits, however, depend on the structure of the flame zone.[11] Thus the addition in increasing amounts of a typical inhibitor such as HBr would have the consequences of widening the reaction zone with a small decrease of the maximum flame temperature, both changes occurring because of interference with the kinetics of the chemical combustion. This interference is just as pronounced as in the case of premixed flames and is undoubtedly due to specific chemical interaction. The heat flux to the fuel supply is not greatly affected by the widening of the reaction zone because the flame zone approaches the liquid surface more closely. Therefore there is no appreciable decrease in the burning rate. However, as more inhibitor is added to the oxidizer a point is reached where steady-state operation ceases, the reaction zone being unable to consume all the fuel and oxygen. This picture is appealing and has been tested experimentally insofar as the over-all process is concerned, i.e., the insensitivity of mass burning rate to inhibitor concentration. One would wish to see the laminar diffusion flame be given the same detailed quantitative attention as the premixed case.

Heterogeneous Inhibition of Premixed Flames

Another aspect of chemical inhibition is the effect of solid powders on the extinguishment of premixed or diffusion flames. With the exception of some screening work,[12] few studies have explored this rather complex situation for diffusion flames. However, regarding the effects of powders on premixed flames, several findings have been published recently in which a number of interesting conclusions were reached. According to investigation of Rosser *et al.*,[13] preceded by work of Dolan and Dempster on the inhibition of methane flames,[14] a mechanism of inhibition by powders probably involves the following succession of steps: heating of powder particles to a high temperature by the hot flame gases, partial evaporation of the powder particles, decomposition or reaction of the evaporated materials to provide metal atoms, and inhibition of the combustion process by the

118

ABSTRACTS AND REVIEWS

metal atoms themselves. Let us review briefly the experimental research. Fine powders are dispersed in a premixed gas mixture and the change in propagation velocity is measured as a function of particle concentration for substances of different specific surface area. Relatively little material is required to cause a significant reduction in the propagation velocity of a stoichiometric methane-air flame. While some materials, such as calcium fluoride, calcium carbonate, calcium hydroxide, are completely ineffective to reduce the flame speed by even small amounts, sodium fluoride, sodium chloride, sodium bromide, copper chloride, potassium sulfate, sodium bicarbonate, potassium bicarbonate, sodium carbonate are effective inhibitors to a degree which indicates chemical interference with the combustion process. One notes that the presence of about 1% methyl chloride considerably reduces the effectiveness of sodium carbonate although the methyl chloride itself has very little effect on the propagation velocity of the mixture.

It is interesting to speculate how to account for the observed effects of the particles. The stay-time in the reaction zone and the temperature profile of the flame indicates a considerable degree of evaporation of some of the effective powders by the time they pass through the reaction zone. One would expect a proportionality between powder effectiveness and specific surface area, as was shown by Dolan and Dempster's results, since an increase in specific surface area will result in greater fractional evaporation. What new species are introduced by the inhibitor? For the simple case of sodium chloride, the solid will be evaporating as sodium chloride molecules which can subsequently react with hydrogen atoms to form sodium and hydrochloric acid. Thus both sodium and sodium chloride must be accepted as the major species involving sodium. For the more complicated case of sodium carbonate, which evaporates with decomposition, one may initially have sodium, sodium oxide, sodium peroxide, etc. The depressing effect of methyl chloride, previously mentioned, indicates that sodium chloride is relatively inactive and that inhibition is associated with the sodium atom. The ability to inhibit combustion is probably not limited to the alkali metal atoms in view of the similar results obtained with sodium chloride and copper chloride. The two are of comparable volatility and both would yield some metal atoms. Since both lead tetraethyl and iron carbonyl strongly inhibit hydrocarbon-air flames, a metal atom mechanism may be operative in those cases too, although both iron and lead may also be partially converted to oxides or hydroxides.

The second task is to identify an inhibition mechanism which depends on the presence of metal atoms. Rosser discusses the possibility of interaction with the hydrogen-, hydroxyl- and oxygen atom (which were discussed previously for the homogeneous case), but comes to the conclusion that the metal atom concentration is too low to account for the observed results. Another possibility, namely, that the atom can affect free radical recombination rates by acting as a third body, does not appear promising since other third bodies present in large excess, such as water, hydrogen, or oxygen, also can absorb all or portions of the energy released in the recombination reaction and should therefore be effective inhibitors as well. A third possibility is that the metal atom deactivates energetically excited species, such as excited oxygen, carbon dioxide, C_2^*, CH^*, or OH^*. While the effect of bromine on excited OH has been reported from measurements of emission intensity, it does not appear that minor constituents should have large influence on the deactivation of excited hydroxyl. A more likely possibility is the interaction with excited carbon dioxide which with chain-branching could react with oxygen

119

molecules to form oxygen atoms. Sodium or other metal atoms present in the flames could remove the energy required for this particular reaction with the excitation energy in the sodium radiated away or degraded into thermal energy by collision. This mechanism, the removal of excitation energy by metal atom, provides a qualitative explanation of observed effects. However, it requires that excited carbon dioxide be an important intermediate in the combustion of hydrocarbons, a fact which has not been generally accepted and which would certainly require closer inspection.

Water Quenching of Diffusion Flames

In passing from these cases of flame inhibition, which are difficult though manageable problems in the physical chemistry of high temperature reactions, to the case of extinguishment of flames by water sprays, one is facing situations much less amenable to analysis by the well-known techniques of chemistry and physics. In order to make progress, allowance has to be made for the fact that many parameters are not readily controllable independently, nor that they can be described in detail. One ceases to deal with interactions on the molecular level and seeks recourse to correlations. An intelligent assessment of the variables can lead to insights of sufficient value to help in the solution of practical problems while at the same time uncovering a number of general relations which were only dimly visible before.

The best work in this field, carried out over a span of years with consistency and toward a well-defined objective, is the work of Rasbash and colleagues,[15] dealing with the extinction of liquid fuel fires by the application of sprays of water either from above or the side. Attention has been paid, in particular, to the ability of spray to penetrate to the seat of a fire and to study the mechanism of extinction, the properties of sprays required to extinguish fires of various types, and to define the critical heat transfer criteria for extinguishment.

There are two ways of extinguishing a fire with water sprays: cooling the burning fuel and/or cooling the flame gases. Rasbash came to the surprising conclusion that radiation from the flame to the fuel does not normally play a large part in determining the critical conditions for extinction. The evidence for this is that with sprays of less than critical rate a steady flame condition can be established with a temperature near the liquid surface not greatly in excess of the fire point. Also, the critical water flow rate for extinction is not dependent on the linear size of the fire. It was shown that the most economical way of putting out a fire is for the water spray to reach and cool the burning fuel. The rate at which the spray absorbs heat is generally far less than the rate of production of heat by the fire. Another important finding is that as sprays are directed downward onto a fire against the flame gases moving steadily upward, in order for the bulk of the water to reach the burning fuel, the downward thrust of the spray must be greater than the upward thrust of the flame gases. Lateral application of water from the windward side required a much smaller thrust. The extinguishment efficiency of sprays increases as the drop size is reduced for fires in deep pools of high-boiling liquids, while drop size is of relatively small importance for fires in solids.

Comparison of these systematic experiments with data from actual fires under less than ideal conditions indicates that the amount of water used may be more

120

than ten times what is required to extinguish the flame. Much of the excess undoubtedly is due to the fact that the seat of the fire cannot be reached readily and that, therefore, the water is used ineffectively.

While these experiments have shown some of the significant trends, it is evident that only a first approximation of the truth is available at present. Until a much clearer picture of the conditions of pool burning is available, it is premature to discuss the heat transfer mechanism from flame to spray merely on the basis of extrapolations based on pan size and similar scaling factors. The introduction of water in a downward spray, with the entrainment of a considerable amount of air in the process, changes the aerodynamics of the diffusion flame in a pronounced manner. This alteration in aerodynamics alone can have a profound effect on the heat transfer mechanism from the hot flame gases to the fuel surface, bringing about changes in flow pattern which have to be carefully analyzed before general conclusions can be drawn.

Diffusive Combustion of Liquids

For the detailed understanding of free-burning fires, it is important that reasonable models be available on the basis of which the factors influencing burning rates and fire spread can be assessed. As in all other combustion situations of technical interest, the interplay between combustion and aerodynamics is such that a priori descriptions of the system are difficult. Recourse has to be made to enlightened experimentation and observations. A significant advance in this area was initiated by the publication of Blinov and Khudiakov [16] who studied the diffusive combustion of liquid fuels burning in pans of varying diameters. These studies have now been taken up in a number of laboratories.[17] Blinov and co-workers investigated the burning from surfaces of liquid fuels over a range of pan diameters from .37 to 2290 centimeters for hydrocarbon fuels of different physical properties. The reported data included linear regression rates of the liquid surface and an approximate value of the visible flame height.

This work represents the simplest, though perhaps not the most significant, fire situation from which quantitative data about the interplay between fuel availability (i.e., vaporization by heat feedback from the reaction zone), the structure of the reaction zone and the aerodynamics of the process can be obtained. The results clearly indicate that various burning regimes (laminar, mixed, turbulent) can be distinguished. As pointed out in the analysis of the data by Hottel,[18] serious errors in interpretation may be made by drawing general conclusions from studies of pan fires of too limited size. (For example, the water-spray experiments of Rasbash on pans of 30 centimeters diameter or less are largely in a transition zone between the laminar and turbulent flow regime.) A decrease in burning rate in the laminar combustion regime as diameters are increased is primarily due to the relative decrease in the amount of heat received by the liquid from the flame through the wall of the container. In the laminar regime, the ratio of volumetric burning rate to flame height is substantially constant, while the flame height increases less rapidly than the pan diameter. In the turbulent regime, the flame length/pan diameter ratio is constant at high Reynolds numbers.

These results are reminiscent of work done on diffusion flames of fuel jets burning in air.[19] It is noteworthy, however, that with the pan fires the buoyancy head of the fuel vapor is several orders of magnitude less than the velocity head

of the gas jet experiments of Hottel. The very small length/diameter ratio 1.7 to which pan fires approximate at high Reynolds numbers is only one-fiftieth of the length/diameter ratio of the gas jet flames. It is clearly desirable to obtain more information of the structure of pan fires both in the laminar and fully turbulent regime. It would also seem advisable to treat the process as much as an aerodynamic phenomenon as possible, paying careful attention to the flow of air near the fire (as was done in the experiment by Emmons).[17] What is the predominant rate of heat transfer to the fuel? In Hottel's analysis it is argued that at large pan diameters, heat transfer by conduction through the pan rim will vanish and the radiant heat transfer term will predominate. The minimum in the burning rate curve in the transition region is due to the fact that the radiation term becomes small because of the thinness of the flame for pan diameters which are already large enough so that the first term (conduction) is not significant. The separation of the convective and radiative term is not simple. Ultimately, in order to understand this model, the flame luminosity, the complex flame geometry, the heat losses to the surroundings, and the chemical reaction rates need to be known if this work is to be correlated with the extinction limits.

A monograph on "The Diffusive Combustion of Liquids" by V. I. Blinov and G. N. Khudiakov (Academy of Sciences USSR, 1961) has just been published, in which is collected a large amount of experimental and theoretical material obtained in the Energy Institute, Academy of Sciences USSR and the Heat Physics Laboratory of the Central Scientific Research Institute of Fire Protection. It discusses in detail problems of flame shape and size, oscillation, and radiation. Burning rates, composition changes in multicomponent mixtures and temperature distribution in the liquid are described. On the basis of the experimental observations, conclusions are reached about extinguishing liquid tank fires by mixing, foam or water fog. It is an all-too-rare example of establishing design principles for a fire situation of practical interest by a thorough analysis and investigation of the important variables and represents an important contribution to Fire Research.

"Three-Dimensional" Fire Structures

While studies of "two-dimensional" liquid fires are in a relatively advanced state with regard to meaningful experiments and interpreting the results, the three-dimensional situation is not nearly as well advanced. A first attempt in this direction is described in wood crib experiments by Fons [20] and in a brief note by Thomas.[21] Unless the material of the solid fuel is very simple, or the structure made from porous, noncombustible material impregnated with a continuously supplied liquid fuel, the thermal behavior of the solid needs now to be understood. Wood, unfortunately, is such a complex structure that its behavior under the conditions of crib combustion is highly involved. No satisfactory theory exists at present regarding the processes occurring in crib fires.

Only limited results have been published thus far. The experiments of Thomas do not appear to give constant flame height/diameter values even for the largest linear size of fires (152 centimeters). This indicates that the "three-dimensional" nature of the structure plays a significant role despite the fact that the height of the crib compared to the flame height was relatively small. A number of new variables appear which did not have to be considered in the "two-dimensional"

case, namely, the stacking density of the wood, the surface-volume ratio, the height of the structure, etc. Fons' results are of interest because they demonstrate that a steady-state flame propagation through wood cribs is possible, thus offering a means of looking at the propagation phenomena.

Important work is done in England [22] and Japan [23] on the problem of fires in enclosures with access to outside air, with interest centered on burning rates, temperatures within the enclosure and the flow of and radiation from the gases leaving the enclosure. A substantial amount of useful information is being acquired on the influence of air flow and the distribution of combustible material on burning rate for the cases where insufficient air for complete combustion or adequate ventilation is available.

Fire Convection Columns

The investigation of the convection currents above fires has been pursued actively, theoretically and experimentally, in several places. While it is an inherently interesting problem in fluid dynamics, it has a number of practical applications as well. It is directly related to the design of chimneys and the dispersement of gases from industrial plants. The knowledge of the temperature and velocity distribution in the gas plumes above fires gives information about how safe it is to approach a fire with planes, permits deductions about the interaction between the fire plume and the atmosphere, and finally gives estimates about the interaction of wind and convection column. From the standpoint of fire protection, knowledge of the shape and temperature of the convection column provides design criteria for structures, such as steel towers in the event of fire at their base. Similarly, the flow of hot gases out of windows of the lower stories of burning buildings is part of the same problem.

The simpler problem is that of the buoyant column in an atmosphere of uniform conditions. An extension of the analysis to stratified atmospheres has also been made with reference to reasonable changes of temperature distribution with height.[24] From a number of careful experimental studies, particularly those of Yokoi,[25] temperature and velocity distribution in the convection of line and point heat sources have been explored for turbulent flow. It was shown by Rouse,[26] Yokoi and others that the plume above a line source has the same velocity at all heights, while above a point source the velocity decreases as (height$^{-\frac{1}{3}}$) while the temperature above a line source decreases inversely with height and as a $-5/3$ power for a point source.

As the column rises it cools due to both expansion and the mixing-in of additional ambient atmospheric air. It is commonly assumed that the rate of entrainment at the edge of the plume is proportional to the mean vertical velocity on the axis.[27] If the quantity of heat from fires is known and the dimensions of the real source across which the heat liberation takes place, it is possible to calculate the general shape of the convection column and, in particular, the altitude to which such a column can rise in the absence of side winds. While no measurements in actual fire situations are available, attention should be drawn to the intriguing scaling experiments of Taylor [28] in which a liquid of low density was injected into a tank containing stratified liquids of varying density. The shape of the resulting plume agreed quite well with the predictions. Calculations have been made corresponding to conditions in a burning forest in which a thousand tons of wood

are burned per hour, producing heat at a rate of 5 million kilowatts, with a lapse rate of 6.5° centigrade/kilometer. The plume of smoke will rise to about 7000 ft. in the absence of wind. It was suggested, in fact, that the rate at which a forest fire is burning could be determined by observing the height to which the smoke rises.

Only very fragmentary and preliminary experiments have been carried out regarding the effects of side winds on the convection plume.[29] A number of interesting qualitative interactions between flow and convective columns have been described by Scorer[30] (from the point of view of chimney exhausts) on the circulation of air into valleys and its effects on the products of combustion which have spread out horizontally in a stably stratified atmosphere or the changes in flow brought about during daytime circulation. These problems of wind interaction with a convection column are of such great interest to air pollution that much active work in this area is carried out. Of immediate interest is some understanding of the behavior of the column in the region where the chemical reactions are proceeding. No conclusive results are available in this critical zone.

Ignition of Solids

The review will be concluded by discussing the subject of ignition of solids, particularly the ignition of wood and its components. The ease with which materials are ignited is important in determining the growth and spread of fires. Ignition by radiant heat transfer is the preferred way by which fire spreads in fully developed fires. A quantitative investigation of the thermal decomposition of wood is essential.

One should recall the pioneering publication of Bamford[31] where much interesting material on the combustion of wood is presented. In the theoretical part of the paper, temperatures and rates of decomposition within the wood structure, where the thermal breakdown is accomplished by heat evolution, have been calculated for given initial condition and known rates of heat applied to the surface. The theoretical results were compared with experiments on wood heated by direct contact with a flame or by radiation. A number of simplifying assumptions are made, namely, that the decomposition products remain the same throughout the process, that the rate at which gases escape from the surface is determined by the rate of decomposition and not by the rate of diffusion (which implies considerable porosity of the material), and finally that the thermal decomposition reactions can be lumped together in a single exothermic reaction of the first order. In addition, it was assumed that the thermal constants of wood and its decomposition product remain constant and are the same. Values for the activation energy and reaction constants for the assumed single reaction step were obtained by fitting, in one case suitable values to the experimental time-temperature curve in the center of the specimen. The value of the activation energy so found (33,000 calories) is not unusual for reactions of this type.

The way in which a flame transfers heat to a vertical surface is not readily obtainable from information on heat convection in turbulent and non-turbulent flow. Heat transfer by radiation must be included by estimating the heat transfer from the igniting flame. The calculations permit predictions of the temperature distribution within wood sheets of different thicknesses and estimates of the rate of gas evolution as a function of time. Assuming that a minimum evolution rate

is necessary for spontaneous burning, one can determine how the ignition time would vary with thickness. Experiments were also carried out on the behavior of wood subjected to radiation of constant intensity in which was studied the time for the surface to become "critically hot," the variation of time of forced burning with intensity and the variation of depth of burning with intensity. The paper is full of stimulating discussions and shows how, with a number of simplifying assumptions, progress can be made on a complex problem.

This work has now been supplemented by an exhaustive study in Japan [32] and a series of papers from the Fire Research Establishment in England.[33] The ignition of wood and of other similar high polymers is a case of heat conduction into the material under conditions in which an exothermic reaction proceeds at a comparatively low temperature, leading to a variety of gaseous reaction products. These, in turn, diffuse to the surface where they mix with the ambient air. Ignition of these mixtures may either proceed spontaneously if the temperature is sufficiently high or, in the presence of an independent heat source, it may occur when the gas-air mixture is within the flammability limits. Needless to say the individual steps are of such complexity that a detailed accounting of the over-all event is difficult. The Japanese and English workers have succeeded, nevertheless, to correlate much useful information. The problem can be divided into two regions, the ignition of thin sections where the temperature gradient within the slab is linear, and of semi-infinite solids with a more complex temperature distribution. In either case, radiation intensities of about one calorie per square centimeter per second were required to achieve ignition. At higher intensities the ignition delay is reduced and can be estimated from equations which assume a surface equilibrium temperature of about 500°C.

The nature of the gases escaping from decomposing wood or its component parts (cellulose and lignin) have been investigated at relatively low temperatures and heating rates [34] and in an intense radiation field.[35] Such investigations are of value since chemical impregnants which increase or reduce its thermal stability act largely on chemical grounds. Up to temperatures of 500°C the decomposition products from cellulose in vacuum consist mainly of tar, water, carbon dioxide, and carbon monoxide and a nonvolatile carbonaceous residue. The concentration of carbon monoxide is so low (2% approximately) as to be beyond the lean flammability limit. The bulk of the combustible material appears as volatile tars which have been identified as low-molecular weight sugars (levoglucosans). The amount of volatile tar material appears to depend on where the thermal break in the cellulose chain molecule takes place. A particularly noteworthy task is the investigation of the influence of inorganic salts on the progress of the thermal decomposition.[36] Since fuels are rarely "pure," it is important to know why inorganic compounds have such an effect, positive or negative, on the decomposition of wood.[37]

Conclusions

This survey of some of the main lines of fire research was intended to indicate on how many different fronts the problem requires attention in order to fit together the mosaic of the over-all process. While some areas, such as the burning of "two-dimensional" and "three-dimensional" fires are still in an early stage of development, where much is yet to be learned concerning the important variables,

other fields, such as the inhibition of premixed flames, have reached a considerable degree of sophistication.

It is necessary to have a sense of perspective about what one hopes to achieve by inquiring more deeply into these complex physical and chemical phenomena. From the point of view of practical applications, understanding of some of the more common fire situations would serve as a guide in choosing promising methods of attack which, if one were using the more conventional empirical procedures, might be dismissed prematurely because they were tried under inopportune circumstances. It would permit valid extrapolations into new situations, buttressed by knowledge of the effects of the important variables, and provide a rational basis for regulations and codes whose validity is often based on inadequate theoretical or experimental information. Not least, it would reveal patterns of interactions which can give joy and satisfaction to a perceptive mind.

Fires and disease have much in common. They are unwanted and ancient scourges of mankind. They appear in a bewildering number of forms and go through a similar cycle of initiation, steady state and decay. The individual case presents a different situation from the occurrence "en masse." Much empirical knowledge of the combating of both has been developed over the ages and many practitioners of exceedingly keen insight and judgment have spent their working lives with them.

Will fire research benefit the practitioner as much as medicine has been helped by an intensive research effort? Surely, difficult as it is, it is less difficult, more restricted in scope and more readily analyzable with the precise tools of the physical scientist. The answer should be in the affirmative.

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Survey of Chemical Inhibition in Flames

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When a fire is extinguished by addition of a third substance to fuel and air, the mechanism of the effect obviously may be either blanketing, i.e., separation of the fuel from the air, or cooling, i.e., reducing the flame temperature to the point where flame kinetics is too slow to maintain combustion. However, either of these effects would depend on the specific nature of the third substance only through the generally well-known physical and especially thermal properties of that substance. Practical experience has shown that some extinguishing agents are significantly more effective than can be accounted for on this basis, and this finding has led to the belief that chemical inhibition may play a key role in fire extinguishment. Evidence for this view will be briefly reviewed here. A more detailed review made in 1957 is available.[1]

The most widely known agents believed capable of chemical inhibition of flames of organic fuels fall in two classes: (a) volatile substances containing bromine or iodine; (b) alkali metal salts (except lithium). While one might think it would be relatively simple to demonstrate the superiority of these over other chemical substances, if such superiority exists, by making comparative pan-fire extinguishment tests, this has not proven to be so. One difficulty is the notoriously poor reproducibility of pan-fire experiments, probably largely due to the random nature of the free convective gas motion around such fires. Another complication is that the bromine compounds may themselves be fuels (e.g., methyl bromide) or oxidants (e.g., elemental bromine). In the case of salts, there are problems of knowledge of surface area and degree of dispersion, and the difficulty of knowing the number of salt particles present per unit volume of burning gases. These problems notwithstanding, results of many fire-extinguishment studies tend to show the superiority of the above-mentioned classes of compounds over other substances of similar physical properties.

The combustion scientist, however, would prefer more than statistical evidence from model fire studies. He has made detailed measurements over the past eighty years of flammability limits, burning velocities, and quenching distances of pre-mixed combustible gases at rest or in steady streamline flow, and he has at least partially reliable theories which qualitatively relate these flame properties to the "first principles" of chemical kinetics and gas kinetics. It is only in the past few years that measurements of this kind have been utilized systematically to examine the question of flame inhibition.

Let us first consider flammability limits. For example, methane-air mixtures containing less than roughly five or more than roughly fourteen per cent methane are not flammable, the stoichiometric composition lying in the middle of this range. Upon adding additional nitrogen to any flammable methane-air mixture, a point is reached where it is no longer flammable. Finally, thirty-eight per cent additional nitrogen is enough to render all methane-air mixtures non-flammable. While the mechanism causing such a limit is not rigorously known, most combustion scientists would accept the following explanation. Addition of

128

ABSTRACTS AND REVIEWS

excess diluent, fuel, or oxidant reduces the flame temperature, and hence the rate of heat generation by chemical reaction, according to the Arrhenius law. The rate of heat loss from the flame to the cold surroundings also decreases, but not as much. Thus, heat-loss rate tends to overtake heat-generation rate as the flame is diluted. The effect is amplified by the fact that as the chemical reaction time increases, in the cooler flame, there is now more time for heat loss from the reaction zone to occur. Thus a finite limit of flammability is predictable mathematically, governed primarily by the magnitudes of the chemical reactivity and the heat-loss rate. (The relative importance of convective and radiative heat loss is not yet well understood.)

Now, if elemental bromine vapor [2] is added to methane-air, 2.45 mole per cent is sufficient to render all mixtures nonflammable, compared with 38 mole per cent nitrogen for the same effect. On this basis bromine is some 15 times as effective as nitrogen in extinguishment on a molecular basis, a result which cannot be explained except as a specific chemical effect, presumably inhibition. It follows from the above finding that one bromine molecule can prevent the combustion of four methane molecules. Many other examples of narrowing of the flammability range by additives have been reported.

Let us now consider burning velocity, which is the idealized rate at which a flat combustion wave would propagate through an initially stationary combustible mixture. This velocity may be deduced, to an accuracy of a few per cent, from the knowledge of the shape of a stabilized laminar flame in a known flow field, as a Bunsen burner provides. The magnitude of the burning velocity is determined by the interaction of two important parameters, the chemical reactivity in the flame and the transport properties of the mixture. Since the latter are influenced only slightly by small additions of possible inhibitors, we have a convenient means of measuring inhibition of the chemical reactivity quantitatively by observing burning velocity.

Consider the data below, which show systematic measurements of reduction in burning velocity by a series of volatile bromine and other halogen compounds:

ADDITIVE REQUIRED FOR 10% REDUCTION OF
STOICHIOMETRIC METHANE-AIR BURNING VELOCITY [3]

Additive	Number of halogen atoms	Molecular additives required per 100 molecules CH_4
HBr	1	1.8
CH_3Br	1	1.6
CF_3Br	1	1.2
Br_2	2	0.83
CH_2Br_2	2	0.81
CF_2Br_2	2	0.85
$CHBr_3$	3	0.55
CH_3Cl	1	4.9
CH_3Br	1	1.6
CH_3I	1	1.7

Note that one molecule of bromine added to 100 molecules of methane (and 900 molecules of air) is more than enough to produce a 10 per cent reduction in burning velocity. It can be shown that the burning velocity varies with the square root of chemical reactivity, so this corresponds to a reduction of 21 per cent in chemical

129

reactivity. Such a small addition could not affect the flame temperature significantly, so the effect must be a chemical inhibition. Note that all seven of the bromine compounds show similar effects, the strength of the inhibition being almost directly proportional to the number of bromine atoms per molecule. Note further that iodine is comparable with bromine while chlorine is much less effective.

Consider now the greater variety of chemical substances tested in another investigation:

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ADDITIVE REQUIRED FOR 30% REDUCTION OF
STOICHIOMETRIC HEXANE-AIR BURNING VELOCITY [4]

</div>

Additive	Molecules required per molecule hexane
CO_2	4.05
N_2	4.05
Cl_2	1.54
Br_2	0.33
$TiCl_4$	0.09
PCl_3	0.07
$Pb(C_2H_5)_4$	0.034
$Fe(CO)_5$	0.033

Here the fuel vapor is hexane instead of methane and data are reported on the basis of a 30 per cent instead of a 10 per cent reduction in burning velocity. Note that the most effective substance, iron pentacarbonyl, is more than 100 times as effective as the least effective substances, carbon dioxide and nitrogen. Bromine occupies an intermediate position in this list. New data [5] show that iron pentacarbonyl is such a powerful inhibitor that one molecule, added to 10,000 molecules of a stoichiometric methane-air mixture, reduces the burning velocity by 25 per cent.

It must be mentioned that pure iron pentacarbonyl is flammable in air, so it would hardly be capable of extinguishing an open fire unless used in combination with some other agent. Nevertheless the powerful inhibiting effect produced by traces is highly suggestive.

We turn now to the third premixed flame property frequently measured by combustion scientists, quenching distance. This is the closest distance of approach of a flame to a cold wall, and is readily determined to about one per cent accuracy by observing the minimum width of a rectangular or circular channel through which a flame can propagate. As does burning velocity, quenching distance depends on transport properties and chemical reactivity. The minimum pressure at which a flame would propagate through a stoichiometric propane-air mixture in a 3.73-diameter tube has been reported [6] to increase from 46 mm Hg to 80 mm Hg upon addition of 0.1 mole per cent methyl iodide, or one molecule of inhibitor per 40 molecules of propane. Since quenching distance of propane-air is nearly inversely proportional to pressure, this result is about equivalent to an 80/46 increase in quenching distance at constant pressure. Similar effects were observed with bromine-containing agents, while carbon tetrachloride was much less effective. Another investigator [7] has measured the depth of flame penetration into a tapered tube of gradually decreasing diameter, the diameter of the tube at the position of furthest flame penetration being taken as the quenching distance. An 8 per cent increase in quenching distance is reported to be produced by addition of one molecule of bromotrifluoromethane per 1000 molecules of stoichiometric methane-air, hydrogen bromide being not quite as effective.

The above examples, based on precise measurements of flammability limits,

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130

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burning velocities, or quenching distances of premixed hydrocarbon-air mixtures, clearly show that trace quantities of certain gaseous substances can substantially reduce flame reactivity and thus make extinguishment easier. Similar data, although not so quantitative, are available for effects of suspended sodium and potassium salts on flames.

Let us now examine what is known about the chemical mechanisms by which these agents act, a necessary preliminary to rational development of more potent or less toxic agents.

Considering first the bromine and iodine inhibition, we note that the effectiveness of a variety of carrier molecules correlates well with the number of halogen atoms per molecule, so it is reasonable to assume that breakdown to some simple halogen-containing molecule occurs in the flame, the latter being responsibile for the inhibition. In the case of bromine inhibition, Br_2 will not exist at flame temperature, so Br and HBr are the candidates. However, to inhibit the flame, it seems probable that the inhibitor must deactivate the most abundant chain-carrying radicals present, H and OH. Monatomic Br could not do this except by slow three-body processes while HBr can easily react by a rapid two-body process, e.g.,

$$H + HBr \rightarrow H_2 + Br \text{ or } OH + HBr \rightarrow H_2O + Br$$
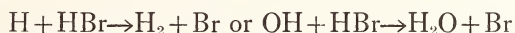
with inhibitor regeneration by hydrogen abstraction

$$Br + HR \rightarrow HBr + R.$$
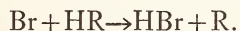
The radical R must be presumed less reactive (or less capable of upstream diffusion) than the H or OH it replaces. Since H has the unique ability to lead directly to chain-branching via

$$H + O_2 \rightarrow OH + O$$
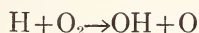
any inhibiting mechanism capable of removing H (or OH, since $OH + CO \rightleftharpoons H + CO_2$ is rapid) looks promising. The reaction of H with HBr to form H_2, however, is not a satisfying explanation of inhibition since the H_2 would rapidly oxidize, giving more H atoms. Thus OH radicals may be the key species inhibited by HBr. This kind of speculation was first published by Rosser et al.,[3] and others who have considered the problem generally utilize this approach as a working hypothesis. However, neither the theory of chain-reaction-governed flames nor knowledge of individual rate constants is sufficiently advanced to permit a theory like this to be proved. Rosser et al.,[3] have observed that the 3064 Å emission line from excited OH decreased in intensity as bromine was added, but confirmatory evidence obtained by observing unexcited OH in absorption would be highly desirable.

According to the above ideas, HI should behave similarly to HBr, and HCl and HF are too stable to react rapidly with free radicals, so the behavior of the entire halogen family is accounted for if one accepts the foregoing type of mechanism.

Considering now the inhibition produced by other substances, especially metal compounds, we find much less understanding. The mere fact that powerful inhibition can occur is good evidence that chain carriers are being taken out of circulation, and the further fact that hot fuel-oxygen flames are less susceptible to inhibition than cooler fuel-air flames is readily attributed to the much higher radical concentrations believed present in the hotter, faster-burning flames, making them harder to inhibit. To progress beyond this point to specific mechanisms is difficult. Metal atoms might react with O, OH, or H to form oxides, hydroxides, or hydrides, or metal atoms might remove energy from active species by becoming

electronically excited and then radiating. When the metal-containing substance is added in dispersed condensed-phase form, there is a choice between assuming surface reaction or vaporization. A paper in this symposium [8] suggests that vapor reactions are the important ones. Much more research is needed in this area.

Finally, attention must be given to the problem of relating information on inhibition of chemical reactivity in a premixed flame to the extinguishment of a fire, which is more nearly a diffusion flame. The rate of combustion in a diffusion flame is determined by fuel-air mixing rate for a gaseous fuel, or by rate of heat transfer from flame to fuel supply for a slowly volatilizing liquid or solid fuel, and does not depend on chemical kinetics, generally speaking. Thus, introduction of an inhibitor which would cause a moderate reduction of reactivity in a premixed flame would be expected to have no measurable effect on a diffusion flame. Nevertheless, a gaseous diffusion flame as maintained on any of several types of laboratory burners can be extinguished when a sufficient concentration of inhibitor is mixed with the air supply, the necessary concentration of inhibitor being roughly that which would extinguish a premixed flame of the same fuel. This gaseous diffusion-flame extinction process may be attributable to the presence of one or more local regions in the flame, generally at the base, which serve to anchor or stabilize the flame. Such a region, which might be very small, could contain fuel and air which mix before they burn, while in the bulk of the flame, mixing and burning are simultaneous. The inhibitor may exert its entire action in this small region. Detailed studies of this effect have apparently not been made.

A potential method for studying effects of inhibitors on diffusion flames is Potter's experiment [9] in which coaxial opposing jets of fuel and air of equal flow rates meet at a flame surface. At sufficiently high flow rates, the flame ruptures, as indicated by appearance of a hole. Effects of inhibitors on this process have not yet been reported, but such experiments are currently under way in our laboratory.

In conclusion, the fundamental knowledge of flames and inhibition thereof is sufficient to show promise that practical methods of fire control may evolve from this approach, but such knowledge is as yet quite fragmentary, and more basic research is required.

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132

Extinguishment Studies of Hydrazine and Unsymmetrical-Dimethylhydrazine Fires

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Introduction

The employment of new high-performance liquid propellants has resulted in new problems of fire protection for personnel and facilities in the vicinity in which these chemicals are stored, handled, or used. By their very nature these propellants are reactive. Toxicity of the fuels or their combustion products may exist. Many of the fuel and oxidizer combinations are hypergolic, requiring no outside ignition source to start a fire. In other cases, these materials may burn as monopropellants without an outside oxidizer, making a particularly difficult extinguishment problem. The materials under discussion may be used in a wide variety of situations or geometries. This produces a wide variety of possible fire and explosion events. Yet, if these propellants are to be used, some form of fire protection must be provided.

This investigation was undertaken to determine the materials and techniques necessary for the extinguishment and control of fires involving two of these new propellants, hydrazine and unsymmetrical-dimethylhydrazine. Some properties of these fuels are shown:

Fuel	Formula	Boiling point (°F)	Density (gms/cc)	Flash point (closed cup) (°F)	Fire point (°F)	Flammability limits in air Lower	Upper
						(vol per cent)	
Hydrazine	N_2H_4	236	1.008	104	126	4.7	100
UDMH	$(CH_3)_2N_2H_2$	146	0.786	34(?)	5	2.5	95

The program also included studies of the 50–50 mixture of these fuels, the fuel JP-X (a solution of UDMH in JP-4, a petroleum fuel), and fires involving all these fuels in contact with nitrogen tetroxide in either liquid or vapor form. This paper is limited to a summary of data for the hydrazine or UDMH and air combinations. Further details including results from the other combinations, are available from the progress reports.[1]

While the primary objective of the investigation was to determine the requirements for fire protection systems capable of coping with fires involving these propellants, an important by-product was the development of basic knowledge in the use of small models for fire-extinguishment research. Since the application of the results of this investigation to fire-extinguishment practice depends, in part, upon being able to extrapolate laboratory results to very large fires, the appropriate scaling factors must be well known. This involves determination of the mechanisms by which various agents extinguish fires and the effects of agent-application parameters, fire geometries, and fire size on the extinguishing capabilities of the various agents.

133

The experimental approach involved three fire sizes. The smallest test, 6.54-sq in, were conducted in a laboratory hood, providing an extensive amount of data to screen candidate agents and determine the mechanisms of extinguishment, and the optimum methods and rates of application. The burner shown in Figure 1, was a square stainless-steel pan which could be heated to maintain the fuel at a temperature above its fire point. A ¾-inch freeboard on the sides of the pan reduced splashing and fuel spillage. Any propellant spillage or excess extinguishing agent was caught in the stainless-steel tray on the sides of the pan. This tray also served to reduce the updraft caused by the fire and to prevent these updrafts from cooling the sides of the burner.

To evaluate an extinguishing agent, 0.6 to 2.4 cubic inches of fuel (corresponding to about 0.1 to 0.4 inches depth) were placed in the burner, allowed to reach the desired temperature, and ignited by means of a hot wire. After a selected preburn time, usually 10 seconds, the agent was directed onto the fire. The length of time required for extinguishment, the amount of agent required, and the amount of propellant remaining unburned were determined as a function of agent, rate of application, application technique, and propellant.

The larger pans, 49- and 324-sq in, were identical in geometry to the smallest pans and were used to determine the scaling factors necessary for extrapolation of the results to still larger fires. They were located in an outdoor facility around which an eight-foot-high windbreak was built to minimize the effects of variable winds.

In spite of all precautions, a substantial variability in the results of consecutive tests was found. This seems to be characteristic of pan fire extinguishment tests. Hence a large number of tests were made, and averages of a series of identical tests were used to compute each datum point plotted on the curves which follow. A total of 994 test fires were burned to obtain the results discussed herein.

Experimental Results

A. Burning Rates of Hydrazine and UDMH

Burning rates of hydrazine and UDMH were found from burning time vs. fuel depth curves for a series of square pans:

Fuel	Pan Area (sq in)	6.54	49	324
Hydrazine		0.74 in/min	0.47 in/min	1.41 in/min
UDMH		0.088 in/min	0.046 in/min	0.195 in/min

Hydrazine is seen to burn an order of magnitude faster than UDMH. This is ascribed to the ability of hydrazine to burn like a monopropellant; a decomposition flame not requiring oxygen exists close to the liquid surface. The hydrogen produced by this flame then burns with air as a diffusion flame. Addition of water to the hydrazine reduces its burning rate substantially.

The slower-burning UDMH has a burning rate of the same magnitude as ethanol or gasoline, so a decomposition flame is evidently not present.

The variation with pan size for both fuels is explicable on a heat-transfer basis (2, 3) and will not be discussed here.
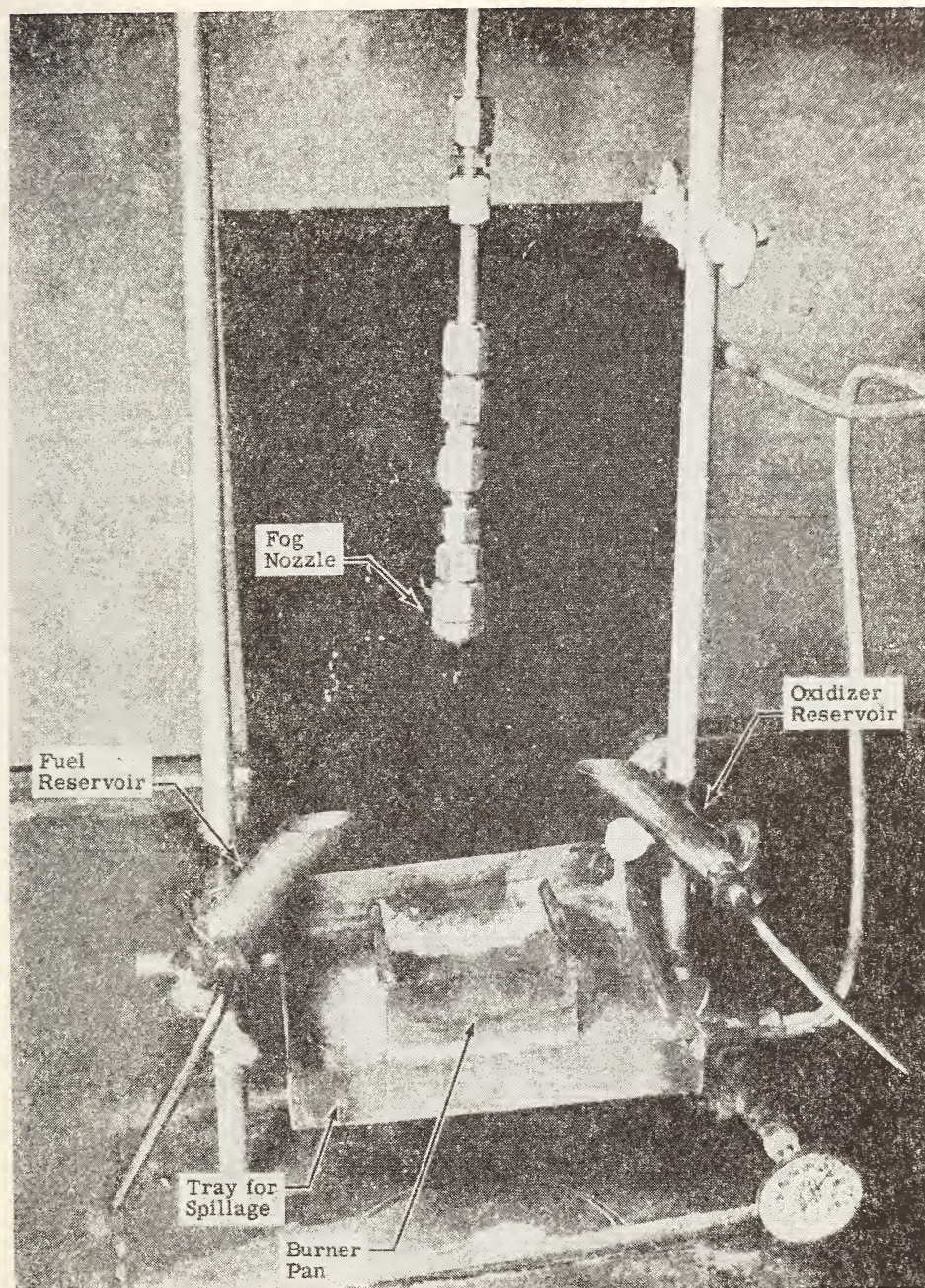
134

ABSTRACTS AND REVIEWS

Figure 1. Burner apparatus with spray nozzle.

135

B. Extinguishment of Hydrazine Fires

1. *Water Sprays*

The mechanism by which water sprays extinguish hydrazine fires appears to be dilution of the hydrazine to a concentration which will not support combustion. As shown in Figure 2, when water was applied to 6.5-, 49-, and 324-sq in hydrazine fires at rates of 0.01 to 0.33 gal water/sec per gal of fuel (0.2 to 1.2 gpm/ft²), the hydrazine concentration after extinguishment indicated a dilution to 40–70 weight per cent. The residue remaining after extinguishment of the larger fires was more dilute than those from the smaller fires. In the larger fires, more heat was radiated to the liquid and therefore the liquid temperature was higher. This meant that more dilute solutions supported combustion. The concentration of hydrazine in the residue remaining after extinguishment was found to decrease as the depth of the fuel was decreased. Decreasing depth is indicated by increasing normalized water spray rate in Figure 2. Since water and hydrazine have approximately the same densities concentration gradients are easily established. Mixing depends mostly on the force with which the water spray impinges on the surface and the depth of the pool. Both effects are responsible for the decrease in the concentration of hydrazine in the residue as the normalized spray rate was increased as shown in Figure 2.
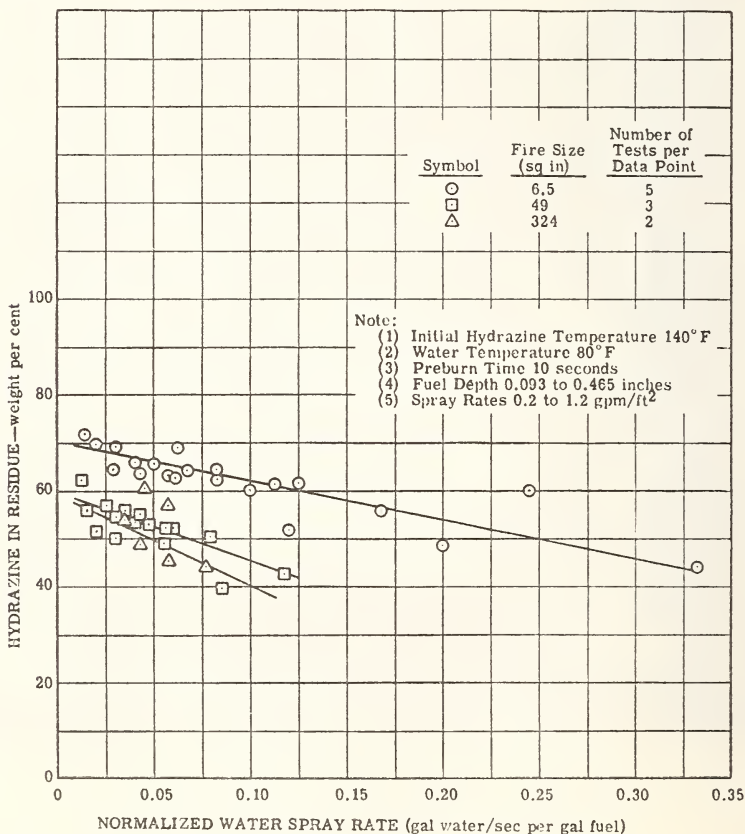
Figure 2. Concentration of hydrazine in residue remaining after extinguishment of hydrazine fires by water spray.

136

ABSTRACTS AND REVIEWS

Since the mechanism of extinguishment is primarily one of dilution, in an idealized case the time that spray must be applied to cause extinguishment should be directly proportional to the amount of fuel present and inversely proportional to the rate of application of spray. However, the simplicity of the dilution mechanism is complicated by the following factors:

1) As the fire progresses, some of the fuel is consumed, leaving only the remainder to be diluted.
2) Some of the water which does reach the burning liquid is later vaporized.
3) Some of the water is vaporized in the flame and never reaches the burning liquid.
4) Mixing rate of the water and fuel is not instantaneous.

Because of the above factors, the length of time that spray must be applied is not simply proportional to the volume of fuel or the inverse spray rate. However, as shown in Figure 3, the data may be correlated by plotting the logarithm of the extinguishment time versus the logarithm of a normalized rate of application of spray (gal water/sec per gal of fuel). In view of the above complicating factors, the fact that even an empirical correlation can be obtained is indeed fortuitous. The slopes and intercepts of the curves would be expected to be complex functions of the properties of the fuel, pan size, and agent. The main conclusion from the curves is that larger fires require a longer application of spray before extinguish-
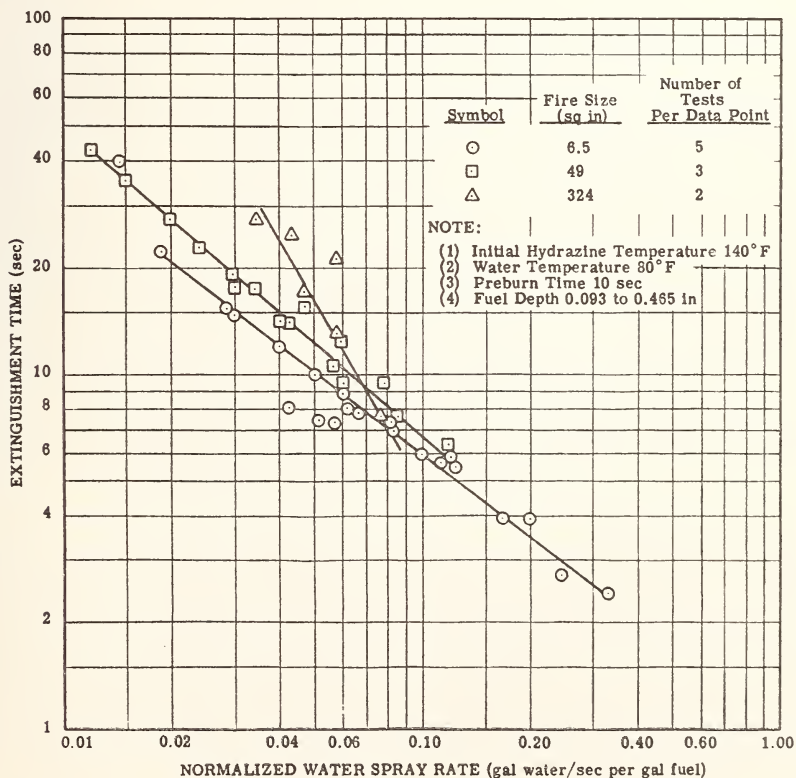
Figure 3. *Effect of normalized spray rate on extinguishment time of hydrazine fires.*

137

ment occurs, for the same normalized spray rate, but that the increased time is slight when compared to the increased fire size.

The percentage of original fuel remaining after extinguishment, an expression of the efficiency, is presented in Figure 4 as a function of the rate of application of water. As can be seen, faster rates of application are more efficient on this basis than slower ones, and deeper pools of fuel are more efficiently extinguished than shallow ones.
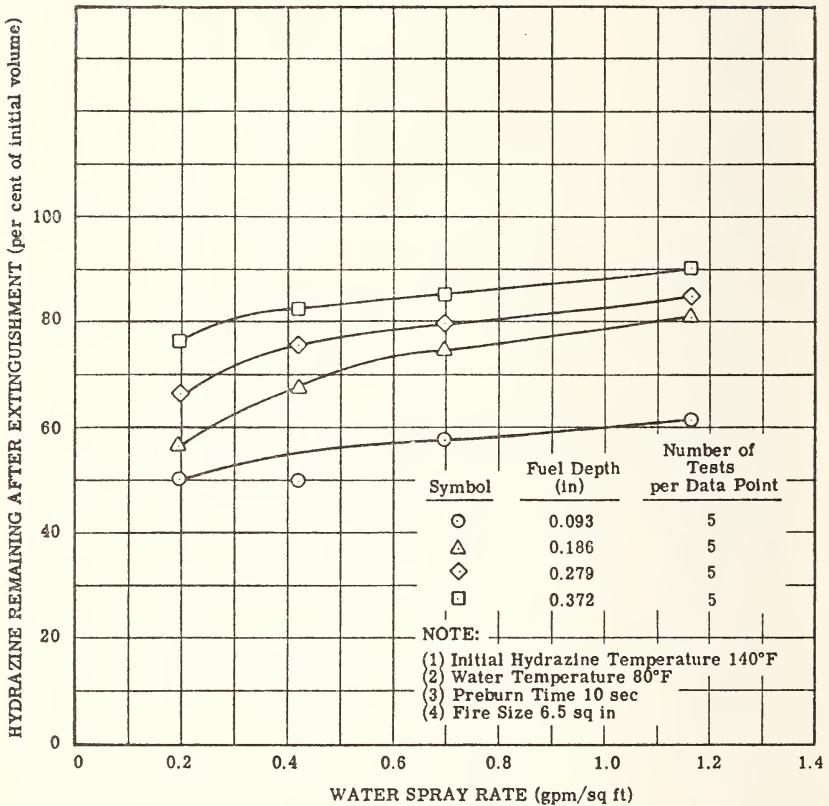

Symbol	Fuel Depth (in)	Number of Tests per Data Point
⊙	0.093	5
△	0.186	5
◇	0.279	5
☐	0.372	5

NOTE:
(1) Initial Hydrazine Temperature 140°F
(2) Water Temperature 80°F
(3) Preburn Time 10 sec
(4) Fire Size 6.5 sq in

Figure 4. Effect of water spray rate on amount of hydrazine remaining after extinguishment.

Because dilution is the mechanism by which water sprays extinguish hydrazine fires, the major scaling factor for extinguishment is a function of the amount of fuel present and is not a function of diameter, per se. However, spray rate, liquid depth, and fire diameter do influence scale-up slightly. Since dilution to 50 weight per cent concentration appears to be adequate, the amount of water required for extinguishment would be about one gallon per gallon of fuel. Any consumption of fuel or vertical concentration gradients would reduce the amount required. Conversely, any vaporization of water in the flame would increase the amount of water required.

138

The weight average particle size, $\overline{D}_w$, of the spray used on each fire size was:

Pan Size sq in	$\overline{D}_w$ microns
6.5	160
49	245
324	290

2. Fog

Measurements with the 6.5-sq in burner indicated that water fog was less effective than coarse water sprays against hydrazine fires. Since the concentrations remaining after extinguishment were comparable, the lower efficiency was probably due to increased vaporization of the fine droplets in the flame. Fog was less effective against 49-sq in fires than against 6.5-sq in fires, again because of vaporization in the flame, preventing liquid dilution. The fact that as much as 1.5 gallons of water per gallon of fuel originally present were required for extinguishment, in comparison to 1.0 gal/gal for spray, indicates the magnitude of the vaporization, especially since most of the fuel originally present was consumed in the fire.

Fog is not a good extinguishing agent for hydrazine fires and would probably fail to extinguish very large fires.

3. Foam

The mechanism by which foam* extinguishes hydrazine fires appears to be dilution of the surface of the burning liquid below the concentration which supports combustion. Since the hydrazine causes the foam to break down rapidly, a surface layer of water is built up over the fuel. The foam on top of the water film is stable until it contacts fresh hydrazine further out on the burning pool. When the foam blankets the entire surface, the fire is extinguished.

As shown in Figure 5, the amount of foam required for extinguishment is a function of application rate, depth of liquid fuel, and size of the fire. Faster rates of application require less foam because the foam has less time to break down and is therefore able to blanket the fire more quickly. Figure 6 shows that times required to extinguish the 49-sq in fires were about 10 seconds longer with 0.2 gpm/ft² application than with 0.32 gpm/ft². The slower rate of travel across the hydrazine surface at the lower application rate permits more breakdown of the foam, and therefore more foam is required.

The decrease in the amount of foam required per gallon of fuel for deeper pools of hydrazine confirms the mechanism of surface dilution. Although the concentrations of hydrazine remaining after extinguishment shown in Figure 7 are decreased by the collapse of the foam blanket remaining after extinguishment, the fact that the final hydrazine concentration may be as high as 86 weight per cent shows that the concentration gradients are very steep.

The mechanism of surface dilution suggests that scaling factors are strongly dependent on surface area of the fire as well as liquid depth and stability of the foam. Any agitation of the fuel would disturb the concentration gradients and

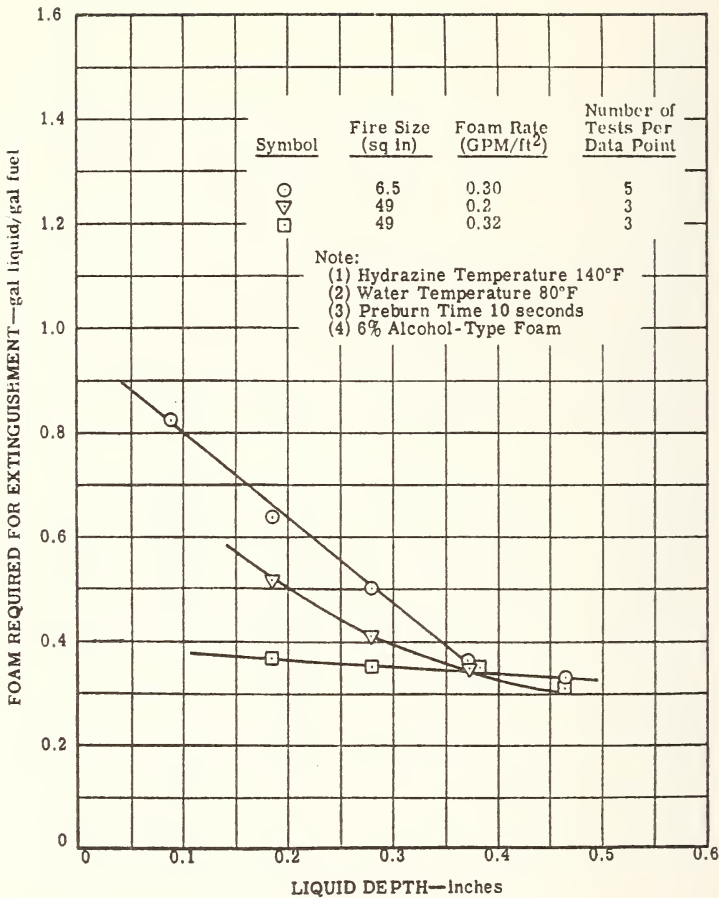* A 6 per cent alcohol-type foam was used at a 10 to 1 expansion ratio

Figure 5. Effect of liquid depth on amount of foam required for extinguishment of hydrazine fires.

140

render the foam less effective. The foam should be distributed evenly over the surface and applied at as fast a rate as possible. Although foam is a more efficient extinguishing agent than water spray, the ease of application of water sprays and the required dilution below the fire point, which eliminates the reignition hazard, make water sprays more attractive than foam.
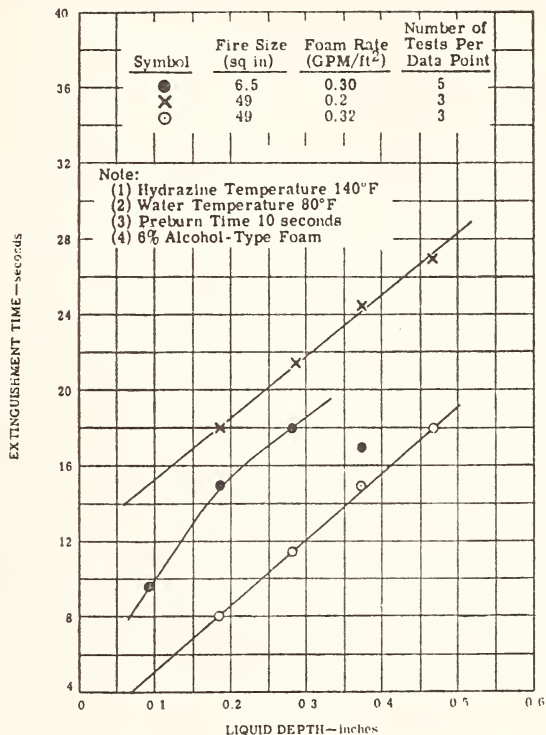

Figure 6. *Effect of liquid depth on time required for extinguishment of hydrazine fires by foam.*

4. Dry Chemical

A modified sodium bicarbonate powder of 50 micron average particle size was very effective in extinguishing fires involving hydrazine and air. As seen in Figure 8, when as little as 0.016 lbs/sec/ft² was applied, the fires were extinguished in less than four seconds. The depth of burning liquid had no observable effect, but complete coverage of the burning surface was required before extinguishment occurred. This requirement is probably the cause of the apparently anomalous results in which more time was required for extinguishment at the faster rate. These results are similar to those obtained in the 6.5- and 324-sq in burners, in which 0.016 lbs/sec/ft² extinguished the fires in less than three seconds. After extinguishment the fires could be reignited by the hot wire igniter. In practice, therefore, some other agent such as water might have to be applied in addition to the dry chemical to prevent reignition after extinguishment had been achieved.

141

A solution of 8 per cent by weight sodium bicarbonate in water applied as a water spray at a rate of 0.6 gpm/ft² showed no improvement over water as an extinguishing agent in the 6.5-sq in burner. This is consistent with other work which has shown that extinguishment by dry chemical involves reactions in the flame.

A potassium bicarbonate powder of 25 micron diameter was as effective as the sodium bicarbonate. However, an ABC Type powder was ineffective against the hydrazine fires.
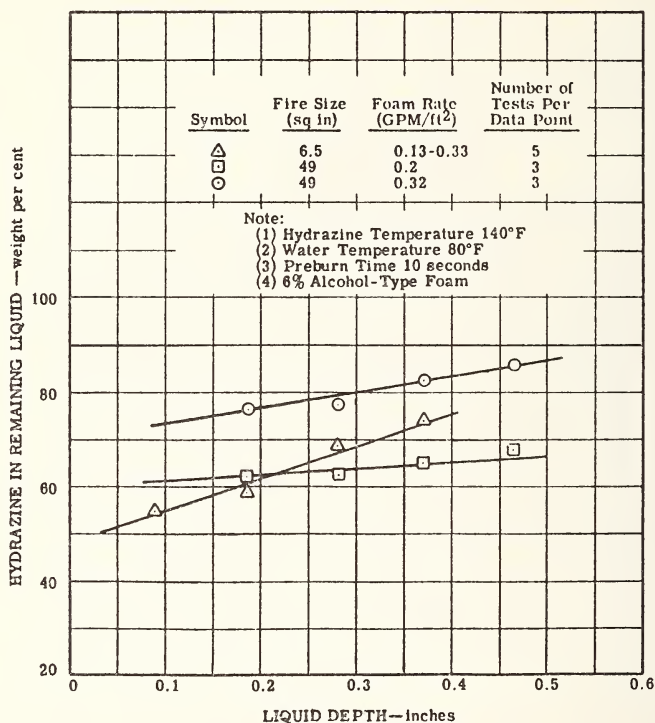

Figure 7. Effect of liquid depth on concentration of hydrazine remaining after extinguishment of hydrazine fires by foam.

Scale-up in dry chemical extinguishment is a function of fire area. Good results with this agent are dependent on the ability of the extinguishing system to completely blanket the fire and thereby prevent flashover from reigniting the extinguished areas. Dry chemicals are attractive in that they can extinguish the fires in a comparatively short time with the minimum weight of agent.

5. Chlorobromomethane

Chlorobromomethane (CB) was sprayed on hydrazine fires at a rate of 0.11 gpm/ft² through the nozzles also used for water spray. The CB reacted with the hydrazine, increasing the intensity of the fire and producing dense white fumes. The fires continued to burn until the hydrazine was consumed. CB is ineffective as an extinguishing agent for hydrazine fires under these conditions.

142

ABSTRACTS AND REVIEWS

6. Investigation of Other Agents

Several screening tests were made to determine if chemicals other than sodium bicarbonate could inhibit the combustion of hydrazine-type fuels. Since aniline is capable of trapping the $NH_2 \cdot$ radical believed to be involved in the combustion process, this chemical was the first to be investigated. When 2 weight per cent aniline was added to hydrazine, the burning rate of the hydrazine was reduced by only 10 per cent. Since the alkali metal bicarbonates in powder form
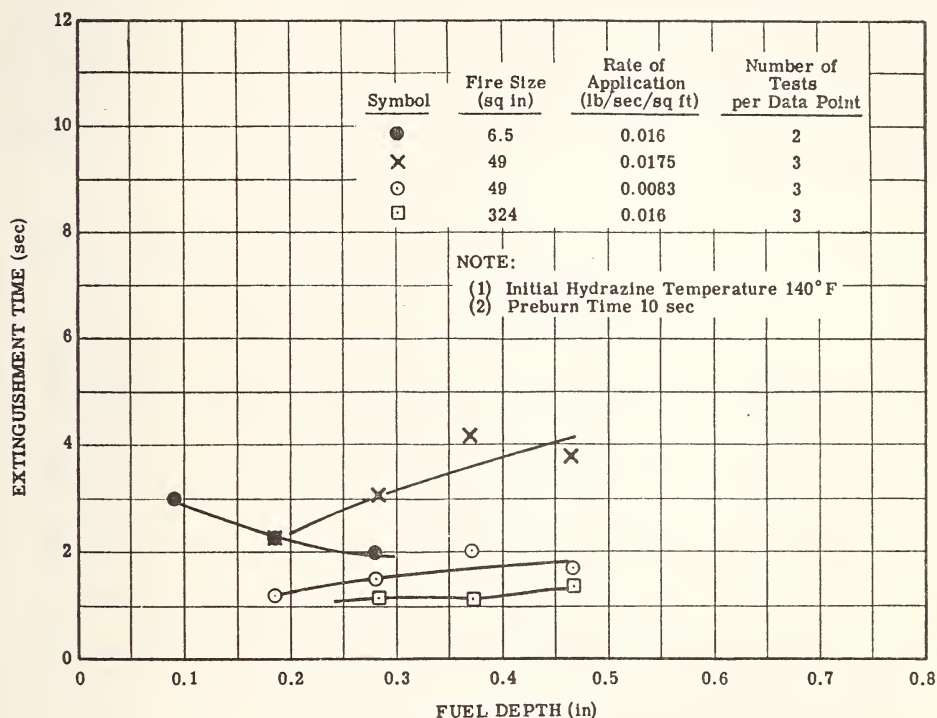
Figure 8. *Effect of fuel depth on extinguishment time of hydrazine fires by sodium bicarbonate.*

were so effective against hydrazine fires, other methods of applying alkali metal salts were investigated. A solution containing 8 per cent by weight sodium bicarbonate showed no improvement over a plain water spray. Since potassium iodide is very soluble in hydrazine, a solution containing 20 grams of potassium iodide per 100 grams of hydrazine was burned. The combustion was slowed down considerably by the formation of a molten slag over the burning liquid, but all of the hydrazine was consumed. Addition of 10 weight per cent boric acid (a constituent in some ABC powders) had a similar effect. It was thought that an inert liquid might blanket the surface of burning hydrazine and prevent combustion. However, a silicone oil added to burning hydrazine formed a film on the surface, but did not extinguish the flame.

143

C. Extinguishment of UDMH Fires

1. *Water Sprays*

As was the case with hydrazine fires, the length of time that water sprays must be applied before extinguishment of UDMH fires occurs is a function of the amount of fuel present and the rate of application of the spray. This indicates that the mechanism of extinguishment of UDMH fires is also one of dilution of the burning liquid to a concentration which will not support combustion. The UDMH fires required a longer application of spray than did the hydrazine fires because more dilute solutions of UDMH will support combustion and the UDMH burns at a slower rate, thus consuming fuel more slowly. Figure 9 shows that the fires in the 6.5-, 49- and 324-sq in burners were extinguished when the UDMH concentration was reduced to approximately 30 weight per cent. This final concentration was the same for all spray rates, pan diameters, and liquid depths. Since water is more dense than UDMH, it is believed that good mixing occurred as the water settled through the UDMH.
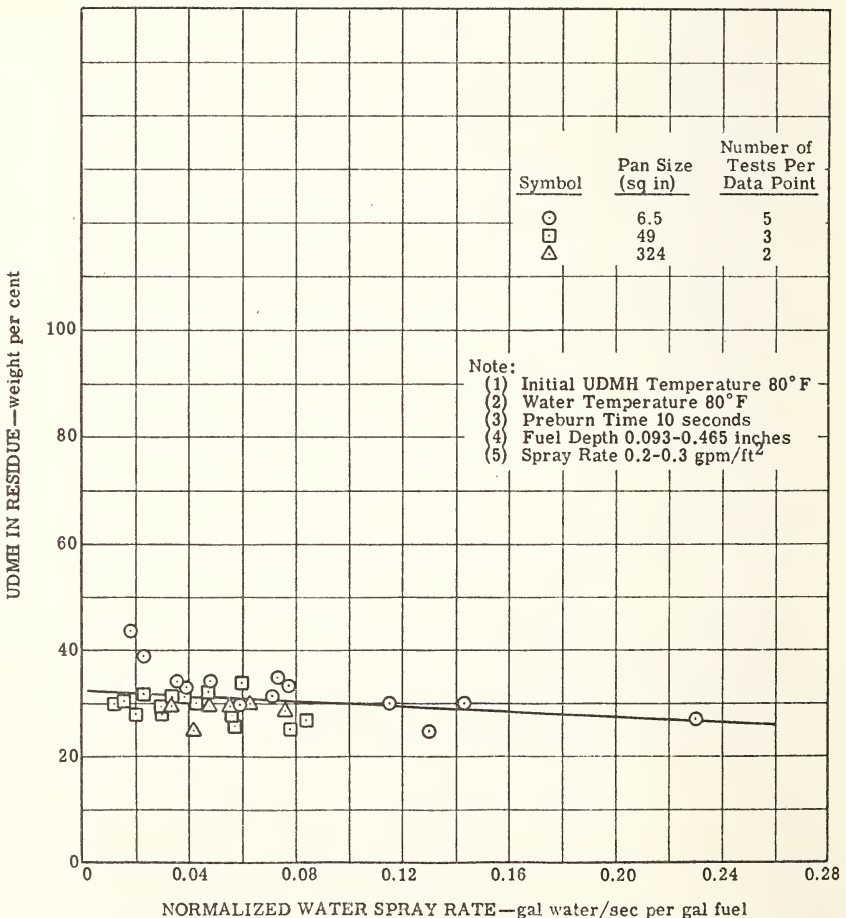
Figure 9. *Concentration of UDMH in residue remaining after extinguishment of UDMH fires by water sprays.*

144

ABSTRACTS AND REVIEWS

As was the case with the hydrazine fires, the larger fires required a longer application of spray before they were extinguished, cf. Figure 10. Since the concentrations of UDMH remaining in the residue after extinguishment were comparable regardless of fire size, increased vaporization of the water droplets in the larger flames would appear to be the cause of the increased amount of water required for extinguishment.
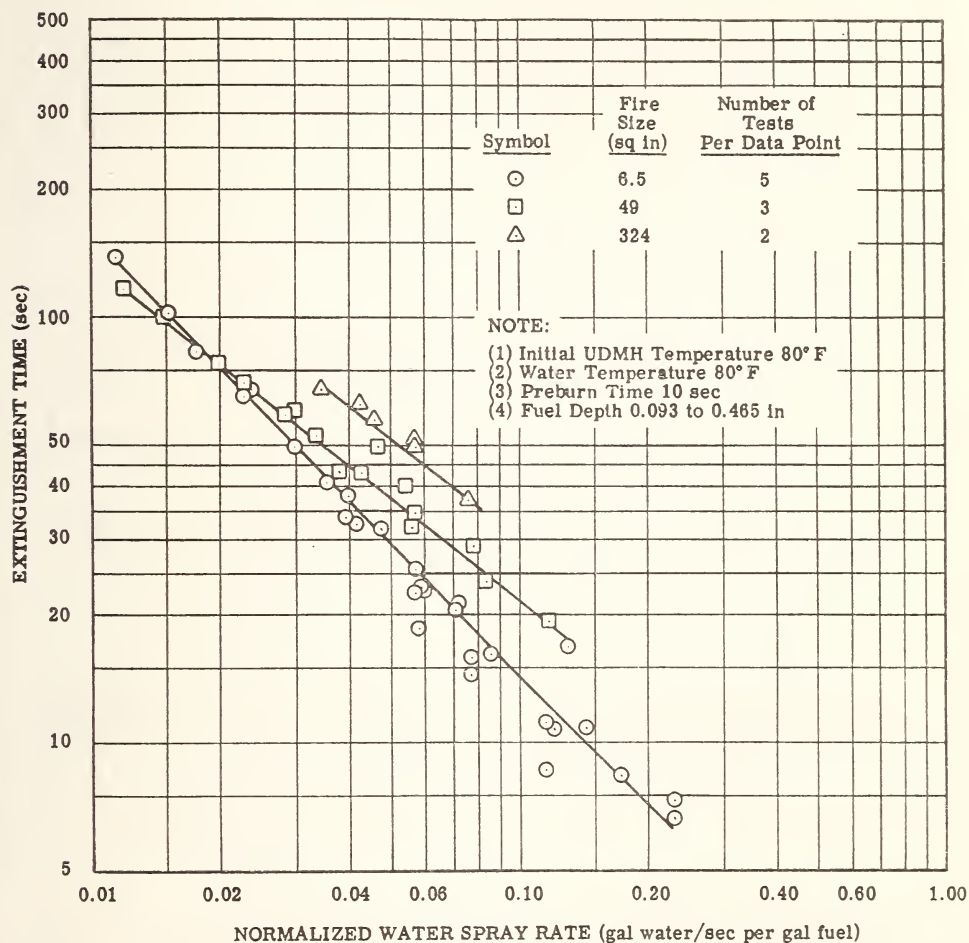

Figure 10. *Effect of normalized water spray rate on extinguishment time of UDMH fires.*

The percentage of UDMH remaining after extinguishment as a function of spray rate is presented in Figure 11. As can be seen, faster spray rates are more effective for extinguishing UDMH fires than slower rates. There is little or no change in the percentage of fuel remaining after extinguishment as the depth of UDMH is increased. This indicates that a basic difference in extinguishment behavior arises from the more complete and rapid mixing of water with UDMH than with hydrazine.

145
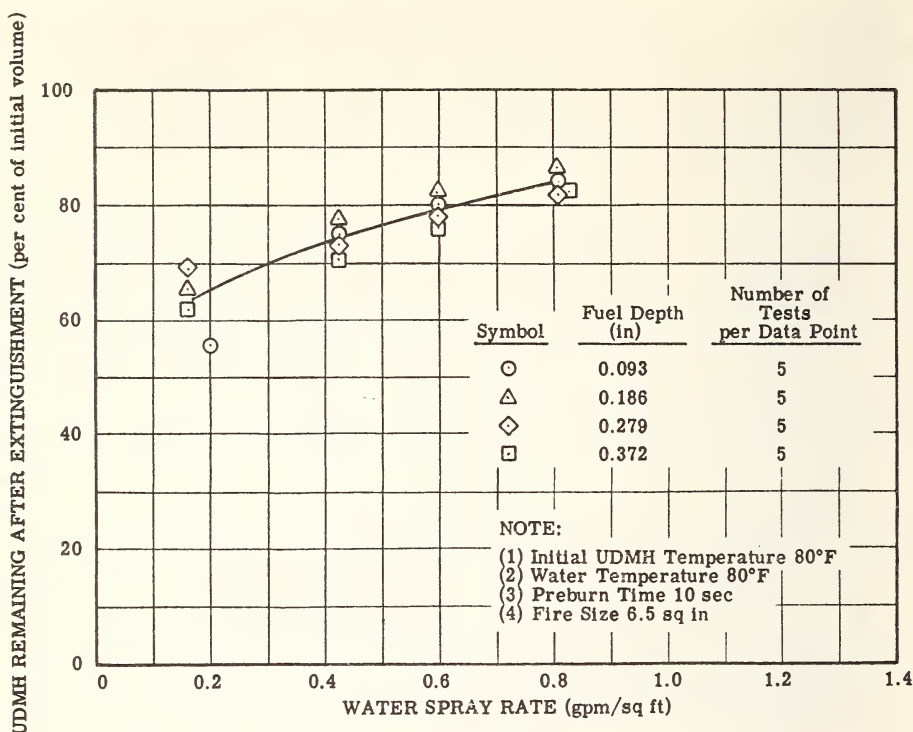
Figure 11. *Effect of water spray rate on amount of UDMH remaining after extinguishment.*

2. Fog

Fog extinguished UDMH fires by the same mechanism as water sprays, i.e., dilution. Fog applied at a rate of 0.2 gpm/ft^2 against the 49-sq in fires required 2.13 gal/gal of UDMH as compared to 1.46 gal/gal of UDMH for water spray at the same rate. Fog does not seem as desirable as water spray against UDMH fires, since part of the fog evaporates and is unable to dilute the fuel.

3. Foam

Although UDMH caused the alcohol-type foam to break down, it neverthe-less extinguished UDMH fires. As with hydrazine, the mechanism of extinguish-ment appears to be one of floating water on top of the burning liquid and diluting the surface below the concentration which will support combustion. Because this is a gentle application of water, concentration gradients are set up and the average concentrations of 35–55 weight per cent are well above the minimum concentra-tions which support combustion. Figure 12 illustrates this. As seen from Figure 13, the relative amount of liquid required for extinguishment decreases as the fuel depth is increased because of the concentration gradients mentioned above. The effectiveness of foam is increased by faster application rates. Increasing the pan diameter did not increase the amount of foam required per gallon of fuel at any

146

ABSTRACTS AND REVIEWS

given depth. The scaling factor would therefore be a function of volume of fuel, depth of fuel, and application rate.

As was the case with hydrazine fires, foam is a more efficient method of applying water to UDMH fires than is spray. However, if an adequate supply
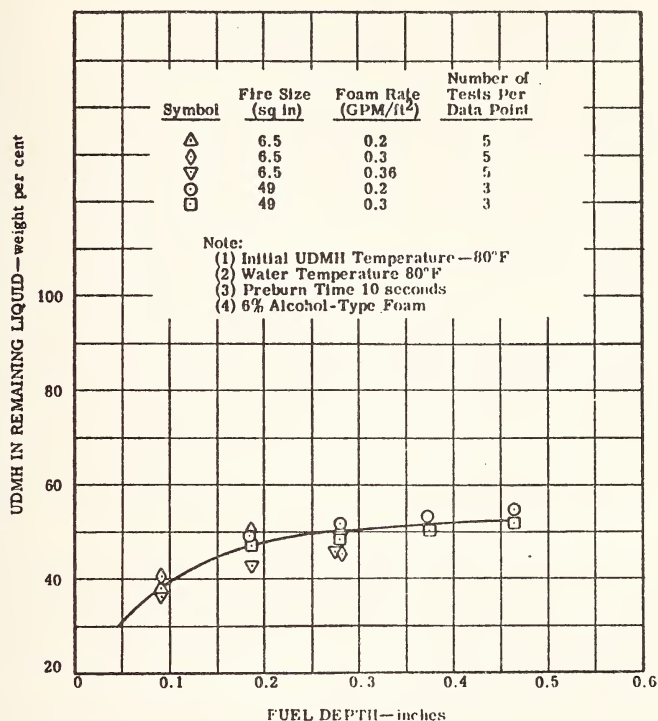

Figure 12. *Effect of fuel depth on concentration of UDMH remaining after extinguishment by foam.*

of water is available, the ease of application and the faster rates at which it can be applied make water spray more attractive.

4. Dry Chemical

Sodium bicarbonate powder rapidly extinguished UDMH fires. When the dry chemical was applied at rates of 0.0175 or 0.0083 lb/sec/ft² and when complete coverage of the surface was obtained, all fires were extinguished in less than 5.2 seconds. Fire size was varied from 6.5- to 324-sq in and depth of fuel from 0.093 to 0.47 in. If complete coverage was not obtained, the fire flashed over the surface when the flow of agent was stopped. As was the case with hydrazine, the fire could be reignited by a hot wire. Dry chemical is particularly suitable when speed of extinguishment is important or when a minimum amount of agent must be applied.
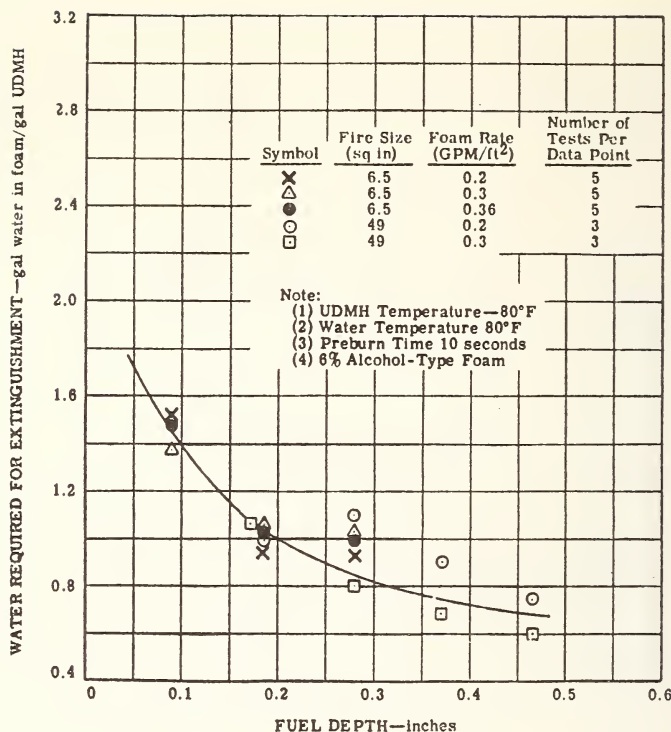
147

Figure 13. Effect of fuel depth on amount of liquid required for extinguishment of UDMH fires by foam.

5. Vaporizable Liquid Agents

As shown below, trichlorotrifluoroethane extinguished 6.54-sq in UDMH fires when applied at a rate of 0.5 gpm/ft². The fires could be reignited after extinguishment, but burned less intensely. Since trichlorotrifluoroethane has a boiling point of 115.7°F, and the fire point of UDMH is 34°F, cooling of the UDMH does not appear to be a mechanism of extinguishment. Although dense white fumes were given off when the trichlorotrifluoroethane contacted the burning UDMH, there was no increased intensity of the fire such as occurred when chlorobromomethane was added to hydrazine. Trichlorotrifluoroethane might be useful in locations where limited access to the fire is available. It appears to be somewhat more effective than water spray or foam.

EXTINGUISHMENT OF UDMH FIRES BY TRICHLOROTRIFLUOROETHANE

Liquid depth (inches)	Extinguishment time (seconds)	Gallons of agent per gallon of UDMH
0.093	6.9	0.99
0.186	6.7	0.48
0.279	9.5	0.45
0.372	24.0	0.86

Notes:
1. Application rate: 0.5 gpm/ft²
2. UDMH temperature: 80°F
3. Preburn time: 10 seconds
4. Fire size: 6.5 sq in

148

D. Extinguishment of Fires Involving a Mixture of Hydrazine and UDMH

Although an investigation of fires involving a mixture of 50 parts each by weight hydrazine and UDMH is incomplete, enough data have been obtained to indicate that this mixture behaves very much like pure UDMH in regard to burning rate and quantity of agents required for extinguishment. The reason is that the vapor pressure of UDMH is much greater than that of hydrazine, so that the vapors above the mixture are essentially UDMH.

In addition to the agents applied to UDMH fires, several other agents have been tested against small fires involving the mixture. These agents were bromotrifluoromethane and carbon dioxide.

Bromotrifluoromethane, when applied at a rate of 0.04 lb/sec/ft^2 (0.18 gpm/ft^2), failed to extinguish fires involving the 50–50 mixture in the 6.54-sq in burner. The agent was applied in gaseous form and directed on the fire both from above and from the side. It did not react with the burning fuel. Further tests are in progress, with other methods of application.

Carbon dioxide when applied at a rate of 0.17 lb/sec/ft^2 failed to extinguish fires involving the 50–50 mixture in the 6.54-sq in burner. The carbon dioxide was applied in the gaseous form and no attempt was made to direct "CO$_2$ snow" on the fire.

Conclusions

Based on results to date the following conclusions are drawn:

1. Hydrazine fires can be extinguished by water sprays, alcohol-type foams, or dry chemical powders containing primarily sodium bicarbonate. Water sprays are best suited for spill-type fires. At least one gallon of water per gallon of fuel must reach the surface of the burning liquid. Foams can be used for deep pools or in chases where the water supply is limited. Dry chemicals should be used in cases where rapid extinguishment is necessary or when the amount of agent available is limited, and where reignition is not a problem. Chlorobromomethane should not be used against hydrazine fires.

2. UDMH fires may be extinguished by water sprays, alcohol-type foams, dry chemical powders containing primarily sodium bicarbonate, or trichlorotrifluoroethane. Water sprays are best suited for spill-type or deep-pool fires. Dry chemicals are effective when rapid extinguishment is necessary or when the supply of agent is limited, and reignition is not a problem.

3. Fires involving the 50–50 mixture of hydrazine and UDMH behave essentially as UDMH fires. The same quantities of agents are required for fires involving the mixture as for fires consisting of pure UDMH. Neither bromotrifluoromethane nor carbon dioxide have extinguished fires involving the 50–50 mixture, in tests to date.

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149

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Surface Flammability of Fire-Retardant and Conventional Paint Assemblies

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Introduction

The results of a previous study [1] have shown that paints and other thin coverings applied to a flammable base material can provide a new surface of substantially lower flammability than that of the untreated base. Although with coatings of more than 50 mils (0.050-inch) thickness the particular base material used did not appreciably affect the flame spread index of the assembly, it appeared that with thinner finish coatings the base material had an important bearing on the flame spread results obtained. In cases where the coating is intended to be applied to a specified substrate, the surface flammability of the prescribed assembly is required. However, in cases where a particular substrate is not specified and a comparative evaluation of coatings only is desired, a suitable standard substrate material is required.

In choosing a standard substrate for paints, the use of an incombustible material such as asbestos cement board would obviously restrict the range of the flame spread index values and therefore the evaluation of the effectiveness of the paint film in reducing surface flammability. A study was therefore undertaken for measuring the surface flammability of a number of conventional paints and fire-retardant coatings as applied to common combustible building finish materials. The primary objects of the investigation were:

1) to evaluate the effectiveness of typical fire-retardant and conventional coatings applied to several combustible substrates at various spreading rates,

2) to evaluate those characteristics of the substrate material which were important in surface flammability measurements on painted assemblies, and

3) to select, if possible, one substrate as a standard for paint flammability measurements.

Material and Preparation

Five fire-retardant and three conventional interior paint finishes were applied to each of four substrates: paper wallboard, plywood, fiberboard and tempered hardboard. The coatings were applied to the smooth finished side of each substrate. Table 1 lists and briefly describes the substrates and Table 2 gives the schedule employed in the preparation of these test assemblies. With the exception of coating systems 7, 7a, and 7b, the effective spreading rate employed in the preparation of the assemblies was 125 ft²/gal (two coats at 250 ft²/gal). This rate, unusually heavy for conventional paints, was fairly representative of the spreading rates commonly used and recommended for fire-retardant coatings. The paints consisted of two alkyd flat paints (Nos. 3 and 8), one latex water

151

emulsion paint (No. 6), four fire-retardant paints (Nos. 1, 2, 4, and 5), and one coating system consisting of an intumescent fire-retardant main coat plus a supplemental top coat (No. 7). The fire-retardant paints selected were typical proprietary materials.

TABLE 1

SUBSTRATE MATERIALS

Symbol	Substrate	Thickness in	Density lb/cu ft
A	Paper Wallboard—Factory Finished One side	$\frac{3}{16}$	35.0
B	Plywood—Douglas Fir, exterior grade	$\frac{1}{4}$	39.0
C	Fiberboard—Interior Insulating Board, Class D (factory-finished)	$\frac{1}{2}$	19.4
D	Hardboard—Tempered	$\frac{1}{4}$	67.6
E	Hardboard—Tempered	$\frac{1}{4}$	55.1

The first step in preparing the test assemblies was to coat the substrate boards, at a spreading rate of 450 ft²/gal, with a white pigmented primer-sealer conforming to Federal Specification TT-P-56. After 72 hours the primed substrates, with the exception of those reserved for coatings 7, 7a and 7b, received two coats of the paint under test at 250 ft²/gal per coat, allowing 72 hours between coats. Sample 7 consisted of a flat fire-retardant main coat at 250 ft²/gal plus a supplemental gloss fire-retardant top coat at 250 ft²/gal. Sample 7a received only one main coat at 350 ft²/gal. Sample 7b was coated in the same manner as sample 7 but with spreading rates of 350 ft²/gal and 500 ft²/gal for the main and top coats, respectively. The coatings on samples 7, 7a and 7b were purposely varied to study the effect on flame spread behavior of different rates of spreading of the same paints.

TABLE 2

COATING SCHEDULE

Coating system	Main Paint Coating				Supplemental Top Coat			Description
	Density lb/gal	Color	No. of Coats	Spreading Rate ft²/gal	Density lb/gal	No. of Coats	Spreading Rate ft²/gal	
1	11.9	Aqua	2	250	——	—	—	Fire-Retardant Paint
2	12.8	White	2	250	——	—	—	" " "
3	12.2	"	2	250	——	—	—	Flat Alkyd Paint
4	10.6	"	2	250	——	—	—	Fire-Retardant Paint
5	13.6	"	2	250	——	—	—	" " "
6	11.5	"	2	250	——	—	—	Styrene-Butadine (Latex) Water Emulsion
7	12.3	"	1	250	11.95	1	250	*Main Coat*—intumescent, resin-base, flat, fire-retardant coating. *Top Coat*—interior gloss fire-retardant paint.
7a	12.3	"	1	350	——	—	—	Same as 7 Main Coat
7b	12.3	"	1	350	11.95	1	500	Same as 7
8	12.1	"	2	250	——	—	—	Flat Alkyd Paint

Note: A primer-sealer (10.8 lb/gal density) was applied to all substrates, at a rate of 450 ft²/gal, before coating

152

ABSTRACTS AND REVIEWS

In another study of the effect of spreading rate, one flat alkyd (No. 3) and one latex water emulsion type (No. 6) were applied to a tempered hardboard substrate (E). The rates and film thicknesses are given in Table 3. These paints were applied directly (without primer-sealer) to the smooth substrate surface in a sufficient number of coats to obtain the desired effective spreading rate, allowing 24 hours between coats.

TABLE 3

SPREADING RATES AND FILM THICKNESSES FOR TWO CONVENTIONAL PAINTS
APPLIED TO TEMPERED HARDBOARD SUBSTRATE (E)

Number of coats	Effective spreading rate ft²/gal	Paint Film Thickness	
		Computed * mils	Measured ** mils
1	900	0.6	0.3
1	500	1.1	1.2
1	250	2.1	1.6
2	125	4.2	4.4
3	60	8.8	8.5
6	30	18.	21.

* 530 divided by effective spreading rate; based upon one-third nonvolatiles by volume.
** Average for paints 3 and 6, based upon microscope measurements across smooth-sanded edge surface.

After the application of the finish materials, the assemblies were dried for not less than 72 hours and then cut to produce five specimens, each 6 by 18 inches. The specimens were then dried in an oven at 160°F for 24 hours and again conditioned, in a room maintained at 73°F and 50 per cent relative humidity, for not less than one week prior to testing. An alternate drying procedure, 24 hours at 140°F, was used for half of the test specimens prepared for the spreading rate study. However, no appreciable difference in the test results could be attributed to the effect of the slightly different drying procedure.

Test Procedure

The apparatus used for the tests has been described in detail.[2, 3] It consists of a radiant panel, a frame for support of the test specimen, and associated measuring equipment.

The radiant panel consists of a cast iron frame enclosing a 12- by 18-inch porous refractory material. The panel is mounted in a vertical plane, and a premixed gas-air mixture supplied from the rear is burned in intimate contact with the refractory surface to provide a radiant heat source. The energy output of the panel, which is maintained by regulating the gas flow according to the indication of a radiation pyrometer, is that which would be obtained from a black body of the same dimensions operating at a temperature of 670°C. A stack placed under the hood above the test specimen receives the hot products of combustion and smoke.

For test, the 6- by 18-inch specimen was placed in a metal holder and backed with a ½-inch sheet of asbestos millboard of 60 pound per cubic foot density. At time zero, the specimen was placed in position on the supporting frame facing the

153

radiant panel and inclined 30 degrees to it. A pilot igniter fed by an air-acetylene mixture served both to initiate flaming at the upper edge of the test specimen and to ignite combustible gases rising from the specimen. Observations were then made of the progress of the flame front, the occurrence of flashes, and so forth. An electrical timer calibrated in minutes and decimal fractions to hundredths was used for recording the time of occurrence of events during the tests. The test duration was 15 minutes, or until sustained flaming had traversed the entire 18-inch length of the specimen, whichever time was less.

The flame-spread index, I_s was computed as the product of the flame spread factor, F_s, and the heat evolution Q, thus

$$I_s = F_s Q$$

where:

$$F_s = 1 + \frac{1}{t_3} + \frac{1}{t_6 - t_3} + \frac{1}{t_9 - t_6} + \frac{1}{t_{12} - t_9} + \frac{1}{t_{15} - t_{12}}$$

The symbols t_3 . . . t_{15} correspond to the times in minutes from specimen exposure until arrival of the flame front at a position 3 . . . 15 inches, respectively, along the length of the specimen. $Q = 0.1 \Delta\theta/\beta$, where 0.1 is an arbitrary constant, $\Delta\theta$ is the observed maximum stack thermocouple temperature rise, in degrees F, at any stage of combustion of the specimen minus the maximum temperature rise observed with an asbestos-cement board substituted for the specimen, and β is the slope of the line obtained by plotting the maximum stack thermocouple temperature rise as a function of the corresponding measured heat input rate, in Btu per minute, as supplied by a diffusion-type gas burner placed near the top of an asbestos-cement board specimen during normal operation of the radiant panel.

Results and Discussion

A minimum of four replicate tests were run on each test assembly. The mean flame spread indices and the coefficients of variation are listed in Tables 4 and 5. The weight of the smoke deposit listed is the mean for replicate tests. Although not directly related to surface flammability, the smoke deposit is considered to be an indication of possible parallel hazards, such as toxicity and the interference to be expected in evacuation and fire-fighting procedures. The smoke deposit values represent the contribution of both the coating and substrate materials as evidenced by the somewhat higher mean smoke deposits for coatings on hardboard (D) than on the other substrates. The fire-retardant coatings tested did not produce significantly greater smoke deposits than the conventional paints.

Intumescence was exhibited by paints 1, 7a, and 7b. Paints 2, 4, 6, and 7 blistered, whereas the alkyd paints 3 and 8 did not blister or intumesce. Paint 5 flaked off from the substrate during test. Blister and intumescent formations were responsible for a wide variation in flame spread indices for the paints which exhibited these properties.

Of the four substrates used, the plywood and the hardboard showed the widest range in flame spread index values, affording good opportunity for discrimination between coatings. The hardboard values, however, had lower coefficients of variation than the plywood values, and much lower than those obtained with the other two substrates. Considering the results obtained with the hardboard, the conventional paints 3, 6, and 8 appeared to be comparable to the fire-retardant paints

154

1, 4, and 5, when applied to this substrate at the same effective spreading rate of 125 ft²/gal. The intumescent fire-retardant coating, 7a, showed both the lowest flame spread index and the lowest smoke deposit value of any of the coatings.

At effective spreading rates of 250 ft²/gal or greater, the flame spread index was found to be strongly affected by the spreading rate as shown in Figure 1. One coat of a flat alkyd paint applied at a rate of 250 ft²/gal reduced the flame spread index of a tempered hardboard substrate by a factor of almost 5. Similarly, a
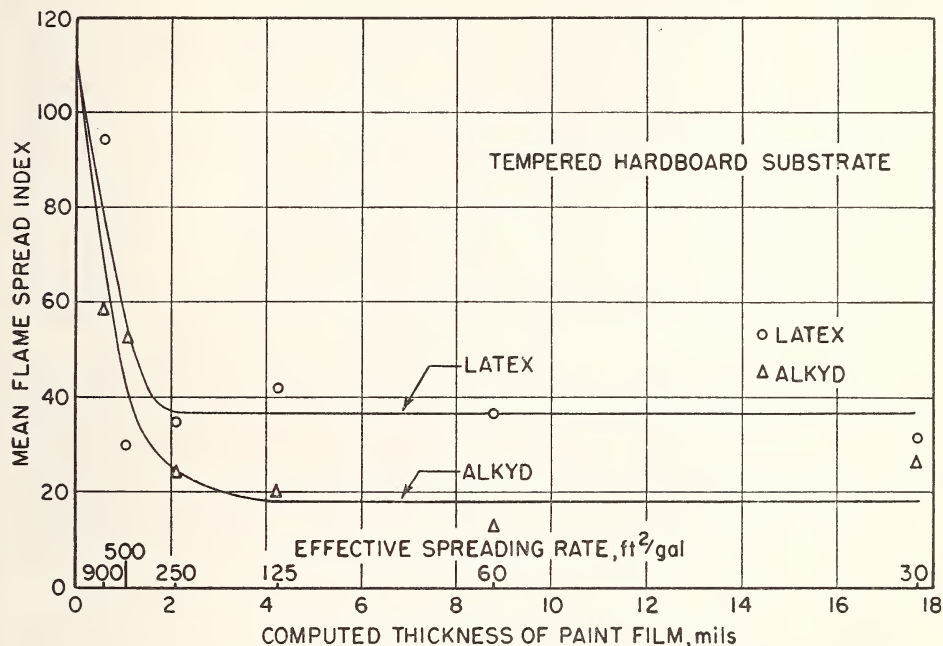
Figure 1. Effect of paint film thickness on mean flame spread index for two conventional paints.

coat of a latex paint effected a more than three fold reduction. For film thicknesses greater than those corresponding to 250 ft²/gal, the additional improvement in flame spread index was quite small. The effect of very thick films, such as might be encountered on surfaces frequently repainted, was not investigated. It is possible, however, that a higher flame spread index might result from the formation and disintegration of blisters, from cracking, peeling or other separation from the flammable substrate, or by the direct involvement of the thick paint layer.

The effect of paint thickness upon surface flammability properties refers only to typical combustible cellulose-base substrates in contrast to noncombustible substrates such as plaster, concrete or metal.

In another study, in which nonflammable substrates were used, it was found that the flame spread index increased with increasing thickness of a paint coating applied on steel sheet. For example, the flame spread index of a No. 18 gage, red lead primed steel sheet had values of 1, 7, 69, and 110 for oil-base paint coat-

155

TABLE 4

MEAN FLAME SPREAD INDEX AND MEAN SMOKE DEPOSIT OF
COATED ASSEMBLIES BASED ON FOUR REPLICATE TESTS SUBSTRATE

	A Paper Wallboard			B Plywood			C Fiberboard			D Hardboard		
Coating system	Mean I_s	Coeff. of var.* %	Mean smoke mg	Mean I_s	Coeff. of var. %	Mean smoke mg	Mean I_s	Coeff. of var. %	Mean smoke mg	Mean I_s	Coeff. of var. %	Mean smoke mg
Uncoated Substrate	126	11	—	167	7	0.3	83	16	0.2	150	9	2.6
1	44	48	2.5	21	85	3.1	35	115	3.1	29	39	4.1
2	48	37	1.5	75	25	1.7	17	96	1.0	75	21	4.5
3	20	56	1.1	27	6	1.4	7	62	0.7	28	15	5.0
4	34	62	2.6	34	21	2.2	18	71	1.9	37	5	3.6
5	9	55	1.6	14	42	2.6	6	70	1.6	33	7	4.9
6	60	39	2.2	46	60	2.8	15	101	2.5	42	25	5.1
7	8	64	2.1	9	69	2.7	9	103	1.4	40	54	3.2
7a	1.2	86	1.3	2	71	1.8	1.2	151	1.5	1.5	73	1.2
7b	9	183	1.6	7	94	1.5	9	96	1.9	6	54	1.9
8	46	30	1.0	42	76	1.4	13	54	0.9	28	15	3.9

* Defined as the ratio of the standard deviation to the average, expressed as a percentage

ings of 5, 10, 15, and 20 mils, respectively. An assembly of a 10 mil coating of the same paint applied to ⅛-inch thick asbestos-cement board had a flame spread index of 2. Thus it appears evident that the flame spread behavior of coatings applied to either flammable or nonflammable substrates depends not only on the type and thickness of the paint film but also on the characteristics of the substrate.

For a conventional paint, such as flat alkyd (No. 3) applied at an effective spreading rate of 125 ft²/gal, the ratio of the flame spread index of the painted

TABLE 5

MEAN FLAME SPREAD INDEX OF TWO CONVENTIONAL PAINTS AT
VARYING SPREADING RATES APPLIED TO TEMPERED HARDBOARD

Paint	Effective spreading rate ft²/gal	Number of tests	Mean flame spread index	Coeff. of variation per cent	Mean smoke deposit mg
Uncoated Substrate	—	4	116	8	2.1
Alkyl Flat No. 3	900	4	58	13	2.4
	500	4	52	11	2.4
	250	4	24	13	2.7
	125	4	20	4	2.4
	60	4	13	8	2.4
	30	5	27	77	1.7
Latex No. 6	900	4	94	2	2.6
	500	5	30	25	2.0
	250	4	35	9	1.8
	125	4	42	24	2.0
	60	5	37	10	2.7
	30	5	32	91	3.4

ABSTRACTS AND REVIEWS

assembly to that of the substrate was found to be related to the density of the substrate material. The effect at other spreading rates was not explored. As shown in Figure 2, this paint was most effective on the low density fiberboard sub-strate. A majority of the other paints tested were also most effective on the low density substrate. However, for critical evaluation of a paint for fire-retardancy, the burden of effective performance should be placed upon the paint without ascribing to the paint undue advantage resulting from the properties of the sub-strate. For this reason, tempered hardboard is considered a more suitable substrate.
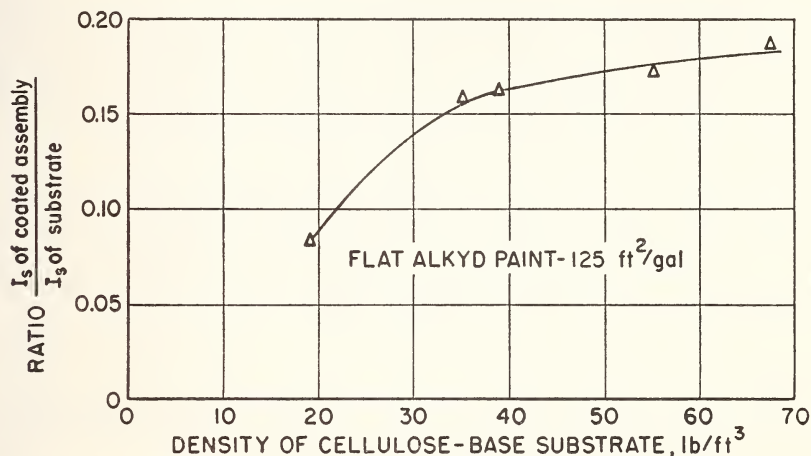
Figure 2. *Effect of substrate density upon flame spread index ratio.*

An analysis of the data was made to provide a statistical measure of variability. Particular attention was directed toward evaluation of the substrate materials both from the standpoint of (a) selection of a standard material for paints and other liquid coatings and (b) interpretation of previous and subsequent flame spread data on coated assemblies employing a variety of substrates.

The analysis showed that although the wallboard and fiberboard substrates gave a more consistent behavior of dispersion about the mean than the plywood and hardboard substrates, the coated hardboard assemblies did exhibit:

a. A substantial range of flame spread index values for the coating materials, and
b. The lowest coefficients of variation.

It should be noted that considerable variation was observed in the rankings of the coatings on the four substrates. In addition, the coefficients of variation were considerably higher than those obtained in an earlier investigation of con-ventional paints on the same or similar substrates.[1] This is not unreasonable when consideration is given to the special types of coatings and rates of application employed here. Inasmuch as the hardboard did result in the lowest coefficient of variation and provided a substantial range of flame spread index values for the coating materials tested, its choice as a standard substrate is indicated.

157

Conclusions

On the basis of the work reported, the following conclusions seem justified:

1. Tempered hardboard may be considered a suitable choice as a standard substrate for evaluating the fire-retardant effectiveness of paints and other thin surface coatings. Of the substrates studied, it gave results with the lowest coefficient of variation, provided a substantial range in flame spread index values for the coating materials tested, and placed the burden of effective performance upon the paint under test.

2. The fire-retardant effectiveness of paints and other coatings is highly dependent upon the effective spreading rate of the paint and on the type and density of the substrate material, as well as on the coating composition and the undercoat-overcoat combination employed. Coatings of latex and flat alkyd paints applied to a tempered hardboard substrate at an effective spreading rate of 250 ft²/gal reduced the flame spread index of the uncoated substrate by factors of 3 and 5, respectively.

3. In general, conventional paints of the flat alkyd and latex emulsion types tested, when applied at the heavy rate common for fire-retardant coatings, appear to have flame spread indices comparable to those of the fire-retardant coatings. However, one intumescent fire-retardant coating showed a flame spread index significantly lower than that of any other tested.

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Uncontrolled Diffusive Burning of Some New Liquid Propellants

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Introduction

The safe use of new liquid fuel-oxidizer combinations for rockets requires evaluation of the hazards that may result from accidental spillage and ignition. One such system is based on hydrazoid and amine type fuels consisting essentially of mixtures of unsymmetrical dimethyl hydrazine (UDMH) and diethylenetriamine (DETA). The mixtures are designated as MAF-1 and MAF-3: MAF-1 is (b.w.) 41 per cent UDMH, 9 per cent CH_3CN,* and 50 per cent DETA; MAF-3 is 20 per cent UDMH and 80 per cent DETA. Materials of this type present special problems in fire fighting. They are water-soluble, possibly toxic, and more likely to be chemically reactive with their environment or fire extinguishing chemicals than common hydrocarbon fuels. Fires of these new fuels may be less readily extinguished by common extinguishing agents. Burning deep pools of blended fuels may boil over, etc. Laboratory-scale techniques for evaluating such hazards and defensive measures are obviously useful. This paper reports techniques (and results) which were developed and which should be extendable to other similar fuel-oxidant systems. These techniques were used to measure burning rates of large pools of fuel, radiation from flames, temperature profiles in flames and liquid beneath, composition of combustion products, and limits, in terms of water dilution, of fire points and of hypergolicity.

Measurement and Discussion—Burning Rates in Large Pools

Single-Component Fuels

The work of Blinov and Khudiakov [1, 5] and our own more extensive work with other single-component fuels [2, 13] show that the burning rate in shallow trays approaches constancy as the tray diameter increases (Figure 1). Burning rates taken with trays a meter or two in diameter can be extrapolated to yield burning rates in very large trays. This extrapolation for single-component fuels and the basis for it are discussed in references 2 and 13. Based on these discussions, the burning rates of single-component liquid fuels in large pools, v_∞, in centimeters per minute, are given by equation 1:

$$v_\infty = 0.0076 \frac{\Delta H_{comb.}}{\Delta H_{vap.} + \int_{T_a}^{T_b} C_p \, dt} \qquad (1)$$

where $\Delta H_{comb.}$ is the net heat of combustion and $\Delta H_{vap.}$ is the heat of vaporization at the boiling point, T_b. The integrated heat capacity in the denominator deter-

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* The boiling point of acetonitrile is near enough to that of UDMH to justify neglect of this minor component of MAF-1 as a separate entity in the considerations that follow.

159

mines the temperature dependence of the burning rate, normally about ½ per cent per degree centigrade variation of the initial liquid temperature, T_a. The dependence of burning rates of such fuels on thermochemical properties is shown by Table 1.[2, 13] Values for UDMH and DETA are included in Figure 1 and Table 1.

TABLE 1

RELATION OF LIQUID BURNING RATES TO
THERMOCHEMICAL PROPERTIES OF FUELS

Fuel	ΔH_c (net)	ΔH_v (sens.)	$0.0076 \dfrac{\Delta H_c}{\Delta H_v}$	$v\infty$, cm/min
	kcal/mol			
Hydrogen	58.2	0.22	2.02	1.4
Butane	623	5.95	.81	.79
Hexane	916	9.77	.72	.73
Benzene	751	9.20	.63	.60
Xylene	1038	14.72	.55	.58
UDMH	432	9.53	.35	.38
DETA	735	26.1	.22	.16
MeOH	150	9.18	.13	.17
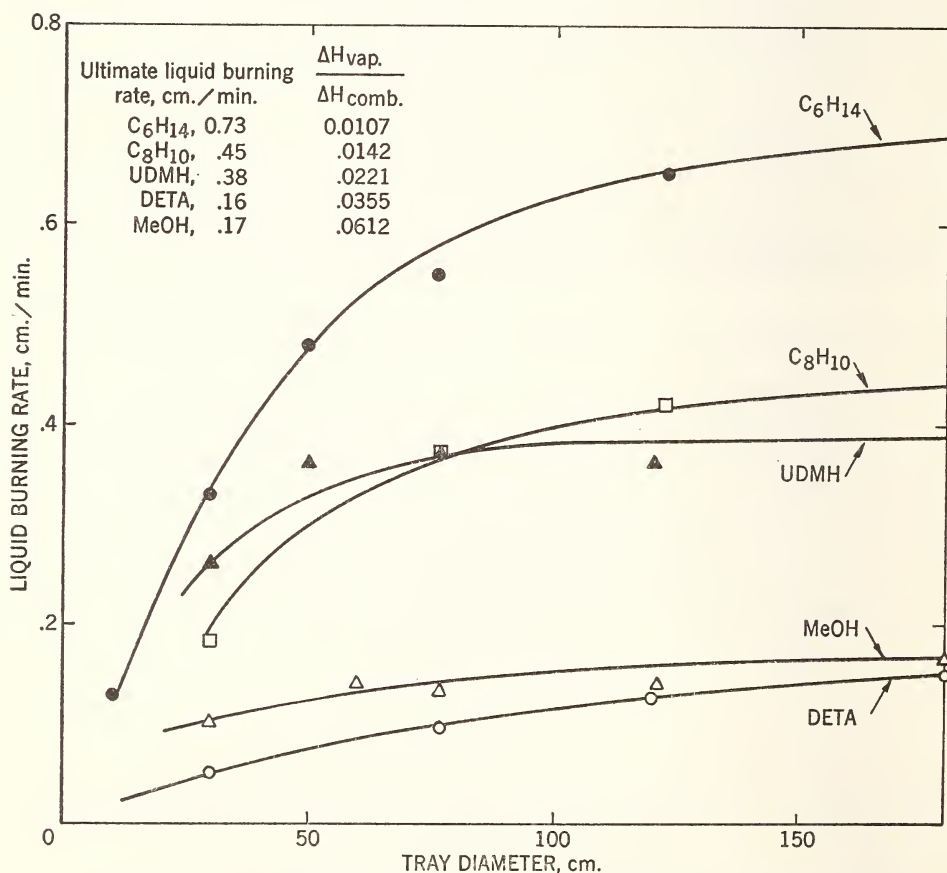
Figure 1. *Variation of liquid burning rate with tray diameter.*

160

ABSTRACTS AND REVIEWS

Blended Fuels

Fires in pools of blended fuels, especially of those whose components differ widely in their volatility, do not burn at a uniform rate. In the beginning, the burning rate is characteristic of the high volatile component. During the middle portion of the burning, the less volatile component still must be brought to the boiling point of the blend. Finally, as the fractionation proceeds, the burning rate becomes characteristic of the higher boiling fraction. The burning rates of a blend are given by:

$$v_\infty = 0.0076 \left[\frac{n_1 \Delta H_{comb._1} + n_2 \Delta H_{comb._2} + \ldots}{n_1 \Delta H_{vap._1} + n_2 \Delta H_{vap._2} + \ldots + m_1 \int_{T_a}^{T_b} C_{p_1} dt + m_2 \int_{T_a}^{T_b} C_{p_2} dt + \ldots} \right] \tag{2}$$

where n_1 and m_1 refer to mole-fraction composition in the vapor and liquid phases, respectively. For such blends as gasoline, whose specific heats of combustion and of vaporization of the components are comparable and $n_1 \approx m_1$, equation 2 leads to a simple mixture rule:

$$v_\infty = n_1 v_1 + n_2 v_2 + \ldots \tag{3}$$

On burning an unleaded gasoline in a 122 cm diameter tray, we found a steady burning rate of 0.54 cm/min. From distillation data furnished by the supplier, the value given by equation 2 should be 0.57–0.60 cm/min. In the absence of distillation data covering compositions of liquid and vapor, equation 3 may be used for rough estimates of v_∞ or v for medium-sized trays. The average burning rate of a 2:1 benzene-xylene blend in a 76 cm diameter tray was given by equation 3, using experimental values for the individual burning rates of benzene and xylene (0.47 cm/min (exp) versus 0.48 cm/min (calc)). Even for blends with components of widely separated boiling points, equation 3 yields rough estimates, except during the first and last stages of the fire. For example, the major components of MAF-1 and MAF-3 differ very widely in their volatility: UDMH boils at 63°C, and DETA, at 207°C. However, for the 76 and 122 cm trays predicted values exceed observed averages for the middle half of the burning time by about 15 per cent for MAF-1 and about 50 per cent for MAF-3.

Figures 2 and 3 confirm our analysis that for blends with appreciable concentrations of components of widely differing volatility the initial burning rate is about that of the most volatile component, and the final burning rate is about that of the least volatile. The radiation records in Figure 3 show that the steady burning rate for DETA was approached at the end of the burning of MAF-1 and MAF-3 in a 122 cm tray.

Flame Radiation and Absorption

Radiation from flames and absorption of radiation by fuel vapor and liquid affect the burning rate, as discussed in references 2 and 13. In addition, consideration of absorption of radiation by the *liquid phase of the fuel* or by water in the gaseous or liquid state is *pertinent to attenuation* of heat radiated to the liquid fuel or to the surroundings. About 24 and 28 per cent of the heat of combustion was radiated to the surroundings by flames of UDMH burning on the 76 and
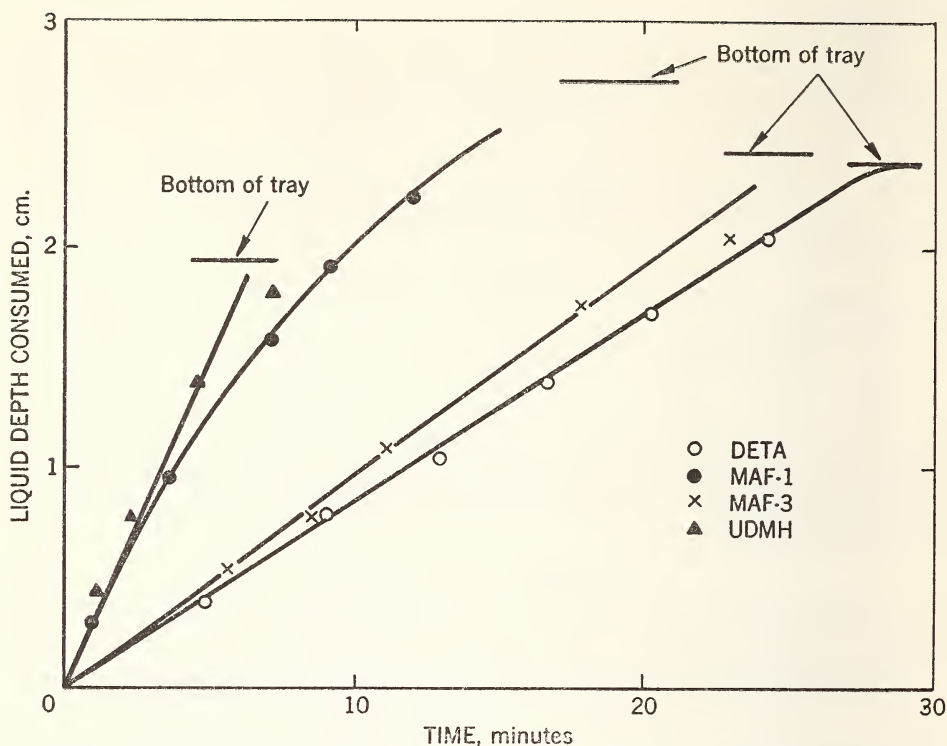
161

Figure 2. Burning time in 76 cm i.d. tray of UDMH, DETA, and the blends MAF-1 and MAF-3.

122 cm diameter trays, respectively (Table 2). Combination of photographic and radiation data gave the magnitudes and variations shown in Table 3 in the specific radiation from such a flame.* The data in Table 2 can be used to compare the radiant flux from large UDMH and hexane flames of the same diameter; that is, ratio of linear burning rates × ratio of liquid densities × ratio of heats of combustion × ratio of percentages radiated =

$$\left(\frac{7.0 \text{ mm/min}}{3.5 \text{ mm/min}}\right)\left(\frac{0.66 \text{ gm/cc}}{0.78 \text{ gm/cc}}\right)\left(\frac{11.5 \text{ kcal/gm}}{7.9 \text{ kcal/gm}}\right)\left(\frac{42\%}{26\%}\right) \approx 4.$$

A four fold reduction in radiation level compared to hydrocarbon flames should be a significant factor in safety considerations.

Furthermore, data in Table 4 and Figure 4 show that UDMH and MAF flames resemble flames of methanol more nearly than those of benzene with regard to self-absorption of radiation from their respective flame. Liquid UDMH and the MAF's are good self-absorbers since a depth of 0.3 cm of liquid absorbs about all the radiation.

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* Cycling of flame size may be due to partial self-smothering which causes the flame to lengthen. This lengthening of flame improves the diffusion and entrainment of air, causing the flame to shorten. Evidence for this explanation of fluctuating flame size comes from studies of smoke limits of flames in ethylene-air mixtures. Limit flames emitted smoke only when the flame was in the tallest stage (3).

162
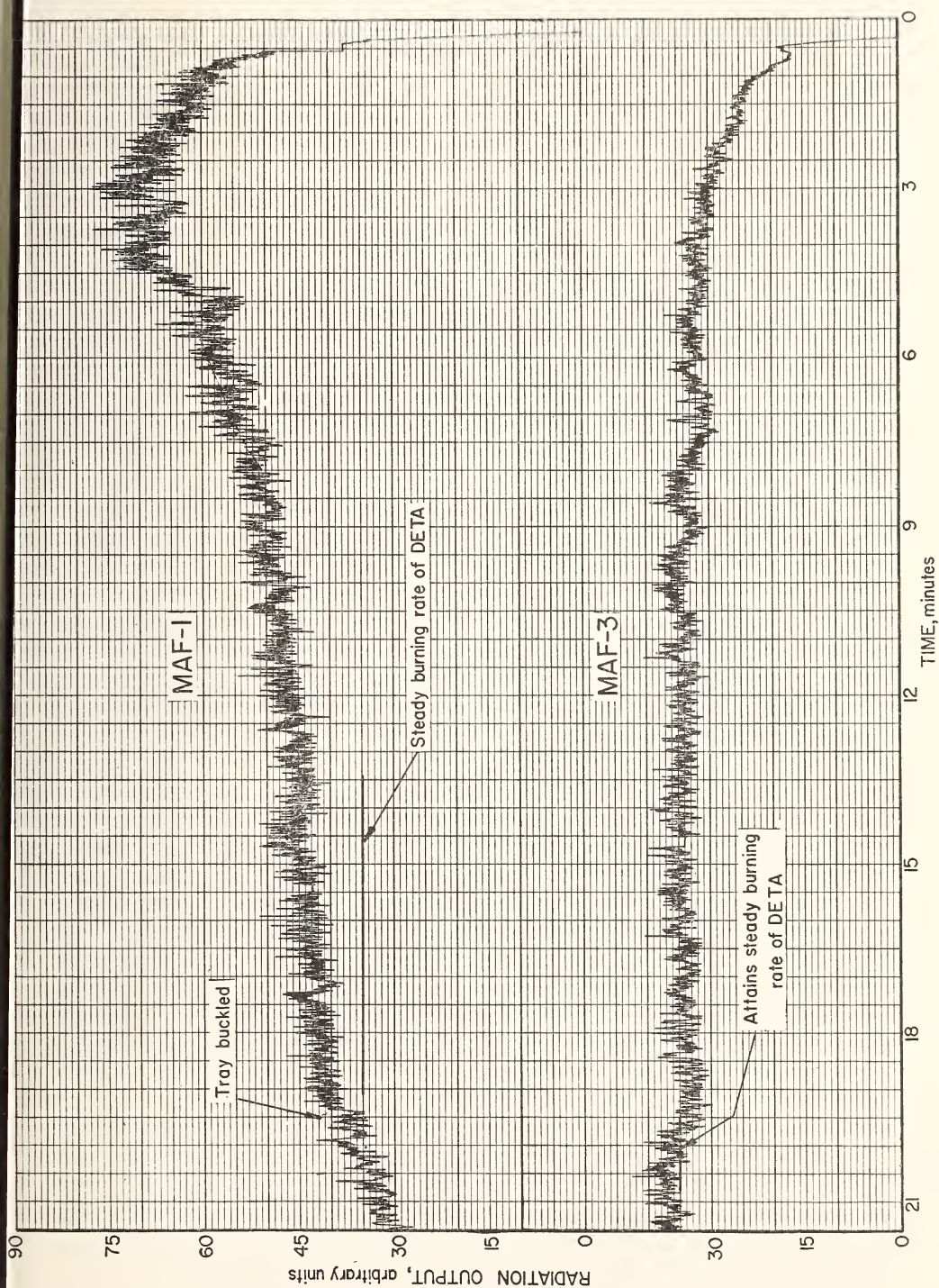
Figure 3. Radiation records of MAF-1 and MAF-3 burning in 122 cm i.d. tray.

163

TABLE 2

RADIATION BY DIFFUSION FLAMES OF LIQUID FUELS

Fuel	Burner diameter, cm	$100 \times \dfrac{\text{Radiation output}}{\text{Thermal output}}$
DETA	76	35
DETA	122	28
MAF-1	76	26
MAF-3	76	42

TABLE 3

SPECIFIC FLAME RADIATION FROM DIFFUSION FLAME OF UDMH.
(POOL DIAMETER 76 CM)

Time, minutes	Specific flame radiation,[1] watts/cm.^{2}
1.0	6.75
1.5	9.15
2.0	9.90
2.5	7.90
3.0	6.50
3.5	8.40
4.0	7.25
4.5	12.9
5.0	9.6
5.5	12.4
6.0	13.2
6.5	6.1

[1] $\dfrac{\text{Radiation output}}{2 \times \text{vertical cross section of flame}}$

TABLE 4

TRANSMISSION OF FLAME RADIATION

Flame of fuel	Cell length, cm	Transmission per cent		
		Through water vapor at 165° C	Fuel vapor at 100° C	Fuel liquid
UDMH	0.3			1
MAF-1				1
MAF-3				0.3
UDMH	8.9	82	57	
MAF-1		89	[1]61	
MAF-3		81	[1]65	
DETA		—	—	
Methanol		87	73	
UDMH	18.4	72	49	
MAF-1		72		
MAF-3		76		
DETA		77		
UDMH	37	70		
MAF1		69		
MAF-3		70		
DETA		69		

[1] Predominant vapor was UDMH.

164
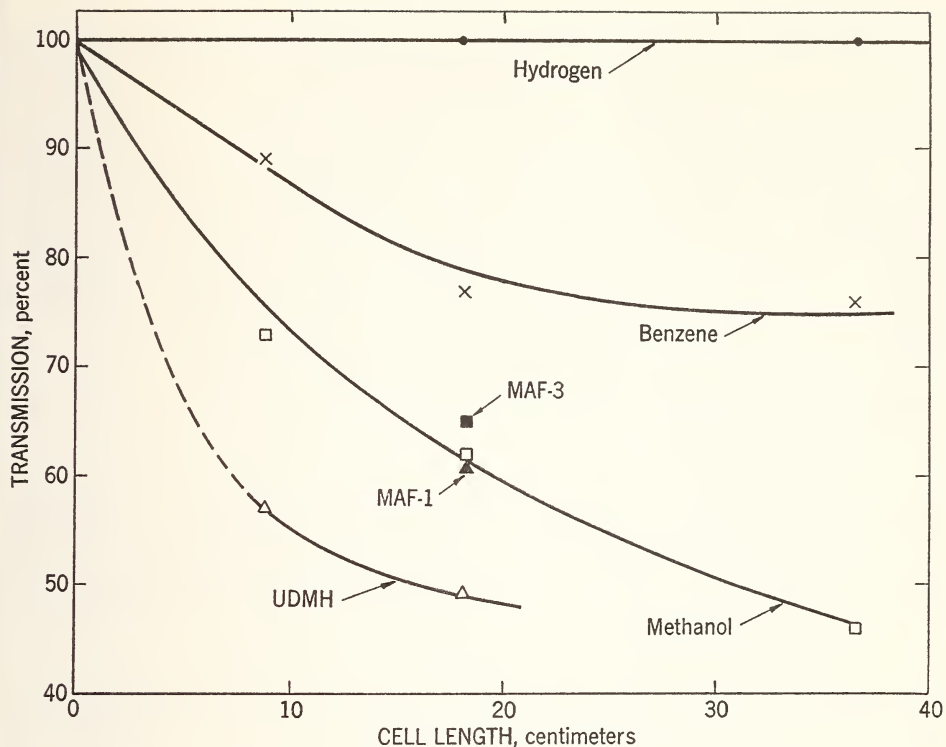
Figure 4. Transmission of flame radiation through cells filled with vapor of burning fuel.

An additional factor to be considered is the absorption of flame radiation by atmospheric water vapor. When a flame is only weakly luminous, its emission spectrum may differ from that of a black-body, a large proportion of the energy being emitted within the emission bands of water and carbon dioxide. This energy is susceptible to absorption by atmospheric water and carbon dioxide, and in the case of hydrogen fires or methanol fires, atmospheric absorption is a factor to be considered. In the case of UDMH and MAF fires (Table 4), absorption of radiation by water vapor roughly follows Lambert's law for the two shortest path-lengths of water vapor but not for the whole range up to 37 cm. This means that radiation from UDMH and MAF fires cannot be blanketed by long distances through moist air.

Temperature Profiles in Flames and Liquid; The Boilover Problem

Temperatures observed underneath a small UDMH diffusion flame and at its surface are given in Table 5. A flame burning on a 50 mm diameter Petri dish and standing about 23 cm high was probed with a ceramic coated (NBS ceramic A-418) platinum platinum 10 per cent rhodium unshielded 10 mil thermocouple. It is apparent that high temperatures (about 600°C) are obtained in the unburned gas about a centimeter or so above the liquid (liquid level was about a centimeter below the rim of the dish). Maximum temperatures at the flame front are about

165

TABLE 5

TEMPERATURES IN A DIFFUSION FLAME OF UNSYMMETRICAL
DIMETHYL HYDRAZINE IN AIR

Tray diameter 50 mm., flame height about 230 mm

Height above dish, mm	Distance from axis, mm					
	0	5	10	15	20	25
	Temperatures, °C					
0	600	600	600	650	730	[1]1080
5	600	620	640	700	[1]1120	480
10	660	700	750	[1]1120	1040	
15	820	840	930	[1]1120	810	
25	770	670	680	[1]1000	950	
50		1040	[1]1080	1050	1060	

[1] Approximate position of flame edge.

1100°C. Similar temperatures have been observed in diffusion flames of hydro-
carbons [10-12] and of alcohol, benzol, petrol, and kerosene.[8] Calculations of adiabatic
flame temperatures for premixed flames are given in Table 6 for comparison with
values observed in the diffusion flame. The temperatures observed in the gas
phase beneath the diffusion flame of UDMH are consistent with the radiation
measurements showing self-absorption of flame radiation. The radiation absorp-
tion measurements also showed that the liquid absorbed strongly; thus, a steep
temperature gradient is to be expected at the liquid surface of burning UDMH.
Such steep gradients were observed at the liquid surfaces of fires of UDMH and
DETA. Conceivably, such hot layers at the surface of a burning deep pool of
MAF-1 or MAF-3 may cause violent bumping and splashing of burning fuel.
Violent expulsion of fuel (called boilover) may occur with oil tank fires, owing
generally to an immiscible layer of water below the oil which is suddenly converted
into steam.[4, 9]

TABLE 6

ADIABATIC FLAME TEMPERATURES OF DIETHYLENETRIAMINE AND AIR
MIXTURES AND OF UNSYMMETRICAL DIMETHYL HYDRAZINE AND
AIR MIXTURES AT ONE ATMOSPHERE INITIAL PRESSURE[1]

DETA,[2] per cent	UDMH,[2] per cent	Flame temperature, °K (Calc)
3.0		2387
4.0		2288
5.0		2058
6.0		1766
7.0		1482
8.0		1276
9.0		1220
	11.5	1314
	17.5	1177
	31.6	974

[1] Calculations by E. B. Cook of this Laboratory
[2] Initial temperatures of gaseous mixture: DETA = 423° K, UDMH = 330° K.

166

ABSTRACTS AND REVIEWS

Somewhat different circumstances than with oil fires may lead to boilovers ·
with the MAF's—a mechanism involving instabilities of convection currents in
the liquid. Consider that at room temperature the density difference between high
and low boiling components is more extreme in UDMH-DETA blends than in
most hydrocarbon blends, and that the viscosities of DETA and of UDMH-DETA
blends are quite comparable to the viscosities of higher hydrocarbons. A hot,
metastable layer may therefore form at the surface of a deep, burning pool of
MAF and suddenly fall to the bottom, boiling out UDMH from cold bottom
layers. For this to occur, a considerable mass of metastable hot liquid must gather
at the surface. Otherwise such a layer would not contain much heat, and as it
fell it would only accelerate the heat front downward; it could not produce a boil-
over. However, if the gravitational forces downward were almost counterbalanced
by the viscous forces holding the layer in place, a large mass might accumulate at
the surface. Secondly, boilover is possible only if the density of the hot liquid at
the top is greater than the density of the initial liquid. Thirdly, the likelihood of
boilover increases if the viscosity of the hot liquid is equal to or greater than that
of the initial liquid. If the hot layer falls and the viscosity of the hot liquid is
less than the viscosity of the initial liquid, viscous shear will tend to disperse the
hot liquid and prevent the sudden transport of such heat to the bottom layer. The
data in Table 7(A) indicate that there is no danger of boilover due to accumula-
tion of boiling DETA at the surface. Table 7(B) indicates that boilover is possible

TABLE 7

(A) COMPARISON OF DENSITIES AND VISCOSITIES OF MAF–1 AND MAF–3
AT 25°C WITH THOSE OF DETA AT ITS BOILING POINT

(B) COMPARISON OF TEMPERATURES OF DETA AT WHICH ITS DENSITY OR
VISCOSITY EQUALS THAT OF MAF–1 OR MAF–3 AT 25°C

(C) COMPARISON OF TEMPERATURES OF DETA AT WHICH ITS DENSITY OR
VISCOSITY EQUALS THAT OF MAF–1 OR MAF–3 AT 60°C

| | A | | B | | C | |
| | Density, ρ gm/cm³ | Viscosity, η, centipoise | Temperatures, °C | | Temperatures, °C | |
Fuel			ρ	η	ρ	η
MAF–1	0.869	1.22	120	80	158	138
MAF–3	.916	3.5	60	40	98	> 100
DETA	.785	.43				

as long as the surface layers atop cold MAF-1 are colder than above 120°C and
those atop cold MAF-3 are colder than about 60°C. In Table 7(C), a comparison
is based on 60°C, the approximate temperature at which MAF-1 and MAF-3
start to distill. Hot surface layers of DETA up to about 160°C appear to be
metastable compared to MAF-1 at 60°C, and correspondingly up to about 100°C
for MAF-3. The temperature difference for MAF-1 (158°–60°) is about twice
that for MAF-3, about the same as for the comparison in Table 7(B). It appears,
therefore, that if metastable layers form atop MAF-1 or MAF-3, the heating po-
tential in the MAF-1 case is more than double that in the MAF-3 instance. On
the basis of these analyses, a boilover with MAF-3 is far less likely than with
MAF-1.

167
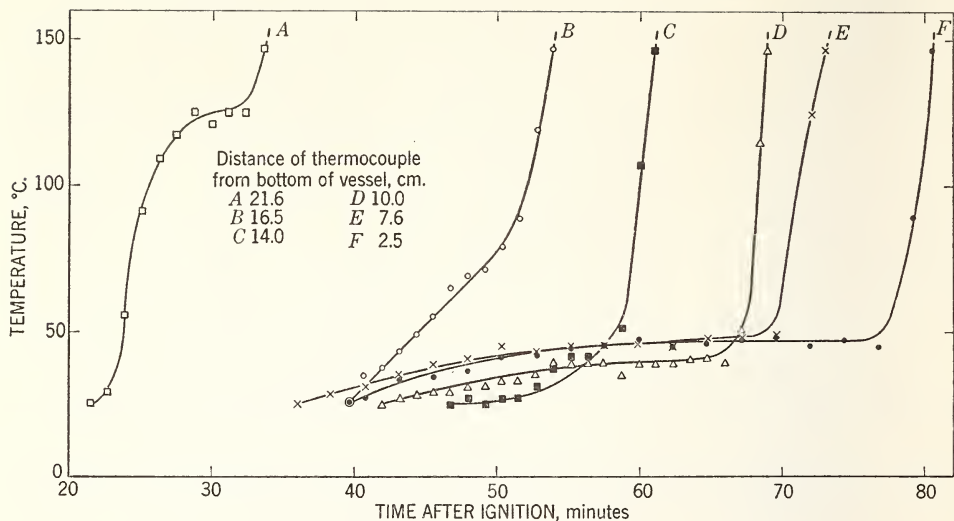
Figure 5. Temperature profiles near liquid surface of MAF-1, burning in 47 cm i.d. vessel.
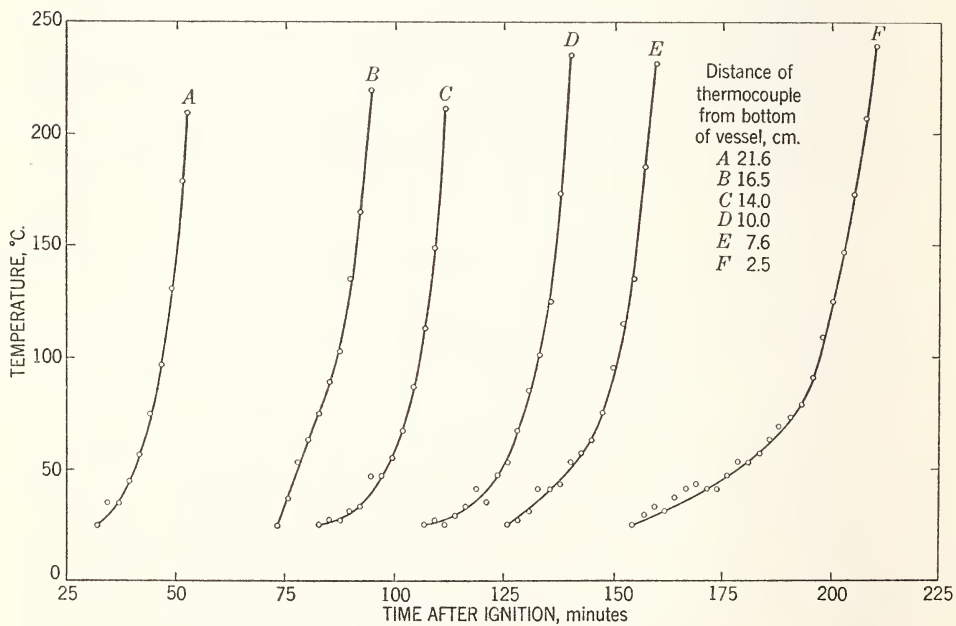
Figure 6. Temperature profiles near liquid surface of MAF-3, burning in 47 cm i.d. vessel.

168

ABSTRACTS AND REVIEWS

Experiments were performed with MAF-1 and MAF-3 in which 38 kg of MAF-1 and 47 kg of MAF-3 were burned in an instrumented drum measuring 30 cm in depth and 47 cm inside diameter. Temperature profiles as a function of time are given in Figures 5 and 6. The history of selected isotherms is given in Figures 7 and 8. The temperature profiles were observed by means of thermocouples in the liquid (at about 0.6 radius from the wall). Temperature-sensitive paints on the sides of the container were also used. In general, thermocouples and paint showed about the same rate of heat travel. Figures 5 and 6 show that a temperature inversion at the bottom of the tank occurred with MAF-1 but not with MAF-3. Figure 7 shows that the heat front moving downward through
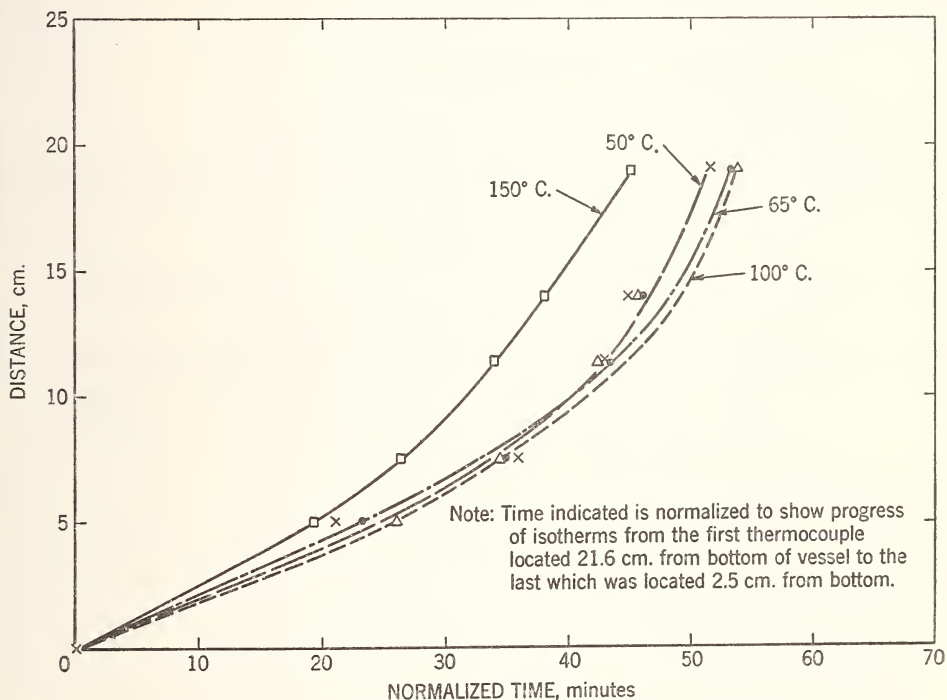
Figure 7. *Progress of isotherms through burning MAF-1.*

MAF-1 accelerated during burning from about 0.2 cm/min to about 0.8 cm/min. Figure 8 shows that the heat front moved steadily downward in MAF-3 at about 0.14 cm/min. The acceleration of the travel of heat front through MAF-1 started after about 1 hour of burning. After 1½ hours of burning, the temperature paints showed that the bottom of the container was at least at 65°C. About the time this heat front reached the bottom of the tank, a vigorous foaming suddenly started and continued for approximately 10 minutes. No appreciable head of foam was apparent, nor was there any bumping of the liquid. Thereafter, as it did before, the liquid bubbled smoothly and quietly over its entire surface until burnout. As soon as the foaming stopped, a sample of fluid was withdrawn through a tap 5 cm from the bottom and about 10 cm from the top of the liquid. The specific

169

gravity of this sample was 0.94 at 27°C, about equal to that of DETA. Therefore, following the foaming all of the UDMH was gone from the MAF-1. Temperatures were fairly uniform throughout the liquid (about 165° to 175°C). About 5 minutes before the foaming started, temperatures were above 140°C, except for the bottom 8 cm of liquid, which was around 65° to 70°C. Within these 5 minutes, temperatures in the bottom 8 cm rose above 140°. These temperatures are in fairly good agreement with temperatures listed in Table 7 for MAF-1. MAF-3 burned smoothly. The only novel observation was the appearance after two hours of burning of very fragile brown clots. Although the observed foaming did not raise or throw liquid, its occurrence and the data in Figures 5 and 7, and Table 7 indicate that boilovers or perhaps only foaming are possible with MAF-1. The weight of experimental and theoretical evidence indicates that boilovers are unlikely with MAF-3.

Composition of Combustion Products

As shown in Tables 8 and 9, samples drawn from UDMH diffusion and premixed flames contain hydrogen cyanide, methyl cyanide, and carbon monoxide.

TABLE 8

MASS SPECTROMETRIC ANALYSES OF COMBUSTION PRODUCTS
OF UDMH DIFFUSION FLAMES

| | Diffusion flames over tray | | | | | |
| | 5.1 × 25.4 × 1.4 cm | | | | 76 cm | |
	(1)	(2)	(3)	(4)	(5)	(6)
Sampling point cm above flames	0	0	0	5	0	5
Analysis, per cent						
Carbon dioxide	4.3	2.9	4.0		3.2	0.3
Carbon monoxide	3.1	2.3	3.2		1.6	0
Methane	4.0	1.3	2.4			
Formaldehyde or ethane[1]	.3	.1	.1		[2]1.6	0
Ethylene	1.8	1.2	1.2			
Acetylene	.3	.1	.3			
Methyl cyanide	.2	.1	.1	0		0
Hydrogen cyanide[3]	1.5	1.1	1.8	0	.7	0
Water	1.6	1.2	1.0			
Hydrogen	3.6	1.8	3.0		1.4	0
Nitrogen + argon	75.6	77.2	76.3	Air	80.5	Air
Oxygen	3.7	10.7	6.6		11.0	

[1] Probably ethane, since Schiff's test for aldehydes was negative.
[2] Total of methane, ethane, ethylene, and acetylene.
[3] Presence or absence confirmed by Prussian blue test for cyanides.

A few centimeters past the flame surface of diffusion flames, these toxic gases are absent. DETA produced as much as 1.5 per cent of hydrogen cyanide on combustion. Therefore, fumes from incompletely burned UDMH, DETA, and the MAF fuels may be unusually toxic. Observed flame temperatures in Table 9 are in good agreement with calculated temperatures in Table 6.

ABSTRACTS AND REVIEWS
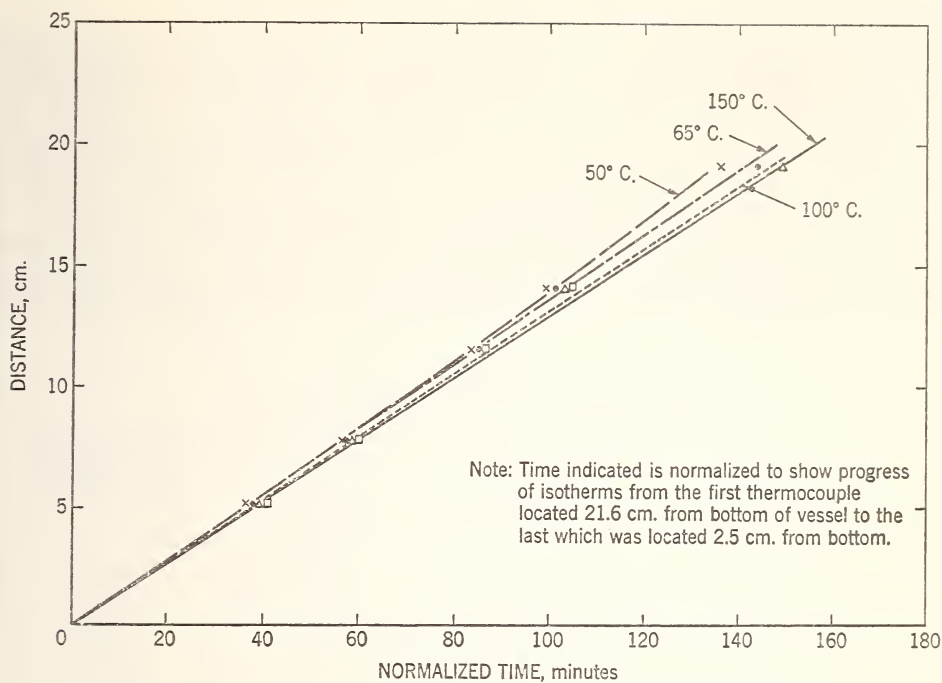
Figure 8. *Progress of isotherms through burning MAF-3.*

TABLE 9

MASS SPECTROMETRIC ANALYSES OF COMBUSTION PRODUCTS
ALONG AXIS OF UDMH-AIR FLAT FLAMES[1]

	UDMH, Per cent				
	11.5	17.5	17.5	17.5	31.6
Distance above blue flame, mm	4	1	2	4	4
Observed flame temperature, °K	> 1340	1240	1250	1270	1030
Analysis, per cent					
Ethylene	2.2	3.4	3.4	3.4	5.5
Hydrogen cyanide	4.4	6.2	4.5	5.6	7.2
Ammonia	.7	1.6	1.5	1.3	4.0
Carbon dioxide	1.8	.2	.5	.7	.1
Oxygen	.2	2.0	1.6	.7	1.3
Nitrogen	63.8	53.2	56.6	55.2	46.2
Methane	1.1	6.3	3.8	3.4	11.6
Carbon monoxide	13.0	11.5	12.6	14.0	8.4
Hydrogen	11.6	14.9	14.8	14.3	14.6
Argon	.8	.7	.7	.7	.6

[1] Data obtained by J. M. Singer of this Laboratory.

171

Fire Points of Aqueous Solutions

Water is the least expensive and generally most available extinguishing agent for fires of MAF fuels. Foam has to be specially prepared and is rapidly disintegrated. Other extinguishing reagents are expensive or soluble or reactive. To evaluate water requirements for fighting fires of the MAF's, measurements were made of the water dilution necessary to render aqueous solutions of UDMH, MAF-1, and MAF-3 nonflammable. About two volumes of water per volume of fuel suffice. (For very deep pools, less water will be required if only the upper portion of the tank's contents must be made nonflammable.) The data are given in Table 10 along with dilutions needed for some alcohols and acetone. The ratios

TABLE 10

FIRE POINTS OF FUEL-WATER SOLUTIONS

Fuel	Temperature, °C	Volume per cent fuel	Heat of vaporization / Heat of combustion
Tray 15 × 76 × 1.6 cm deep			
Methyl alcohol	25	42	
	56	20	0.60
Acetone	25	15	
	60	10	.92
Isopropyl alcohol	25	40	
	66	8	1.09
Tertiary butyl alcohol	25	35	
	64	8	1.01
UDMH	33	50	
	60	34	.22
	63	34	
	[1] Burnout	[1] 28	
MAF–1	34	64	
	60	39.5	[2] .39
	63	38	
MAF–3	25	63	
	60	53	[2] .52
	63	51	
Tray 5.1 × 25.4 × 1.4 cm deep			
Methyl alcohol	25	49	
Acetone	25	21	
Isopropyl alcohol	25	42	

[1] A sufficiently concentrated solution was ignited and permitted to burn to self-extinction. Residual fuel concentration was determined by measurement of specific gravity.

[2] Assumed DETA in aqueous solution did not vaporize or burn.

in the last column of Table 10 of heat of vaporization to heat of combustion indicate that the water requirements can be simply estimated, without recourse to measurement. At worst, the estimates provided a five fold safety factor; for three of the seven tests they provided good agreement with experiment. The estimate is based on assumptions that an aqueous solution of a fuel will not burn when the heat of combustion of the solution equals the heat of vaporization at the boiling point of the liquid, that all of the heat of combustion is transferred to the liquid, and that the compositions of vapor and liquid phases are identical. Errors due to

172

the last two assumptions tend to neutralize each other with regard to the prediction of water concentration at the fire point. It is obviously difficult to compute the heat transfer from flame to liquid. It is also questionable whether vapor phase composition can be computed accurately enough using the liquid composition. Figure 9 shows that equilibrium between compositions of the liquid and the vapor
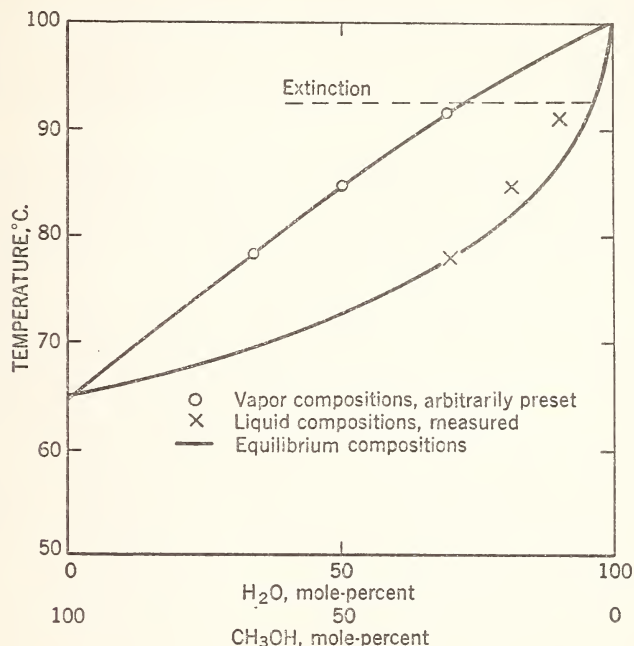
Figure 9. *Fractionation of methanol-water burning in 30 cm i.d. tray.*

burning above it may not be assumed near the fire point. Equilibrium curves were taken from the literature.[6] Experimental points were obtained by adding an arbitrary mixture of methanol-water, e.g., 1:1 on a molar basis to a burning methanol pool. The rate of addition was such as to maintain a constant weight of liquid. Eventually the composition of the liquid, as determined by specific gravity measurements, became constant. (There were no significant concentration gradients in the body of the liquid.) At this stage the composition of the mixture being distilled owing to the flame was identical to that of the mixture being added.

Hypergolicity of Aqueous Solutions

Since the MAF fuels would typically be used with such oxidants as inhibited red fuming nitric acid (IRFNA), there are special problems of preventing hypergolic ignition on simultaneous spillage of fuel and oxidant. It was observed that when the vapors above UDMH and above RFNA were permitted to interdiffuse in a particular closed apparatus at 28°C, there was no ignition. When the temperature was raised to 38°C, ignition occurred. Vapors above either MAF-1 or MAF-3 ignited spontaneously with vapors from RFNA at 45°C but not at 38°C.

173

Impinging jets of the vapors at 60°–100°C in open air led to ignition despite pre-cautions to eliminate liquid spray. Thus, there is a need for new data on flamma-bility limits and spontaneous ignition temperatures with air and inert gases as ignition-preventing diluents.[7]

With regard to liquid phase interactions, it was observed in preliminary spot-plate tests that ignition could be prevented by prediluting the RFNA or the fuel (UDMH, MAF-1, or MAF-3) with 40 volume per cent water and that DETA-RFNA were not hypergolic. These results were duplicated with 100 cc quantities of propellant in Dewars. To estimate the water dilution required for nonignition in large systems with no heat loss, the following conventional concept of hyper-golicity was invoked:

   1) There are fast neutralization reactions, independent of the degree of dilution, yielding about 10–20 per cent of the over-all heat of combustion.
   2) The temperature of the system is thus raised sufficiently to permit slower reactions, such as oxidation or nitration, to lead on to ignition.

Accepting the neutralization step as inevitable, one must dilute sufficiently with water so that the system never exceeds a critical temperature for initiation of second-stage reactions. Figure 10 shows the temperature rises obtained on adding water-diluted RFNA (50–50) incrementally to 200 cc of water-diluted UDMH in a Dewar, the diluted reactants having been precooled in each case to 25°C. Curves A, B, C, and D refer to 10-, 20-, 40-, and 100-per cent initial concentrations of UDMH and the dashed lines depict temperature rises from a hypothetical neutralization yielding 12 kcal/mole. In curves A and B the initial points are below predicted temperatures, and heat evolution has virtually ceased when acid and UDMH are equimolar. However, in curve C, involving 50 per cent acid and 40 per cent UDMH, there is evidence of some additional reaction at the start and of heat evolution extending beyond the equimolar point. At about this dilu-tion of reactants, and depending critically upon apparatus parameters, ignition was found to occur in the gas phase.

As best one can judge from the figure, the highest reaction temperature for safety in any conceivable environment would be about 50°C. From this, if the reactants are initially at 25°C, the minimum dilution should be about 8 grams of water per gram of UDMH-RFNA propellant. There is evidence that less water would be needed with the MAF fuels. For example, 100 cc of (60–40) water-(MAF-1 or MAF-3) were mixed with 100 cc (60–40) water-RFNA with a heat release that was judged to be 15 cal/mole; 100 cc of (50–50) water-MAF-3 were added to 100 cc of RFNA, giving a heat release of 18 kcal/mole. In each case there was no ignition or evidence of delayed reaction.

Conclusions

The MAF fuels are similar in their gross burning characteristics to more con-ventional fuels. The hazards due to accidental fires of these materials appear to be manageable. As with hydrocarbons, radiative heat transfer is the dominant fac-tor in the burning of large diameter pools. Burning rates are expressible as func-tions of the rates of the component fuels and are of the order of those of conven-tional fuels. Temperature profiles indicate that boilover during fires of deep pools is unlikely. About two volumes of water per volume of fuel yield a nonflammable

ABSTRACTS AND REVIEWS
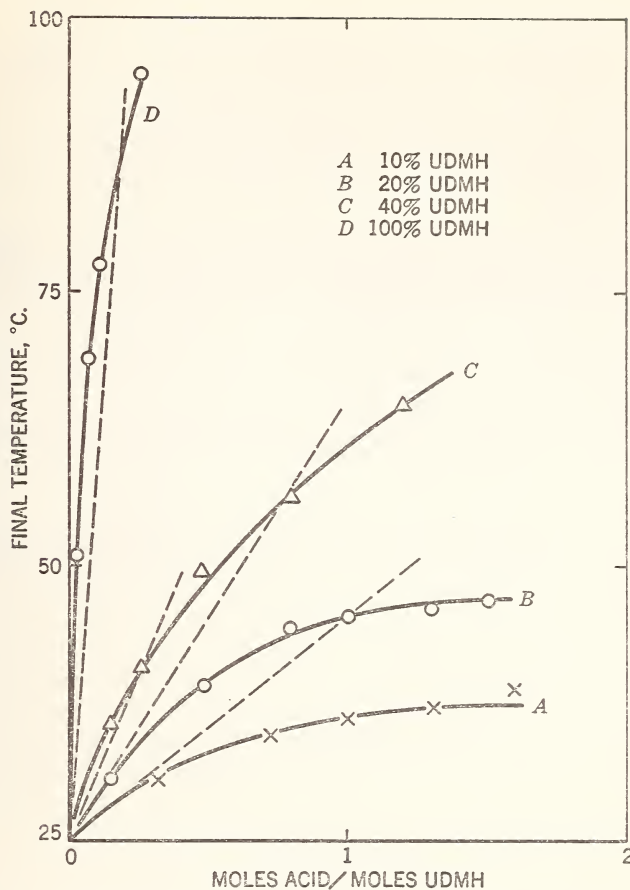
Figure 10. *Temperature rise on addition of water-RFNA (50-50) to 200 cc water-UDMH.*

solution. The products of incomplete combustion of the amines contain cyanides, a factor to be considered in fire fighting. Hypergolicity between the MAF fuels and red fuming nitric acid can be prevented by adding about two volumes of water before mixing. The concepts used in this study should be applicable to other fuel-oxidant systems.

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175

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176

Diffusive Burning of Liquid Fuels in Open Trays

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Introduction

An assessment of the hazards of a liquid fuel requires an estimate of its liquid burning rate (i.e., linear regression rate of the liquid surface) during spill fires in open air. The best known work on this subject is that of Blinov and Khudiakov,[1] who reported on flames of several hydrocarbon blends contained in shallow trays. Their findings, as reviewed and interpreted by Hottel,[3] suggest that the burning rate above large pools is determined by the rate of radiative feedback from the flame to the pool of liquid. The important implication of this rate-controlling process is that burning rate should increase asymptotically to a maximum value at a very large pool diameter; this maximum rate should not be much greater than with pools of moderate dimension, i.e., 1–2 meter diameter.

Some support was given to the picture advanced by Blinov and Khudiakov and by Hottel in an earlier paper from this Laboratory.[2] The present paper gives additional corroborative evidence based on data for methanol, liquefied natural gas, liquid hydrogen, and two amine fuels, as well as for four typical hydrocarbons. The paper also describes the effects of fuel temperature and of wind on burning rate, discusses the special problem of cryogenic fuels, and suggests that burning rate may be predicted with some confidence from the heats of vaporization and combustion of the fuel.

Experimental

Materials

The liquid hydrogen was preconverted parahydrogen, supplied by the U. S. Air Force. Unsymmetrical dimethyl hydrazine (UDMH) used was specification-grade "Dimazine" supplied by the Chlor-Alkali Division of Food Machinery and Chemical Corporation; and diethylenetriamine (DETA) was obtained as a technical-grade product from the Carbide and Carbon Chemicals Company. Liquefied natural gas (LNG) was prepared by total condensation of the local pipeline product, boiling at $-150°C$ (cf. methane, b.p. $-161.5°C$). Reagent-grade hexane and xylene, purified absolute methanol, and technical-grade benzene were used as received from the Fisher Scientific Company, and c.p. butane was obtained from the Matheson Company, Inc.

Procedures

Our burning rate tests followed generally the experimental conditions of Blinov and Khudiakov.[1,3] The noncryogenic fuels were burned in trays of 7–240 cm diameter and about 8 cm depth, particular attention being given to flush filling of the trays at the smallest diameters. Liquid hydrogen was burned

177

in stainless-steel Dewars of 7–33 cm diameter and LNG in insulated trays or within a diked area which had been precooled with liquid nitrogen. Almost all tests were conducted outdoors in winds of less than 1 f.p.s. average velocity.

Radiation from the flames was measured with one or more Eppley thermopiles (CaF_2 windows) spaced around the flames in a horizontal plane and far enough from the flames for the inverse square law to apply. Two typical records appear in Figure 1. The radiant power of a flame was calculated on the assumption that radiation is emitted with spherical symmetry from the center of the fuel tray. The total thermal power was computed on the assumption that combustion is complete, neglecting soot formation, with CO_2, N_2, and H_2O vapor as products.

Burning rates were calculated by assuming that the instantaneous radiation level is proportional to the burning rate at the same point in time and that the area under the radiation record is proportional to the total volume of fuel consumed. Alternative methods were used for specific purposes: (1) The liquid surface level was monitored with a thermocouple and burning rate was computed from the additional rate of fuel required to maintain the level constant. (2) Measured volumes of water-insoluble fuels were poured onto water and burned completely; several depths of fuel, for example, 1, 2, and 5 cm, were burned to comprise each burning rate determination. (3) Small trays, up to 38 cm diameter, were supported on a balance so that fuel consumption could be established intermittently by weight loss. Owing to a difference in convection currents, burning rates in a small elevated tray were generally higher than those obtained with a tray on a broad flat surface.

Results and Observations

Burning Rate as a Function of Time

Typical behavior on ignition is for the burning rate to accelerate through a short "burning-in" period. In the case of benzene, the burning rate was found to reach its steady value at about the time when bubbles appeared on the liquid surface. This induction period was observed at all tray diameters and is illustrated in Figure 2; methanol, UDMH, and the cryogenic fuels H_2 and LNG were exceptions with no induction period.

Methanol and benzene flames at the same pool diameter (7.5 cm) and the same initial vapor pressure (40 mm Hg) were snuffed out after short intervals of burning as shown in Table 1; heat required for fuel vaporization, column 3, was estimated from the weight loss during burning; heat retained in the liquid, column 4, was estimated from the average temperature rise; total heat transfer from flame to liquid, column 5, is almost independent of time and by chance circumstances of the tray diameter, almost equal for the two fuels. The induction period for benzene occurs during the first 2 minutes, while much of the transferred heat is being stored in the liquid phase. Burning rate is constant after the "burn-in."

Burning Rate as Function of Fuel Temperature

Several fuels were burned in small brine-jacketed trays for an estimate of the temperature coefficient of burning rate. Results with ethyl ether, absolute methanol, and 95 per cent ethanol are given in Figure 3. The correlating lines

178

ABSTRACTS AND REVIEWS
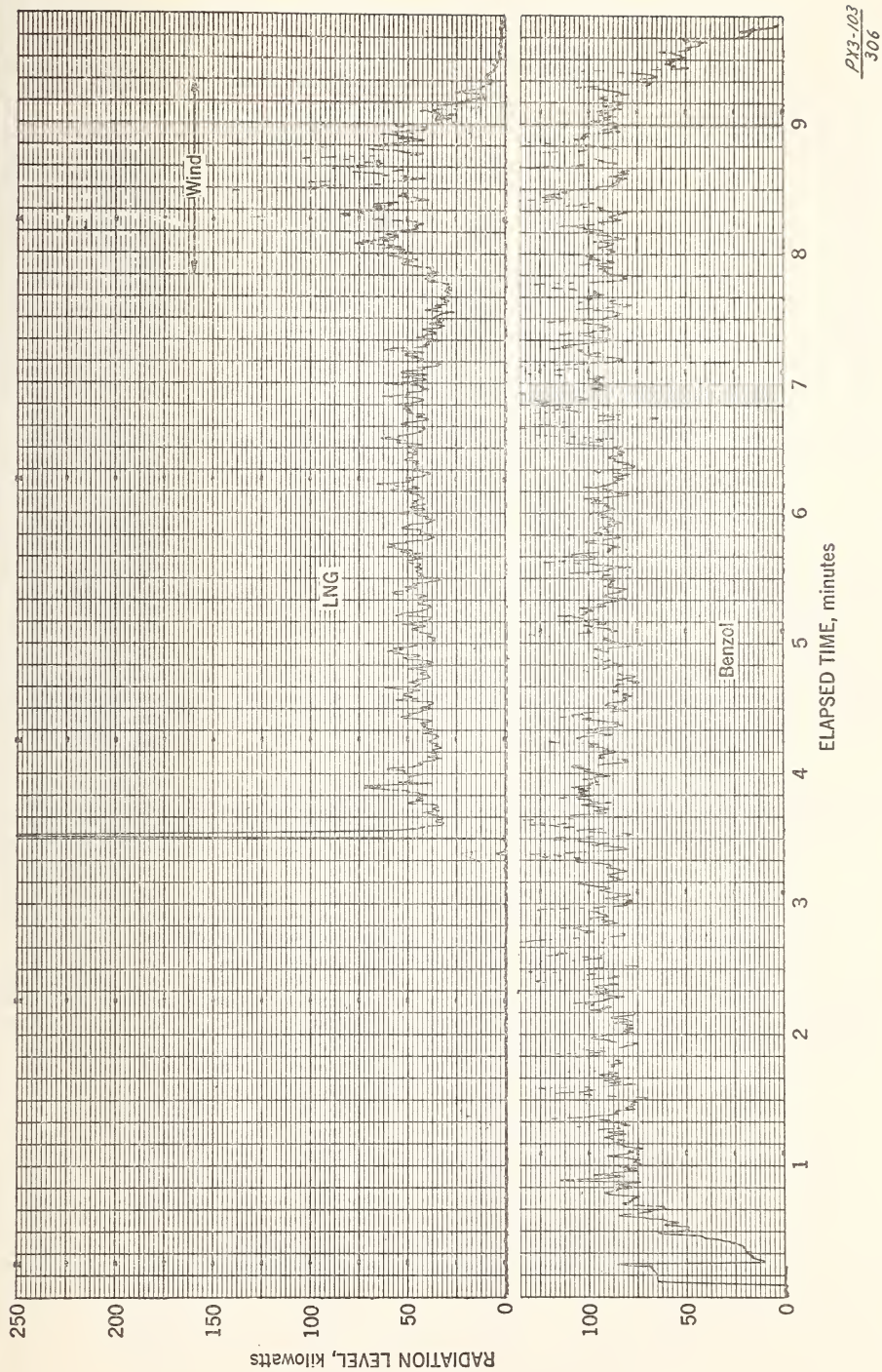
Figure 1. Radiation records on burning about 1 gallon (3640 cc) of LNG and of benzol in 15-inch-diameter tray. LNG poured into warm tray at point A.

179
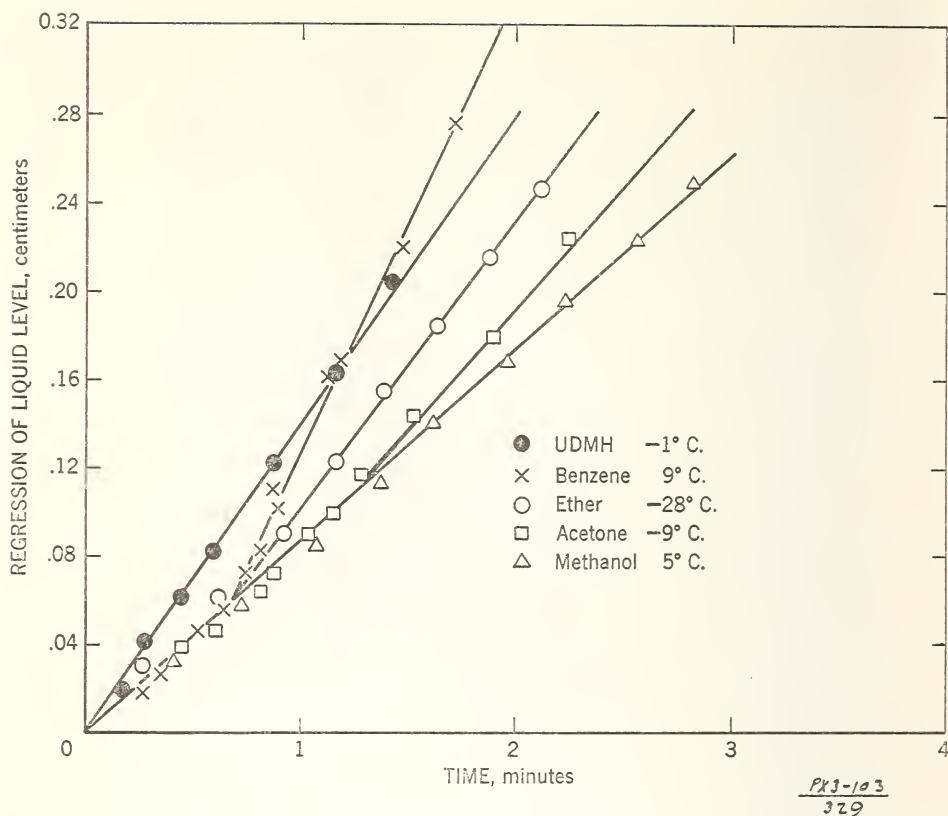
Figure 2. Burning rates of five liquid fuels in 3-inch pyrex vessel (3.5-inch for UDMH). Vapor pressure 40 mm hg at initial liquid temperature.

TABLE 1

HEAT TRANSFERRED TO LIQUID PHASE DURING SHORT
PERIODS OF BURNING

Minutes burned	Grams burned	ΔH_v, cal	ΔH_ℓ, cal	ΔH_t, cal
		Methanol, 5° C, initial		
1	3.8	1,100	250	1,400
2	7.5	2,300	500	2,800
3	11.3	3,400	700	4,100
4	15.0	4,500	900	5,400
5	18.0	5,400	1,050	6,500
		Benzene, 9° C, initial		
1	4.0	500	750	1,300
2	11	1,400	1,250	2,700
3	21	2,600	1,550	4,200
4	31	3,800	1,700	5,500
5	41	5,000	1,800	6,800

180

ABSTRACTS AND REVIEWS

TABLE 2

SUMMARY OF COMPUTED VALUES BEARING ON RADIATIVE HAZARDS OF FIRES

Fuel	κ, cm^{-1}	v_∞, cm/min	Thermal output per unit liquid surface, kcal/cm^2 min	
			Total	Radiated
Hexane	0.019	0.73	5.1	2.0
Butane	.027	.79	5.1	1.4
Benzene	.026	.60	5.1	1.8
Xylene	.012	.58	5.0	—
Methanol	.046	.17	.64	.11
UDMH	.025	.38	2.2	.60
Hydrogen	(0.07)	(1.4)	(2.8)	(0.7)
LNG	.030	.66	3.2	.74

conform closely to our expectation that burning rate should vary inversely with the fuel's sensible heat of vaporization.

Burning Rate as Function of Pool Diameter and Wind Velocity

Steady burning rates in the near absence of wind at various diameters of fuel tray are plotted in Figure 4. The curves represent the empirical expression

$$v = v_\infty (1 - e^{-\kappa d}) \tag{1}$$

wherein v is the linear burning rate and d the tray diameter. Two points for each fuel (solid circles) were used to evaluate the constants κ and v_∞, which are listed in Table 2. Figure 5 presents data specifically for benzene, the points near

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320
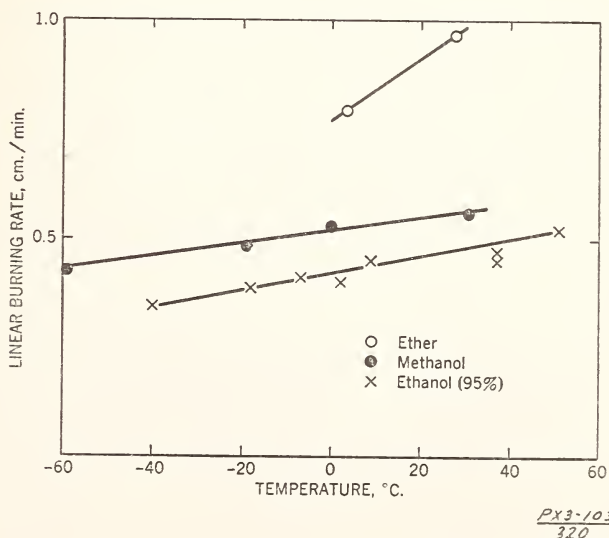
Figure 3. *Effect of fuel temperature on steady burning rates in 7.5-cm diameter brine-jacketed burner.*

181
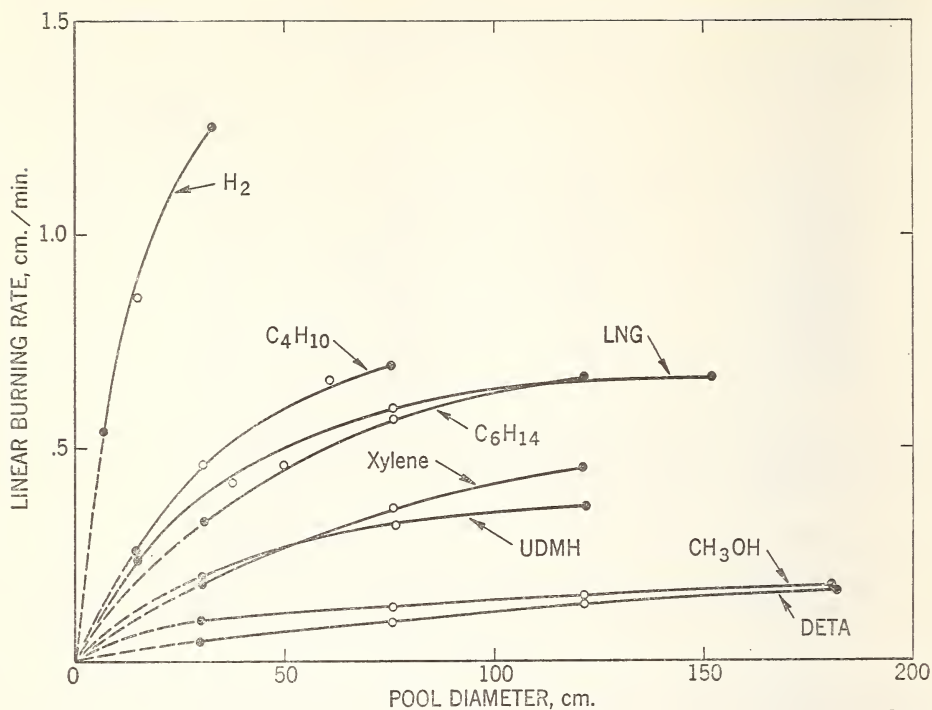
Figure 4. *Dependence of liquid burning rate on pool diameter.*
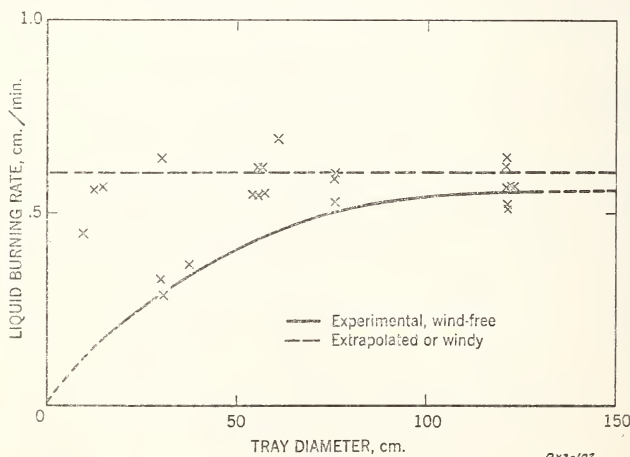
Figure 5. *Effect of wind on burning rate of benzene.*

182

ABSTRACTS AND REVIEWS

the curve resulting from experiments under nearly wind-free conditions. The dashed line represents the extrapolated burning rate, v_∞, and the points near this line were obtained by burning benzene in various natural and artificial winds varying up to 4 meters per second.

Values of v_∞ for the nine fuels studied are given as ordinates in Figure 6.

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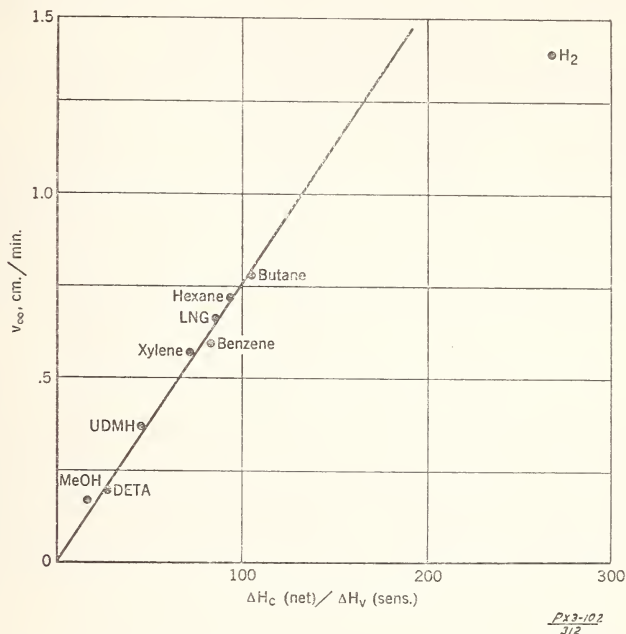
Figure 6. Relation between liquid burning rates at large pool diameter and thermochemical properties of the fuels.

The correlating line has the form

$$v_\infty = 0.0076 \left(\frac{\text{net heat of combustion, } \Delta H_c}{\text{sensible heat of vaporization, } \Delta H_v} \right) \text{cm/min} \qquad (2)$$

No correction was made for incompleteness of combustion, which was particularly evident in the soot-forming benzene flames.

Radiation and Absorption Measurements

The radiative outputs of some gaseous diffusion flames are compared in Table 3 with the total heats of combustion involved. It was demonstrated at several burner diameters that the apparent percentage of heat radiated to the surroundings was independent of the flow rate of fuel supplied. The effect of wind was always to reduce the percentage of heat dissipated radiatively.

Radiative outputs at various diameters of liquid-supported flames are given in Table 4. The percentage of heat radiated in the largest scale test is combined with burning rate values to give the radiant output per unit area of the liquid surface shown in the final column of Table 2. Hazards arising from this radiation

183

TABLE 3

RADIATION BY GASEOUS DIFFUSION FLAMES

Fuel	Burner diameter, cm	$100 \times \dfrac{\text{Radiative output}}{\text{Thermal output}}$
Hydrogen	0.51	9.5
	.91	9.1
	1.9	9.7
	4.1	11.1
	8.4	15.6
	20.3	15.4
	40.6	16.9
Butane	0.51	21.5
	.91	25.3
	1.9	28.6
	4.1	28.5
	8.4	29.1
	20.3	28.0
	40.6	29.9
Methane	0.51	10.3
	.91	11.6
	1.9	16.0
	4.1	16.1
	8.4	14.7
Natural gas (approx. 95% CH_4)	20.3	19.2
	40.6	23.2

TABLE 4

RADIATION BY LIQUID-SUPPORTED DIFFUSION FLAMES

Fuel	Vessel diameter, cm	$100 \times \dfrac{\text{Radiative output}}{\text{Thermal output}}$
Hydrogen	33	25
Butane	30	20
	46	21
	76	27
LNG	38	21
	76	23
Methanol	2.5	12
	5	14
	15	17
	122	17
Benzene	5	38
	46	35
	76	35
	122	36

may be diminished somewhat through absorption of the flame radiations by atmospheric water. Some representative percentages of absorption at various lengths of optical path by water vapor, by fuel vapor, and by the liquid fuel are given in Table 5.

TABLE 5

PERCENTAGE OF ABSORPTION OF FLAME RADIATIONS IN
CELLS WITH CaF$_2$ WINDOWS

	Absorbing medium, path length, temperature		
Fuel	Liquid fuel, 0.3 cm, 30° C	Fuel vapor, 8.9 cm, 100° C	Steam, 8.9 cm, 165° C
Methanol	100	27[1]	13
Hydrogen	—	0	33
UDMH	> 98	43	18
Hexane	71	—	< 6
Benzene	62	11	—

[1] 38 per cent absorbed over 18.4 cm path.

Special Behavior of Cryogenic Fuels

Unconverted liquid hydrogen was poured into a deep Pyrex * Dewar (7.0 cm diameter × 45 cm deep), the bottom 15 cm of which was filled with paraffin at 25°C. The time-dependent vaporization rate is illustrated in Figure 7. The first 20 seconds represent the transfer period during which spattering occurred and the vaporization rate was somewhat uncertain. Thereafter, vaporization seemed to follow a curve given by

$$v \text{ (linear regression rate)} = Kt^{-1/2} \qquad (3)$$

where K has a value consistent with the solution of the one-dimensional, time-dependent, heat-transfer problem,[4] and zero time represents the point at which the paraffin surface was apparently cooled to liquid hydrogen temperature. Similar results were obtained by spilling liquid nitrogen onto warm insulating materials within deep vessels. However, on spillage of the cryogenic liquids N$_2$ and LNG into shallow insulated trays, the time-dependent "tail" corresponding to equation 3 could not be reproduced; as illustrated in Figure 8, the vaporization rate typically decays to a nearly time-independent value which is clearly affected by air currents across the tray.

The result of igniting a cryogenic fuel during the first seconds after spillage is shown in the upper curve (LNG) of Figure 1. Start of spilling is indicated by a pip on the radiation record labeled A. Ignition was accomplished 7 seconds later, and the duration of the radiative flash was no more than 4 seconds. The shape of the radiation record during the first 30 seconds was never found to resemble the vaporization rate curves of Figures 7 and 8. The lower curve of Figure 1 shows the comparable flash on igniting benzene followed by a burning-in period of 30-40 seconds typical of liquid hydrocarbons at room temperature.

The burning rates reported here for liquid hydrogen are less reliable than for the conventional fuels since evaporative losses become very high when one

* Reference to specific commercial products used in this research does not imply endorsement of the products by the Bureau of Mines.

185
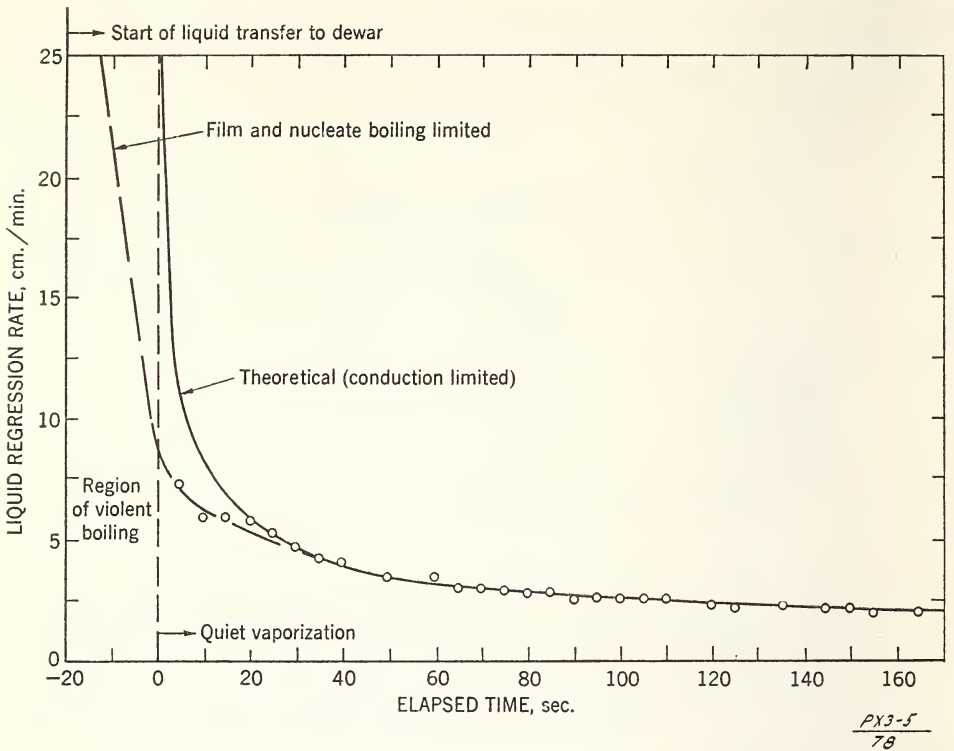
Figure 7. Rate of vaporization of liquid hydrogen from paraffin in a 2.8-inch Dewar. Initial liquid depth 6.7 inches.
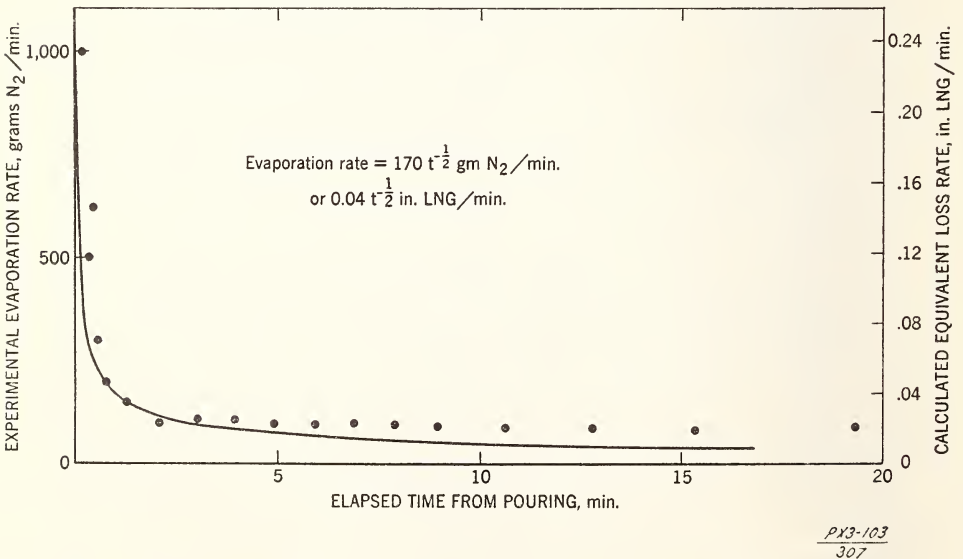
Figure 8. Evaporation of liquid nitrogen after spillage into a warm 15-inch-diameter tray.

186

attempts to flush-fill a container. The liquid was burned in stainless-steel Dewars of three diameters with fuel consumption as shown in Figure 9. Burning rates were obtained from the initial slopes of the curves in Figure 9 corrected for the heat losses of the Dewars. The dashed line of the figure shows this heat loss to be
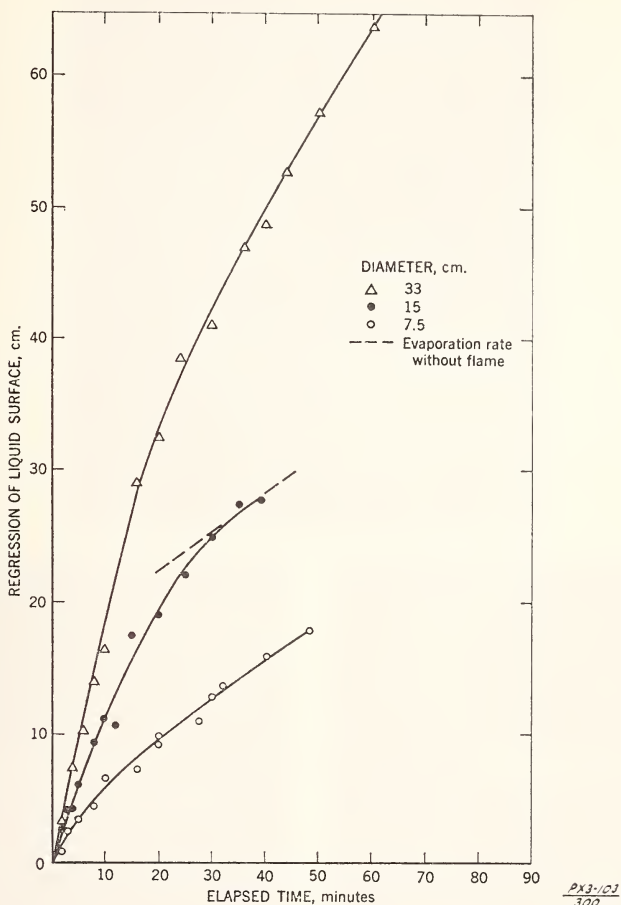
Figure 9. Burning of liquid hydrogen in stainless-steel Dewars of three diameters (reconstructed from flame radiation data, three thermopiles).

about equal to the terminal burning rate as the liquid level approached the bottom of the Dewar. Burning rates in such small-diameter vessels, i.e., 7, 15, and 33 cm diameter, are typically very much affected by such casual crosswinds as occurred during these particular tests.

Other Observations Relative to Rate Measurements

Figures 10 and 11 illustrate phenomena which were observed in large diameter flames and which could be simulated by benzene flames above small Pyrex dishes. The underside views of Figure 10 show the distribution of soot through the vapor zone between flame and liquid surface. The density of soot is increased by

187
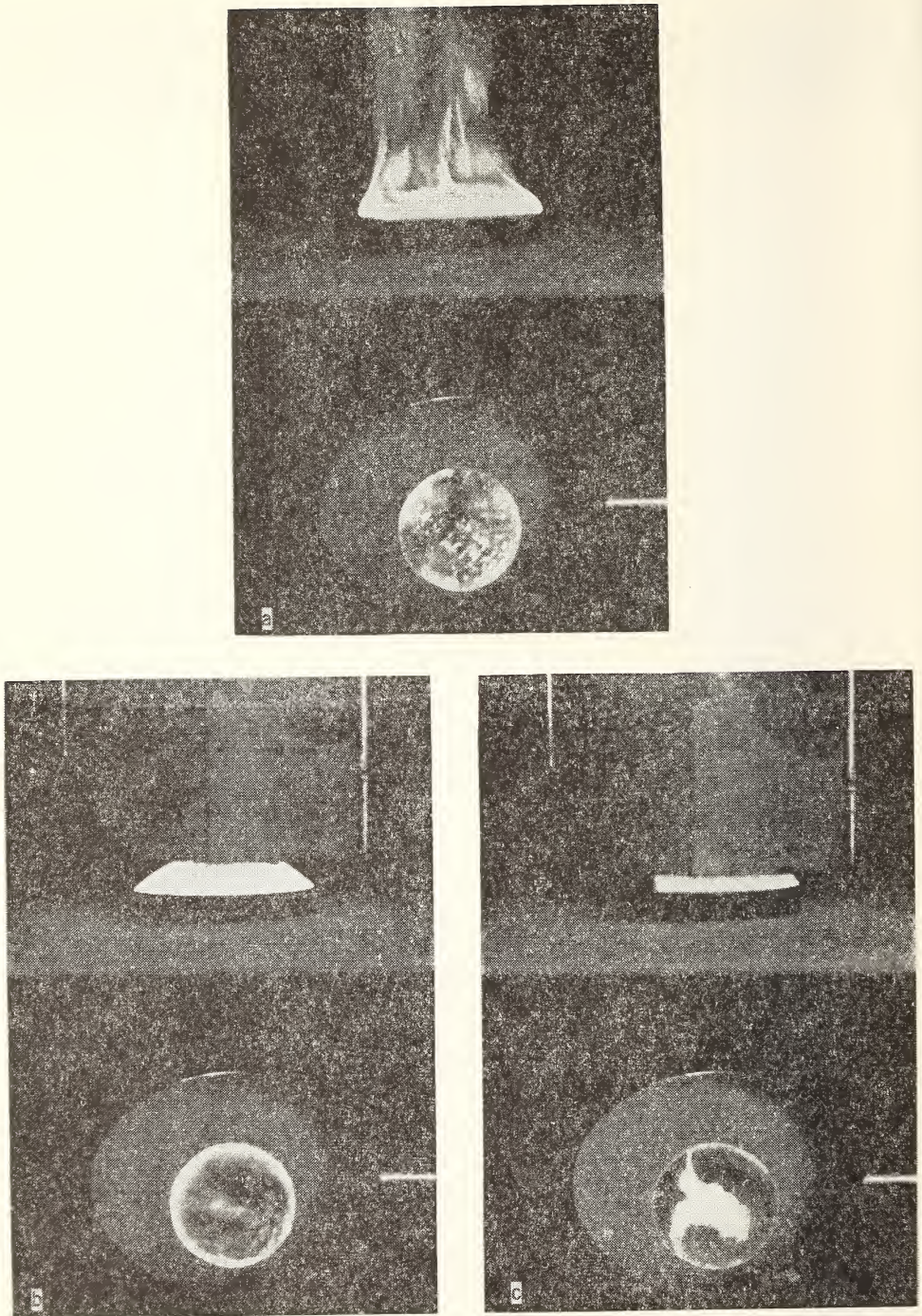
Figure 10. Side views and under views of benzene flames in 6-inch diameter dish. (a) Flame undisturbed. (b) Radial draft induced by chimney. (c) Flame torn from rim of tray.

188
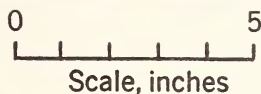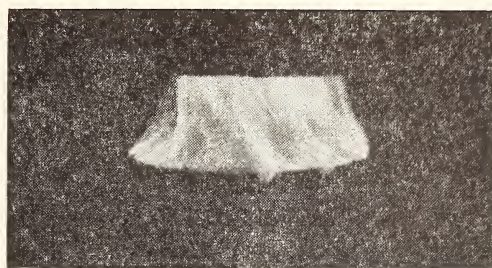
Figure 11. *Creeping flame on lipless dish. Below: Compared with noncreeping flame on dish with ½-inch lip.*

increasing the radial draft with a chimney as in Figure 10b. Soot has also been observed under ethylene flames in open air. The shape of the flame in Figure 10b is quite similar to that of a large flame in quiet air; the burning rate, plotted in Figure 5, is comparable to v_∞. Figure 10c shows the flame dislocated from the rim of the tray by an excessive draft. With rectangular trays this tearing of the flame occurred with winds of about 3 to 4 m/sec, although the critical velocity was sensitive to the configuration of the apparatus. The burning rate typically decreases at this point of incipient blowoff, but if premixing of fuel vapor and air occurs at a point of flame stabilization, then a much hotter flame develops (note the bright zone in Figure 10c), and burning rates can exceed v_∞.

In Figure 10 the Pyrex dish is set into the bench top so that the rim of the dish is ½ inch above the surrounding flat surface. The flame is then stabilized at the rim. In Figure 11 the rim of the dish is mounted flush with the surrounding surface, and one observes the "creeping" of the flame as heavy fuel vapors diffuse outward along the surface against the radial inflow of air. This phenomenon was noted particularly with butane flames and brought about the discontinuance of measurements above 76 cm diameter. Burning rates and radiation levels increased appreciably (>20 per cent) during each period of this flame instability.

It was confirmed that linear burning rates increase at tray diameters below 5 to 10 cm, such rate values being omitted from Figure 4 to avoid confusion. Flames at very small diameter are simple laminar diffusion flames, and heat transfer to the liquid is demonstrably an edge effect of no interest in large-scale experiments. For example, methanol burning in a 7.5 cm diameter, water-jacketed

189

brass tray was consumed at a rate of 3.8 cc/min; when an empty, concentric inner tray of 4.4 cm diameter was added, there was no change in the consumption rate of fuel; when the inner tray had a diameter of 5.4 cm, the volumetric rate fell to 3.1 cc/min. Thus, the "edge" of interest in small methanol flames is an annulus slightly wider than 1 cm.

Discussion

The Dominance of Radiative Heat Transfer

From their studies of hydrocarbon flames, Blinov and Khudiakov concluded that burning rates are controlled by heat flux from the hot zone to the liquid surface. This concept was put into semiquantitative form by Hottel in his review of the Russian paper [3]

$$\frac{q}{\pi d^2/4} = k_1 \frac{T_F - T_B}{d} + k_2 (T_F - T_B) + \sigma T_F^4 F (1 - e^{-kd}) \tag{4}$$

(Heat flux = conductive + convective + radiative components)

where T_F is the flame temperature; T_B the liquid surface temperature, presumably the boiling point; k_1 and k_2 are conductive and convective coefficients, respectively; d is the pool diameter, σ the Stefan-Boltzman constant; F a flame shape factor for radiation to the liquid; and k an opacity coefficient. Dividing both sides of equation 4 by the volumetric heat of vaporization, $\rho \Delta H_v$, and neglecting conductive and convective terms gives

$$v = \frac{\sigma T_F^4 F}{\rho \Delta H_v} (1 - e^{-kd}) \tag{5}$$

Conductive heat transfer becomes negligible at large diameters by virtue of being an edge effect. If one assumes that the Blinov and Khudiakov burning rates at small diameter are completely conduction controlled, then by equation 4 the contribution of conduction is less than our experimental uncertainty at all diameters represented in Figure 4. It is not so easy to dispose of convective transfer, especially with the slower burning flames. We have noted a steep temperature gradient at the interface between liquid and vapor phases in both methanol and benzene flames. The presence of soot particles above the benzene pool as show in Figure 10 is also suggestive of convection. The strong absorption of flame radiation by methanol vapor, Table 5, dictates that the flame stand very close to the liquid surface, which again favors convection as the heat-transfer mode. On the other hand, we can rule out convection with the faster burning butane and hydrogen flames since there was no sharp rise in temperature as a thermocouple emerged from the liquid phase into the vapor zone. Assuming for the sake of further discussion that heat transfer in large trays is exclusively radiative, equation 1 becomes the empirical equivalent of equation 5. On this basis, the empirical constant κ of equation 1 may be identified with Hottel's opacity coefficient k, and our extrapolated burning rate, v_∞, is given by

$$v_\infty = \frac{\sigma T_F^4 F}{\rho \Delta H_v} \tag{6}$$

190

No precise explanation is offered for the simple correlation of data given by equation 2 and Figure 6. Qualitatively, the relationship is easy to understand. The reciprocal of $(\Delta H_c/\Delta H_v)$ is the fraction of the flame's heat that must be fed back to the liquid to maintain a steady rate of vaporization. The smaller this fraction, the taller the flame must be to limit the efficiency of heat transfer; but the height of a diffusion flame, other things being equal, is determined by the rate of fuel feed, i.e., the burning rate. The linearity of the curve in Figure 6 and the small degree of scatter of data were unexpected.

Since equation 2 is expected to have some practical significance in predicting the relative hazards of fuels, it is important to list its limitations. The data involved only single-component fuels (the LNG used was more than 90 per cent methane) burning in unvitiated air under unusually calm atmospheric conditions at one atmosphere pressure. We know from experiments with methanol that the effect of atmospheric humidity must be minor. It is particularly important to note that no fuel studied was a monopropellant and that decomposition flames could hardly conform to the heat-transfer picture described above.

The Effect of Wind on Burning Rate

The effect of minor winds (Figure 5) may be rationalized on the basis of the three variables T_F, F, and k in equation 5. If the effect of the wind is only to move the flame around, then T_F and F could reasonably be expected to remain unchanged; but as the flame's hot zone is ruffled, the opacity is visibly increased, and the result of Figure 5 could arise from such an increase of k, the opacity coefficient, that e^{-kd} becomes negligibly small. The effects of wind and of large pool diameter should therefore be identical.

Some caution is necessary in applying this concept to practical problems. In the case of an idealized spill in which the liquid surface is flush with the surrounding terrain and there are no velocity gradients in the moving air, one would expect v_∞ to be the highest attainable burning rate. At higher wind velocities than those of Figure 5, the flame begins to blow off. However if the fuel is contained behind a bluff body (consider for example a half-empty fuel tank) one may no longer be dealing with a diffusion flame but with a turbulent premixed flame in which T_F is hundreds of degrees higher than in diffusion flames. We have observed burning rates equal to twice v_∞ under such circumstances and know of no upper limit.

Special Problems with Cryogenic Fuels

The data for liquid hydrogen and for liquefied natural gas were made consistent with other data in Figures 4 and 6 by either minimizing or correcting for any heat flow from the warm surroundings. However, in actual spills with ignition occurring at or shortly after spillage, heat conducted from the ground may be the dominant factor in the fuel's rate of vaporization. For example, when hydrogen was spilled onto warm paraffin (Figure 7) about 7 cm of the liquid depth was vaporized in chilling the paraffin surface; thereafter, the liquid regression rate still remained faster for several minutes than the liquid burning rate obtained with insulated pools (Figure 9). With typical soils, the thermal diffusivity is higher than with paraffin, and a liquid depth of 20 cm can well be dissipated within the first minute after spillage.[4]

191

We have no radiation records for the initial flash on spilling a large depth of liquid hydrogen into an ignition source. The data that we do have pertains to LNG, and Figure 1 is representative. The area under the initial spike is never comparable to the radiation expected from fuel vaporization curves. We can only suppose that a large fraction of the fuel vapor escapes unignited.

Conclusions

Owing to the dependence of burning rate on radiative heat transfer from flame to liquid, the burning rate approaches a maximum and constant value with increasing pool diameter. This constant burning rate is proportional to the ratio of the net heat of combustion to the sensible heat of vaporization. Winds raise the burning rates of unshielded fires to approach the large diameter value unless the flame is disrupted. The radiative flux to the environment is about 20 to 40 per cent of the heat of combustion.

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Effect of Potassium Bicarbonate on the Ignition of Cellulose by Radiation

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ABSTRACT

In accord with the established effectiveness of $KHCO_3$ as a fire extinguishing agent, it has been shown that $KHCO_3$ treatment of α-cellulose papers prior to their exposure to thermal radiation reduces their sensitivity to transient flaming and that sustained flaming may be completely prevented without adding more than 1.5 per cent by weight. On the other hand, $KHCO_3$ treatment greatly increases the sensitivity of cellulose to glowing ignition, apparently by increasing the rate and degree of pyrolysis. Treatment particularly enhances the production during pyrolysis of such combustible gases as H_2, CH_4, C_2H_4, and C_2H_6 at the expense of high molecular weight, tarry materials.

Introduction

Most combustion reactions of interest in the field of fire control involve cellulosic materials. For such materials the fire reactions may be considered as proceeding in essentially two steps—first, a pyrolysis of the solid phase which yields, among other things, combustible gaseous products and, second, a highly exothermic gas-phase oxidation reaction. Since most of the energy in the fire is produced in the gas-phase reactions (and incidentally, since simple gas-phase reactions lend themselves more readily to study), most research programs on fire extinguishment have considered primarily the gas-phase flame reactions.

Investigations into the action of flame extinguishing agents have established that, besides the obvious physical effects (cooling, smothering, etc.), a chemical effect, attributed to a chain-breaking reaction, also occurs in the gas phase. On the other hand, the possible chemical effect of the extinguishing agent on the pyrolysis reactions of the solid has frequently been overlooked in the fire extinguishing field (although such an effect forms a basis of chemical theories of flame-proofing of wood and fabrics). However, fire extinguishment procedures generally attempt to bring the extinguishing agents in intimate contact with the solid fuel. Here the agents can affect pyrolysis to give gaseous products differing in kinds, amounts, proportions, or temperatures, and thus, so to speak, affect the gas-phase flame reactions before they occur. This possibility is strikingly illustrated by the observation that many of the highly recommended fire extinguishing materials, including potassium bicarbonate (which also is a major constituent of the mineral component in natural fuels), can "catalyze" the combustion of carbohydrates (for example, make sugar cubes burn).[1]

The present report describes some of the results obtained in a series of experiments undertaken at the United States Naval Radiological Defense Laboratory (NRDL) to determine how impregnation of cellulose with small amounts of

potassium bicarbonate alters the combustion characteristics of the material and the gaseous products evolved in the pyrolysis. Purified alpha-cellulose, in the form of specially prepared papers, had been in use for a number of years in studies of the thermal decomposition and ignition of cellulosic materials by thermal radiation,[2-4] an important phase of the Laboratory's program investigating the effects of thermal radiation from nuclear detonations. Such papers had been selected for study in an attempt to insure reproducible results which could be of direct value in interpreting the behavior of heterogeneous, highly variable, natural fuels. The present experiments were undertaken when it became evident that the low ash content of these papers might give results which differed markedly from results obtained with impure natural fuels and that indiscriminate application of fire-extinguishing and fireproofing materials might lead to undesirable consequences.

Apparatus and Procedures

Test Materials

In 1953, the Forest Products Laboratory, Madison, Wisconsin, prepared, from a single batch of wood pulp, a series of alpha-cellulose papers[5] for use in the program of the Thermal Radiation Branch, NRDL. These papers were made up in varying thicknesses and densities, and carbon black was added to some to provide a gradation in optical properties. The paper (No. 4095) chosen for the present experiments was made with 2.5 per cent (dry weight basis) carbon black added to the pulp. The density of the dry paper was 0.67 g/cm³, its thickness was 0.54 mm, and its radiant absorptance for the spectral distribution of the radiant energy source was 0.9 as measured with a General Electric Model 8 PVI reflectometer.

Chemical analysis of this paper indicated an ash content of 0.15 per cent consisting largely of Ca, Mg, Na, Fe, and Si. As a result, it was decided that the minimum addition of $KHCO_3$ that would be profitable to investigate was 0.15 per cent, doubling the ash content of the sample. To investigate the influence of more drastic changes in composition, a 10-fold increase—to 1.5 per cent—was selected. Finally, a few experiments were conducted with 15 per cent $KHCO_3$ added to a limited number of samples.

Initial attempts were made to distribute the $KHCO_3$ throughout the cellulose by adding it in aqueous solutions. Because of the tendency of the paper to warp and swell when wet, this approach was abandoned in favor of one in which the $KHCO_3$ is produced within the cellulose by the neutralization of alcoholic KOH with moist CO_2. With such a procedure no noticeable change in the appearance of the paper could be detected.

For the treatment, three solutions of KOH in anhydrous methanol were prepared, with concentrations 0.02 M, 0.2 M, and 2 M. The paper samples, 1½ by 1¾ inches in size, weighed 0.63 ± .02 g, so the treatment consisted of adding to each sample 0.5 ml of the appropriate solution from a repeating pipette and placing the samples immediately on racks in an atmosphere of CO_2 saturated with water vapor. The atmosphere was maintained by bubbling tank CO_2 through water and removing excess water from the stream by passing it through a cellulose filter. After an overnight exposure to the moist CO_2 atmosphere, the samples were mounted in standard holders and left exposed to the normal atmosphere until they were used.

194

ABSTRACTS AND REVIEWS

In appearance, the treated samples were indistinguishable from the untreated samples, and no change in absorptance was detected with the reflectometer. Evidence that the treatment did indeed convert the KOH to $KHCO_3$ was obtained in two ways: (1) A number of samples were weighed before and after treatment, the weight changes being in accord with the stoichiometry, (2) the same samples were leached with a small amount of distilled water, and the pH of the resulting solution was compared with that of an aqueous $KHCO_3$ solution of the expected concentration. As a final check on the method of sample preparation, the effects of exposure to radiant energy were compared for a limited number of the samples treated with aqueous $KHCO_3$ solution and those treated with alcoholic KOH. The results showed only negligible differences between the two groups of samples.

Radiant Energy Source

For these experiments, samples were exposed to an intense beam of thermal radiation produced by means of a high current carbon arc and a relay-condenser optical system. The source [6] can provide a maximum irradiance level of 30 calories per square centimeter per second, uniform over a circular area of four square centimeters. The spectral distribution of the thermal output from the source, as operated, approximates that of a 5,500°K black body emitter. Attenuation of the whole beam to the desired irradiance level was accomplished using Libby-Owens-Ford "color-clear" plate glass, ground to produce a diffusing surface of appropriate attenuation. Exposures were made by means of a high speed square-wave shutter capable of providing exposures as short as 0.1 seconds reproducible to 0.01 seconds. The samples of test materials were individually mounted for exposure in brass shim-stock holders through which an accurately centered ¾ inch diameter hole had been punched. A water-cooled aperture with a slotted guide received the holders and automatically aligned them into the focal spot.

Phenomena Observed

The effect observed when a particular cellulose sample is exposed to radiant energy depends upon both the irradiance and the time of exposure. At sufficiently high irradiance, the first ignition phenomenon observed is transient flaming—a flaming which terminates promptly at the end of the exposure. For somewhat longer exposures at a particular irradiance level in this range, sustained flaming occurs—the flaming extends beyond termination of the exposure and results in the nearly complete combustion of the sample. At somewhat lower irradiance levels, transient flaming never occurs; whenever the exposure is sufficiently long to permit initiation of flaming, it is always sustained. At still lower irradiance levels a sufficiently long exposure produces glowing ignition, and the sample may be consumed without the appearance of flame.

Analytical Procedures

The principal evidence concerning the influence of $KHCO_3$ on the combustion characteristics of cellulose was obtained from visual observation of the effects on exposed samples. However, to gain some insight into possible explanations for the observed results, a few comparative measurements were made of the quantities

195

of the principal volatile pyrolysis products generated by treated and untreated samples exposed to the same thermal input.

At two irradiance levels and exposure times chosen on the basis of the ignition effects in air, first an untreated sample and then a sample impregnated with $KHCO_3$ were exposed in a helium atmosphere. The volatile products were swept by the helium carrier into a two-stage gas chromatography system.[7] As a means of confirming the identity of the components, the effluent stream from the liquid-partition stage of the two-stage system was monitored by a Bendix time-of-flight mass spectrometer. A combination of the chromatographic retention time and the mass spectrum gives ample proof, in general, of the identity of each component.

Results and Discussion

Method of Quantification

The result observed when a single test sample is exposed to one specific pulse of thermal radiation is a "go – no go" phenomenon. That is, for a given irradiance, if the critical exposure time (threshold for a particular effect) is exceeded, the effect will occur (a success); if the critical time is not exceeded, no effect, or a different, lesser effect will be observed (a failure). To obtain an estimate of the critical value, then, a series of samples must be exposed to different values of the variate. From the results, an estimate of the critical value, usually defined as that value for which just half of all samples would exhibit the effect, that is, the LD_{50} in biological experimentation, may be obtained.

For a given sample population, the value of the estimate depends upon such factors as the variability in sensitivity of the samples in the population as a whole with external factors—temperature, humidity, etc. For experiments with the present exposure apparatus, additional variability is introduced as a result of uncertainties in the delivered dose. The source is not equipped for continuous monitoring. It is calibrated by mounting a calorimeter in the position at which samples will subsequently be exposed. However, the irradiance is not invariate with time. It has short time fluctuations (1 to 2 per cent in seconds as the carbons rotate) and long time fluctuations (5 to 10 per cent over several minutes as the carbons feed in and out or as voltage drifts). Thus, the method of estimating a critical value must take into account all such variations.

The procedure that has been adopted in determining the critical value for a single material is the so-called "up-and-down" method.[8] In this method, fixed increments of the variate, in this case exposure time, are selected. The result of each exposure then determines the next time setting. If a "success" is obtained, the time is set down one increment; if a "failure," the time is increased. Neglecting a long series of steps in one direction as the critical value is first approached, the final estimate is obtained by simply averaging all subsequent exposure times.

For comparing two materials whose critical values differ only slightly, a modified up-and-down procedure was adopted and will be described in a future report. Samples of the two materials are exposed alternately in quick succession, the time setting being adjusted only if the same effect is observed for both samples. Such procedures permit the use of one material as a control to minimize the effect of any long time fluctuations.

ABSTRACTS AND REVIEWS

Critical Values

The regions of occurrence of the various ignition phenomena for the untreated No. 4095 paper are delineated by the curves in Figure 1. These curves represent the composite results of a large number of experiments on this paper and extrapolations from results obtained with the similar papers * of different density and thickness. As may be seen, there is a critical irradiance for the material—a level below which ignition will not occur no matter how long the exposure. For sustained ignition at the high irradiance levels, so-called reciprocity is approached, the effect occurring at approximately the same total exposure regardless of the irradiance level. More obvious from a logarithmic plot than from Figure 1 is the
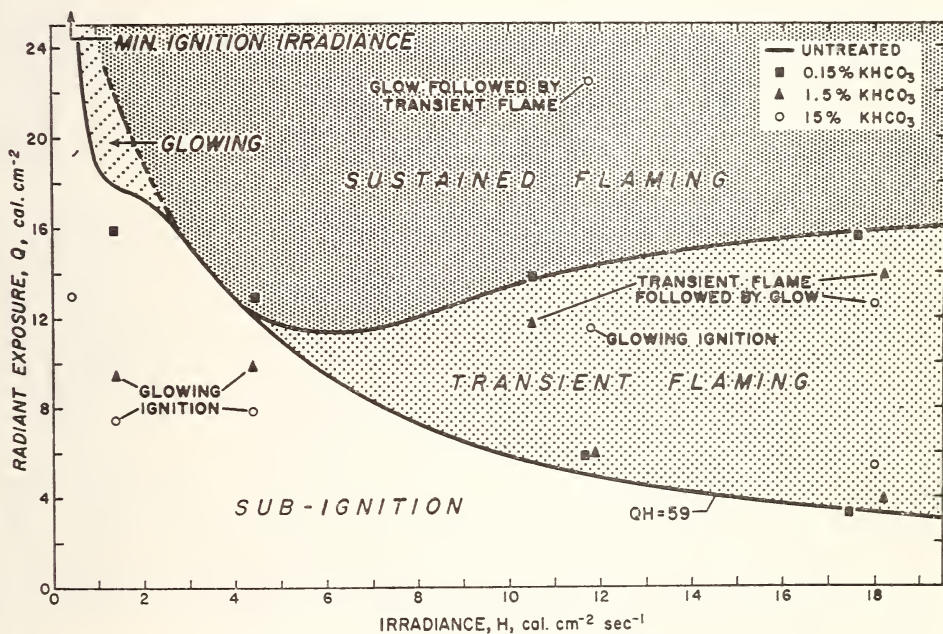
Figure 1. Ignition behavior of No. 4095 a-cellulose paper. Points indicate effect of KHCO$_3$ impregnation.

fact that, for alpha-cellulose papers of the type used in these experiments, the occurrence of transient flaming may be expressed by a constant product of the irradiance and the radiant exposure. The value of the constant is a function of the thermal conductivity, the density, and the heat capacity of the material. For the untreated No. 4095 paper the relationship is given by

$$HQ = H^2t = 59 \tag{1}$$

where

H = irradiance in cal cm^{-2} sec^{-1}
Q = radiant exposure in cal cm^{-2}
t = exposure time in sec

* All of these papers have an ash content of the order of 0.1%. A few experiments with paper containing only 0.01% (but differing somewhat in physical properties) indicate that 0.1% ash markedly alters the combustion behavior of cellulose. In fact, if the cellulose is sufficiently pure, it may be impossible to induce glowing combustion (combustion without flaming) at any irradiance.

For determination of the influence of KHCO₃ impregnation, four irradiance levels were chosen: 11 and 18 cal cm⁻² sec⁻¹, where both transient and sustained flaming are observed for the untreated material; 4.2 cal cm⁻² sec⁻¹, where only sustained flaming is observed; and 1.4 cal cm⁻² sec⁻¹, where only glowing ignition is observed. At each irradiance level, parallel "up-and-down" sequences were obtained by alternating untreated and treated papers. The average irradiance to which the treated material had been exposed was estimated on the basis of the average exposure time for the untreated samples. The results are presented as the points in Figure 1. For those points at which the effects observed differed from those observed at the same irradiance level for the untreated material, the actual effect observed for the treated material is also indicated in the figure.

Several interesting observations may be noted in Figure 1. First, if only 0.15% KHCO₃ is added, the effects are the same as for the untreated materials at all irradiance levels used. At the highest irradiance level, little difference in sensitivity is found between the treated and untreated materials. At the intermediate irradiance levels slightly more energy is necessary to produce a given effect in the treated material. However, at the low irradiance level the treated material is appreciably more sensitive.

Second, under no conditions attainable with this source was it possible to induce a sustained flaming in material treated with 1.5 per cent KHCO₃, except that a brief transient flaming, presumably as the gaseous products of pyrolysis were ignited by the radiant beam, could be produced at the 12 cal cm⁻² sec⁻¹ level at an exposure well beyond that necessary to produce the first glowing ignition. On the other hand, the times to produce a sustained ignition were always much lower for the treated material than for the untreated material, and the minimum irradiance level necessary to produce ignition was much less.

One final point should be made. The highest irradiance levels measured on conventional fires are always less than 2 to 3 cal cm⁻² sec⁻¹. Thus, the largest differences in sensitivity between treated and untreated materials occur in the region of greatest interest from the point of view of fire spread, with the treated material always the more sensitive. The magnitude of these differences is particularly evident in Figure 2 in which is plotted time to ignition as a function of irradiance for levels below 1 cal cm⁻² sec⁻¹.

Analysis of Volatile Pyrolysis Products

A summary of the gas chromatography and mass spectrometry results is given in Tables 1 and 2. In addition to the weight loss during exposure in a helium atmosphere for an untreated 100 mg alpha-cellulose sample and for an equivalent sample impregnated with 2 mg KHCO₃, each table gives the measured weights of various pyrolysis products and their relative ratios (the ratio of weights of the specific constituent divided by the ratio of total weight change). Table 1 gives results obtained after exposure to an irradiance of 4.2 cal cm⁻² sec⁻¹ for 2.5 sec (a time intermediate between those necessary to produce sustained ignition in air for the two materials). Table 2 gives similar results after exposure to an irradiance of 11 cal cm⁻² sec⁻¹ for 1.4 sec (a time somewhat more than the minimum necessary to produce sustained ignition in air for both materials).

Under conditions of these experiments, pyrolysis of cellulose gives a large number of products ranging from the low molecular weight gases to high molecular

198

ABSTRACTS AND REVIEWS
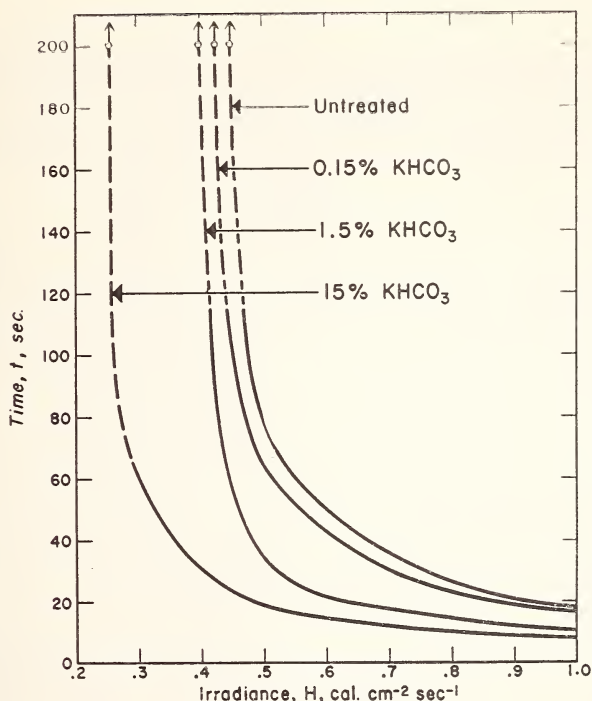
Figure 2. Minimum ignition irradiance for KHCO₃-impregnated No. 4095 α-cellulose paper.

TABLE 1

PYROLYSIS PRODUCTS OF UNTREATED α-CELLULOSE AND α-CELLULOSE
IMPREGNATED WITH 2% KHCO₃ EXPOSED UNDER HELIUM TO 4.2 CAL
CM⁻² SEC⁻¹ FOR 2.5 SEC

Product	Weight produced from		Relative ratio
	Untreated sample (mg)	Treated sample (mg)	
Weight loss [a]	22.7	53.7	1
Total volatiles (B.P. < 150° C)	6.3	33.5	2.2
Total gases (B.P. < 0° C)	1.79	14.4	3.4
CO₂	1.26	9.6	3.2
CO	0.53	4.7	3.8
H₂	0.001	0.009	3.8
CH₄	0.002	0.034	6.3
C₂H₄	< 0.001	0.029	> 12
C₂H₆	< 0.001	0.025	> 11
Water	4.0	16.5	1.8
Other vapors [b] (B.P. 0–150° C)	0.48	2.6	2.3
Total "tars" (by difference)	16.4	20.2	.52

[a] Original sample weight = 100 mg.
[b] Including CH₃CHO, CH₂:CHCHO, CH₃COCH₃, CH₃COCOCH₃
CH₃CH:CHCHO, OCH:CHCH:CH, CH₃OH, CH₃CH₂CHO

199

TABLE 2

PYROLYSIS PRODUCTS OF UNTREATED α-CELLULOSE AND α-CELLULOSE
IMPREGNATED WITH 2% $KHCO_3$ EXPOSED UNDER HELIUM TO 11 CAL
CM^{-2} SEC^{-1} FOR 1.4 SEC

| Product | Weight produced from | | Relative ratio |
	Untreated sample (mg)	Treated sample (mg)	
Weight loss [a]	68.1	79.3	1
Total volatiles (B.P. < 150° C)	16.8	52.0	2.7
Total gases (B.P. < 0° C)	5.5	26.4	4.1
CO_2	3.45	14.7	3.7
CO	1.94	10.2	4.5
H_2	0.009	0.09	8.5
CH_4	0.021	0.65	27
C_2H_4	0.036	0.59	14
C_2H_6	0.007	0.19	22
Water	9.5	19.6	1.8
Other vapors [b] (B.P. 0–150° C)	1.8	6.0	2.8
Total "tars" (by difference)	51.3	27.3	.46

[a] Original sample weight = 100 mg.
[b] Including CH_3CHO, $CH_2:CHCHO$, CH_3COCH_3, $CH_3COCOCH_3$
$CH_3CH:CHCHO$, $OCH:CHCH:CH$, CH_2OH, CH_3CH_2CHO

weight tarry materials. As may be seen from the tables, the volatile fraction
(boiling point less than about 150°C) includes only about 25 per cent of the
weight loss from the untreated samples but more than 60 per cent of the weight
loss from the treated samples. As might be expected, the increased sensitivity of
the treated materials to radiant exposure results in a more complete pyrolysis
(that is, to a larger fraction of low molecular weight materials) for the same
exposure conditions.

The volatile materials may be broken into two categories: gases (boiling
points less than 0°C) and vapors (boiling point 0° to 150°C). For the untreated
sample, CO_2 and CO constitute 98 per cent of the gas fraction. For the treated
samples, the CO_2 and CO components are still quite large, but the other,
combustible, gases show a marked increase. Since the treated samples do not
exhibit sustained flaming, while the untreated samples do, this result is somewhat
surprising.

The principal constituent of the vapors is H_2O, which for both treated and
untreated samples makes up about 80 per cent of the vapor fraction. About
90 per cent of the materials in the "other vapors" category in the tables have been
identified. They include acetaldehyde, acrolein, acetone, biacetyl, crotonaldehyde,
furan, methanol, and propionaldehyde. Here, too, some of the results are rather
surprising. Although $KHCO_3$ treatment does not change the relative ratio of most
of the vapors, several constituents, notably acetone and biacetyl are increased by
an order of magnitude, or more.

The bottom row in each table gives the amount of higher molecular weight
materials lost from the sample. The values are obtained by subtracting the weight
of volatiles from the total weight change so that this fraction would also include
any solid matter lost from the sample. The large increase in volatiles for the
treated samples, of course, requires a corresponding decrease in the relative ratio

200

for the "tars," and this decrease may explain the absence of flaming combustion of the treated samples exposed in air.

As another possible explanation, the difference in ignition behavior of the treated and untreated samples could be due to marked differences in temperatures at which the pyrolyses occur. This has given impetus to a detailed study of the temperature behavior of the samples during exposure, and such experiments have now begun.

Conclusions

As part of a program investigating the mechanisms of action of fire extinguishing agents, a study has been started on the influence of potassium bicarbonate additives on the ignition behavior of cellulosic materials. Pure alpha-cellulose papers and others to which varying amounts of $KHCO_3$ had been added were exposed in air to the intense radiation flux of a refocused carbon arc beam, and the ignition thresholds were determined at several irradiances. Several samples were then similarly exposed in a helium atmosphere, and the gases and vapors generated were passed through a gas chromatography-mass spectrometry analytical system.

From the results of this experimental work it is concluded that adding potassium bicarbonate to alpha-cellulose papers prior to radiant heating reduces the sensitivity to transient flaming and, furthermore, that sustained flaming may be prevented without adding more than 1.5 per cent by weight. Such an observation is in complete accord with the fact that the effectiveness of $KHCO_3$ as a fire extinguishing agent has been repeatedly demonstrated over the years and is beyond question. Not in accord with its proven value in fire fighting is the fact that the addition of $KHCO_3$ increases the rate and degree of pyrolysis of cellulose to volatile substances, and, as an apparent consequence, greatly increases the sensitivity to glowing ignition. Further, $KHCO_3$ treatment markedly enhances the production of gases such as hydrogen, methane, ethane, and ethylene as well as organic liquids (at room temperature) such as acetone and biacetyl.

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ABSTRACTS

I. Ignition Phenomena

Kinbara, T. (University of Tokyo, Tokyo, Japan) and Akita, K. (Fire Research Institute of Japan, Tokyo, Japan) "An Approximate Solution of the Equation for Self-Ignition," *Combustion and Flame* 4, 173–180 (1960)

The equation for heat conduction in the presence of a heat generation term whose rate varies exponentially with temperature requires numerical solution. In this paper the authors offer an approximate solution by substituting a special function of the Form $(1+\beta\theta)$ for the term e^θ in the dimensionless form of the heat conduction equation

$$\partial\theta/\partial\tau = \partial^2\theta/\partial\xi^2 + (m/\xi)\partial\theta/\partial\xi + e^\theta \qquad (1)$$

The authors decide to expand β in terms of a power series with respect to the reduced temperature θ_0 at the center of the specimen

$$\beta = 1 + a_1\theta_0 + a_2\theta_0^2 + a_3\theta_0^3 + \ldots + a_n\theta^n \qquad (2)$$

where the constants a_n depend on the shape of the specimen. In the selection of these constants advantage is taken of the known solution of equation (1) under steady-state conditions [1] which yields the critical temperature θ_c at which self-ignition will occur, i.e., for $\delta > \delta_c$ no steady-state solution exists. By this method for a sphere,

$$a_1 = 0.3691; \qquad a_2 = 0.0908$$

Next the analysis is extended to the nonsteady-state conditions using the same approximation for e^θ as before. The authors recognize the questionable applicability of this procedure, particularly since β was chosen for conditions after the steady-state had been attained. As is to be expected, a comparison of the theoretical temperature rise with experimental data on the ignition of sawdust shows poor agreement. The authors consider this discrepancy to be due to (1) the poor approximation made in the assumption of the form of the parameter β, and (2) the change in mass of reactants during the course of reaction.

Reference

1. Frank-Kamenetskii, D. A. *Diffusion and Heat Exchange in Chemical Kinetics,* Princeton: Princeton University Press (1955)

Subject Headings: *Ignition, solution of equations for.*

H. Wise

Affens, W. A., Johnson, J. E., and Carhart, H. W. (U. S. Naval Research Laboratory, Washington, D. C.) "The Effect of Chemical Structure on the Soptaneous Ignition of Hydrocarbons," *NRL Report 5566* (November 1960)

This is the sixth interim report of the series under the general subject. Hexane isomers and other selected pure hydrocarbons were investigated to show the effect of molecular structures on the spontaneous ignition processes in air.

202

ABSTRACTS AND REVIEWS

Experiments were carried out in a spherical Pyrex flask, in which air was heated uniformly to a basic temperature before fuel was injected. Measurements were made on the time-history of temperature rise and the oxygen consumption. Results were presented in tabulated and graphic forms and these show that minimum ignition temperature, minimum reaction temperature, preignition temperature range, maximum temperature rise, and oxygen consumption are related to the oxidation and ignition resistance of the fuel. The temperature-rise history distinguishes the ignition from the nonignition, but not between hot- and cool-flame ignition. However, the distinction could be made visually in total darkness.

It was found that the oxidation and ignition resistance of aliphatic hydrocarbons is generally increased by decreasing chain length, addition of methyl groups, unsaturation, and particularly chain branching, the effect of which far outweighs that of a double bond. Data on five branched hydrocarbons were approximately the same, which suggests that they pyrolyze to fragments similar in their oxidation characteristics.

Alicyclic compounds were found to be more resistant to oxidation while the aromatic compounds were the most resistant among the fuels tested. Side chains decrease their resistance and this effect increases with the chain length. The cycloparaffins, in general, shows extremely short preignition temperature range and long ignition delays, except in the case of cyclopentane.

The mechanisms of hydrocarbon oxidation are briefly reviewed. Results of minimum reaction temperatures for aliphatic hydrocarbons show agreement with both the experimental reaction rate data and the theoretical methyl retardation factors of Hinshelwood and, therefore, concur with his views on molecular structure and oxidation resistance based on the point of oxygen attack.

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

A. S. C. Ma

Lie, T. T. "Fire Tests on Building Materials," *Bouw* 13, 862–868 (1958) Translation 918, National Research Council of Canada.

During the time-history of a fire, the time from ignition until flashover in a given space is important, since it represents the maximum escape time for persons caught in that space, and in most instances it determines the conditions which will be found upon arrival of fire-fighting forces.

The test method described in this paper has been adapted to the fire behavior of materials in an enclosed space, considering the ease with which the test specimen can be ignited, and the ease with which a fire can develop on the material, expressed as a "spontaneous ignition intensity" (S.I.I.) in calories per square centimeter per second required to bring about flashover in a certain period of time. A flashover time of 15 minutes was selected for test purposes, considering that in an actual fire the inhabitants of a building will have had ample time to leave the building and that in most cases the fire fighters will have arrived.

The apparatus consisted of an asbestos test box, 37 cm x 25 cm x 37.4 cm high, designed to accommodate two 30 cm x 30 cm test specimens forming two opposite sides of the box. The size of two ventilation openings (one in the bottom

203

and one in the top) were so chosen that reduction in size had an unfavorable effect on the development of the fire in the test box. In the center of the test box twelve 0.6 mm diameter chromium-nickel filaments were mounted in a vertical plane parallel to the test specimens; the filaments were connected to a variable current supply. One of the specimens could be exposed to the action of nine 1 mm diameter fuel gas jets, spaced 3 cm apart, with flames 2 cm long, located near the bottom of the specimen. Thermocouples were used to measure the temperature at the center of the test box and at the center of the surface of the specimen not exposed to the gas flames.

The general procedure for making measurements was described as follows:

"The specimen not exposed to the gas jets is first put in place. Then the gas jets are ignited and the second specimen is placed in such a way that it partially closes the box but is itself not yet brought into contact with the gas jets. As soon as the second specimen has been placed, the temperature is measured at the center of the test box. When this temperature has increased to 60°C, the second specimen is pushed further inside so that it is brought into contact with the gas jets, whereupon it is clamped between the asbestos cover and the stays. The temperature at the center of the test box is measured for three minutes. Then, if required, heat may be supplied by way of the filaments. Next, the temperature of the specimen not exposed to the gas jets is measured every other minute. The temperature measurements are continued until flashover occurs in the box, or until 40 minutes have passed, counting from the placing of the second specimen."

The results of tests on twenty-eight different materials are tabulated. The S.I.I. values required to produce flashover in the test box in 15 minutes varied from a high value in excess of 1.4 cal/cm²sec to a low of 0.05 cal/cm²sec. It was found that use of the S.I.I. as a criterion for fire hazard classification of materials enabled a distinction between the behavior of the fire-protection-wise "better materials" (high S.I.I.) which was not found possible using flame-spread test data alone.

A discussion and interpretation of the results of the tests was also made for actual cases. Thus, it is possible to determine, for a certain sheathing material, how much heat must be supplied in a room during 15 minutes, in addition to the heat generated from the combustion of the material, in order to cause flashover. The required heat may be produced in the room, but may also be supplied from outside. A.S.I.I. of less than 0.05 cal/cm²sec is interpreted to mean that there is a possibility of flashover occurring in a room within 15 minutes if the material is brought into contact with a small heat source, such as burning matches, burning paper, etc. This is not the case for materials having a S.I.I. equal to or greater than 0.05 cal/cm²sec. A material having a S.I.I. greater than 1.4 cal/cm²sec will not contribute to the spread of a fire during the first 15 minutes. For materials having a S.I.I. of 0.05 to 1.4 cal/cm²sec, the minimum amount of heat which must have been released in a room within 15 minutes in order to cause flashover on the material within 15 minutes may be specified in terms of an equivalent weight of wood burned to release this heat quantity in the event of fire. This weight of wood may be calculated from the general formula given by the test data, $W = 2 \times 10^{-4} IA$, where

$W =$ Number of kg of wood required to produce the additional heat required, assuming the heat value of wood to be 4,500,000 cal/kg.

$I =$ S.I.I. of the material under consideration, cal/cm²sec.

$A =$ Greatest wall area of the room, cm².

ABSTRACTS AND REVIEWS

If the heat is supplied from the outside by radiation from an adjacent building on fire and flying cinders drop into the room, it may be expected that for a material having a S.I.I. less than 0.05 cal/cm²sec flashover will occur in the room within 15 minutes, irrespective of the radiant heat supplied. If the mean intensity of the incident radiation is smaller than 0.2 cal/cm²sec or equal to it, flashover to the room need not be expected for materials having a S.I.I. equal to or greater than 0.05 cal/cm²sec. If the mean intensity is greater than 0.02 cal/cm²sec, provided that the flashover to the room is not determined by the more combustible material, the materials of which the S.I.I. is greater than the incident radiation are safe. The following formula expresses the condition that no flashover will occur:

$$I > \phi_g \frac{r_1}{100} \frac{r_2}{100} \sigma T^4$$

where

I = S.I.I. of the material under consideration.
ϕ_g = Mean of the configuration factors for different situations.
r_1 = Percentage of window area in a building on fire.
r_2 = Percentage of window area in the room under consideration.
σ = 1.37 x 10⁻¹², cal/cm²K⁴sec (Stefan-Boltzmann constant).
T = Absolute temperature of building on fire (normally 1273°K).

This formula holds true if the mean intensity of the incident radiation is greater than 0.2 cal/cm²sec. If the mean intensity is 0.2 cal/cm²sec, "I" may assume any value equal to or greater than 0.05 cal/cm²sec.

Subject Headings: *Ignition, evaluation of building materials for.*

W. G. Labes

Dorsett, H. G., Jr., Jacobson, M., Nagy, J., and Williams R. P. (U. S. Bureau of Mines, Pittsburgh, Pennsylvania) "Laboratory Equipment and Test Procedures for Evaluating Explosibility of Dusts," *U. S. Bureau of Mines Report of Investigations* 5624 (1960)

The Dust Explosion Branch of the U. S. Bureau of Mines is one of several national research units set up notably by England, France, and Austria as well as America in the first decade of this century. These research units were charged with the job of investigating causes of, and methods of preventing dust explosions. Because of the immediacy of the problem once it had been recognized, many of the methods developed to test the flammability (or otherwise) of the dusts were *ad hoc,* and designed merely to range dusts in a relative order of flammability by some purely empirical criterion. Correlation of such data with known behavior of some of the dusts in actual industrial plants, or underground in coal mines, provided a useful, practical, measure of the probable relative hazard of a new dust; unfortunately, these tests are still largely empirical, and the hoped-for use of their results for accurate, detailed, prediction of the combustion behavior of any dust is still not possible.

Over the past 50 years many such tests have been developed to bring out one practical point or another, and in the paper under review are listed and described the standard range of tests currently used by the Dust Explosion Branch of the Bureau of Mines. Their sequences of tests start with toxicity examination of the dust sample and of its combustion products; if found to be toxic, appropriate venting and handling precautions are taken. The preliminary tests are

205

completed by examining the sample for certain physical properties: particle size distribution; particle shape; and moisture. For the subsequent ignition and combustion tests, an appropriate size fraction and weight of the dust is used in the determination of thermal (relative) ignition temperature in a cloud and a dust layer, electric ignition energy in a cloud and a layer, relatively flammability in the Godbert-Greenwald test furnace by the inert limit method, and low-limit cloud concentration, and explosion pressure with rate of pressure rise, in the Hartmann tube. If required, these various tests are repeated in controlled atmospheres, and are augmented in difficult cases by more intense ignition sources such as E.H.V. discharge, electric arc, guncotton flash, meker burner flame, and an electrically-heated helical coil. These various tests have been standardized against Pittsburgh Coal Dust of specified fineness, and the standard data are tabulated.

For details of construction of the various test methods, and the results obtained on different materials, the reader is referred to the original papers listed in the report. Otherwise, this paper is a most useful summary of the relative flammability tests currently used by one of the major world dust-testing laboratories.

Subject Headings: *Dusts explosions; Explosions, of dusts.*

<div align="right">R. H. Essenhigh</div>

Essenhigh R. H. (University of Sheffield, Sheffield, England) "Dust Explosions in Factories: Ignition Testing and Design of a New Inflammator," *Safety in Mines Research Establishment Research Report No. 188* (May 1960)

This report concerns the design and initial testing of an apparatus for studying ignition phenomena of dust-air mixtures. It was intended that the experimental conditions could be varied independently so that the inherent ignition properties of the dusts could be studied and with as little interference from boundary conditions as possible. Because of their design some types of ignition apparatus reported in the literature have given contradictory flammability ratings among several dust-air mixtures. This was attributed at least in part to different transit periods of the dust in the region of the ignition source.

On open-ended vertically-mounted glass tube 3 inches in internal diameter and 26 inches in length was used in the present apparatus in which dust was blown in through a side arm located near the top. The dust was allowed to fall under the influence of gravity past an electrically-heated igniter of coiled wire located near the bottom. In an ignition experiment a given amount of dust was blown in by releasing air contained in a reservoir at a predetermined pressure attached to the side arm. The fineness and weight of dust sample and dispersion pressure could all be varied independently. The minimum power dissipation of the igniter coil to cause ignition was used as an index of flammability of a dust.

Most of the experiments were carried out with commercial cork dust less than 66 microns in diameter. Flammability was found to be independent of dispersion pressure over the range 2 to 15 lb/in^2, a three fold variation in dust cloud concentration, and fineness of the dust between approximately 60 and 200 microns. A possible explanation for this was that ignition of the cork dust occurred through the distillation and inflammation of the volatile components. The effect of igniter coil size was studied by varying the number of turns and the

<div align="center">206</div>

coil diameter. This showed that for a fixed coil diameter, the ignition current decreased as the number of turns increased.

Subject Headings: *Dusts, ignition testing on; Ignition, testing on dusts.*

<div align="right">C. P. Talley</div>

IV. Diffusion Flames

Akita, K. (Fire Research Institute of Japan, Tokyo, Japan) "Structure of the Diffusion Flame of Liquid and Solid Fuels," *Bulletin of the Fire Prevention Society of Japan* **10,** 6–9 (1961)

The structure of diffusion flames for liquid fuels contained in a vessel and of pulverized solid fuels, such as sawdust, contained in an electrically heated metal pipe were studied photographically. These flames, considered to have basically the same structure as those of a fire, are different from the usual diffusion flame of a bunsen burner in that the initial ascending velocity of fuel gases is very small, and seems to give rise to an essential difference in their structures.

The flames were photographed through a filter which allows only ultraviolet light ranging from 3000 Å to 4000 Å to pass, in order to get a clear profile of the green and faint blue parts, which otherwise are not readily photographed, being prevented by the intense light from the luminous part. The spectra of the light from several parts were also studied with a quartz spectrograph. The result showed that the flame is made of two separate parts, and the outer one which emits C_2- and CH-band radiation forms a sheath wrapping the inner yellowish region where incandescent fine particles emit light.

To clarify the location of these particles, a thin vertical beam of ultraviolet light was directed into the flame and the light scattered by the particles was observed. By this procedure, it was found that the carbon particles appear close to the blue sheath, and that the inner region is a nonluminous one of the fuel gas covered by a thin luminous layer containing carbon particles.

Stream lines in and around the flame were also studied by the particle track method. In a usual diffusion flame such as that of a bunsen burner, it has been believed that air diffuses in through all the surface of the flame. In this case of solid or liquid fuels, however, the air is led into the flame mostly at the rim of the fuel container. No evidence was shown by this experiment that the air diffused in through the side boundary. The fuel gas and the surrounding air seemed to mix and begin to react at the rim of the container and ascend, forming a bluish sheath. The fuel gas inside this sheath ascends vertically without burning until it meets with the sheath, just under which the fuel decomposes thermally and creates carbon particles. These carbon particles burn as they enter into the sheath, and no trace of particles was observed in this region.

Thus, the author concluded that it is most necessary to cut off the flame at its bottom for extinguishing a fire. No effect can be expected from any extinguishing agent applied to the upper or middle part of a flame.

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

<div align="right">T. Kinbara</div>

<div align="center">207</div>

V. Combustion Principles

Berlad, A. L. and Yang, C. H. (Convair Scientific Research Laboratory, San Diego, California) "A Theory of Flame Extinction Limits," *Combustion and Flame* 4, 325–333 (1960)

This paper is another attempt to obtain a theory which can be applied to flammability limits and quenching distances of premixed gaseous flames. Abstracts of papers on this subject by D. B. Spalding and E. Mayer appeared in this Journal some two years ago.* In this present work the flame model is taken to be a moving flame through a reactive mixture held in an infinitely long tube of a given diameter. Spalding treated a stationary flame through which a reactive mixture moved. Average values of temperature and reactant concentrations at each cross section of the tube are assumed. Heat release by chemical reaction and heat losses are approximated by functions of these averages at each cross section.

Conservation equations for energy and for each of the reactants are formulated. The equations for reactant concentration are written to include diffusion in terms of the Lewis number, $D\rho_c/k$; where D is the diffusion coefficient of the reactant being considered, ρ is its density, c is the specific heat, and k is the thermal conductivity. The boundary conditions of the flame are the same as those in the adiabatic case, except that the temperature is said to be equal to the maximum temperature at every cross section of the tube and, therefore, no temperature gradients exist.

Approximate solutions of the equations are presented for two special cases. In the first case for Lewis number equal to zero, the authors (by a series of substitutions and integrations over each cross section of the tube) derive an equation in terms of a dimensionless temperature. This temperature is equated to the heat release rate and the heat loss. The heat loss term is conveniently divided into two parts, conduction and radiation. The conduction loss term is written in terms of tube diameter (quenching distance), temperature difference between wall and gas, and a geometric factor involved in channel quenching. The radiation loss is equated to the product of a constant, the gas emissivity, and the gas temperature raised to the fourth power. Now, a general equation is put forth with three major terms; (1) a term due to heat release by chemical reaction, (2) a term due to heat loss by conduction, and (3) a term due to heat loss by radiation.

Extinction limits are calculated for stoichiometric propane-oxygen-nitrogen flames, and are tabulated along with experimental results from the literature. The agreement is said to be very close even though diffusion is not considered, and the complicated kinetics are oversimplified. Conduction loss is, indeed, the dominant one in the case of quenching. The calculations show 99 per cent heat loss due to this factor. Radiation accounts for more of the heat loss in the case of the flammability limit experiments. For Lewis number equal to one, the authors derive an equation more laborious than that in the first case. In this example, the flammability or pressure limit is calculated.

It is stated that the theory can be extended "with ease" to two- or three-dimensional temperature fields and more complicated kinetics. In conclusion, the authors state that the extinction limit can be changed at will by changing the

* *Fire Research Abstracts and Reviews* 1, 123–126 (1959)

boundary conditions. They point to some experiments on extending flammability limits by heat addition to corroborate their belief. An appendix is included to show how the extinction limit calculations were performed.

Subject Headings: *Limits, calculation of combustion; Flame, extinction limits of.*

C. O'Neal, Jr.

Kaskan, W. E. (General Electric Research Laboratory, Schenectady, New York) "Temperature of Flames Burning on Porous Burners," *Combustion and Flame* 4, 285–288 (1960)

In 1954 Botha and Spalding [1] described the porous flat-flame burner with heat extraction by means of water cooling of the burner assembly. With this device it was shown subsequently [2] that a combustible mixture of fixed equivalence ratio, total pressure, and initial enthalpy may support a laminar flame of two different flame speeds. The existence of two different burning velocities for a given fuel/air ratio was explained in a theoretical analysis of flammability limits. [3] From the experimental results of the burning velocities S as a function of the heat transferred to the burner the temperature of such nonadiabatic flames (T_Q) was computed and compared with experimental flame temperature measurements (T_{TC}) carried out on a similar type burner with the aid of thermocouple probes. [4] Large differences were noted, $70°K < (T_Q - T_{TC}) < 240°K$ for hydrogen-air flames burning at one atmosphere in different equivalence ratios, even after radiation corrections were applied to the temperatures recorded by the thermocouples. However, consideration of different heat losses known to occur, such as radiation, catalytic recombination of radicals, etc. did not reduce materially the discrepancies between T_Q and T_{TC}. The author concludes that other heat losses must be taken into account. Such energy sinks other than the water-cooled burner may cause the flame speed to be a double-valued function of Q, whereas the burning velocity is a single-valued function of the flame temperature.

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Subject Headings: *Flame, temperature of heat loss from.*

H. Wise

Williams, F. A. (Harvard University, Cambridge, Massachusetts) "On the Assumptions Underlying Droplet Vaporization and Combustion Theories," *Journal of Chemical Physics* 33, 133–144 (1960)

Three of the assumptions underlying theories of vaporization and burning are:
a) that the liquid temperature is constant and equal to the boiling temperature for a burning droplet;
b) that the instantaneous vaporization rate of a droplet at a given size is the same as that of a constant diameter sphere of the same size; and

c) that the duration of the unsteady ignition period is much less than the total burning time of a droplet.

The success of the theories for predicting experimental results is a strong indication that these hypotheses are valid in the experimental region. The author of this paper sets out to determine the range of validity of the assumptions theoretically, and to estimate the magnitude of the resulting corrections to the vaporization rate. To do this, the time dependent conservation equations (one for each species present and one for energy) for a spherically symmetrical, infinite gaseous atmosphere surrounding a spherical droplet are set up and converted to dimensionless forms. The boundary conditions of the problem are specified by the known gas properties (mole fractions and temperature) at infinite distance from the droplet, together with the conservation conditions at the gas-liquid interface.

To determine the validity of the *assumption concerning droplet surface temperature*, the other two assumptions are regarded as valid; and the case where only one chemical species is present actually in the droplet is considered. The two conservation equations then give two relations between three unknowns—droplet surface temperature T_o, mole fraction $Y_{1,o}$ at the surface, and the mass flow rate in the gas per unit solid angle, μ. The third relation is provided by the integrated form of the Clausius-Clapeyron equation:

$$Y_{1,o} = \exp\left[-\int_{T_o}^{T_b} (L/RT^2)\,dT \right]$$

where T_b is the boiling temperature of the liquid and L is its latent heat of vaporization. The solutions involve the ratio β of the heat transferred to the droplet to the heat actually used in vaporization.

For pure vaporization without combustion it is found that as the temperature T_∞ at infinite distance from the droplet increases from zero, then for a given T_o the conditions change first from condensation ($T_\infty < T_o$) to evaporization ($T_\infty > T_o$). As T_∞ increases further, T_o approaches T_b asymptotically. T_o also increases with the mole fraction $Y_{1,\infty}$ of droplet vapor. For the specific conditions $\beta = Cp/R$ (c_p is the specific heat of the vapor, assumed constant), $T_b = L/R$, $Y_{1,\infty} = 0.5$, $(T_b - T_o)$ is less than 10 per cent of T_b when $T_\infty > 5\, L/R$. In the neighborhood of a burning droplet T_∞ is usually much larger than this, so that the assumption $T_o \sim T_b$ should be quite accurate.

When combustion also is considered it is found that $T_o \sim T_b$ when the heat of reaction is sufficiently large, but that the approximation becomes invalid if $\beta \gg 1$. The mass burning rate μ is also found to depend logarithmically on T_o, so that a substantial error in T_o only alters μ slightly. For a typical practical case, the assumptions $T_o \sim T_b$ only produced an error of greater than 10 per cent in μ under conditions where few fuels could be ignited.

To test assumption (b) the steady state is again considered, and it is assumed that T_o is known by assumption (a). For condensation under the somewhat unrealistic conditions of constant density (independent of temperature) in the vapor phase, an approximate solution is obtained which shows that in a typical case with $\rho_l / \rho_o \sim 1000$, where ρ_l is the density of the liquid, the assumption that the rate of growth of the droplet is zero only alters the mass rate of condensation on the sphere by about 0.1 per cent. For vaporizing droplets rigorous solutions probably do not exist but arguments are advanced for believing that here too

ABSTRACTS AND REVIEWS

the correction to the evaporation rate is only about 0.1 per cent, and is much less than the effect of the assumption $T_o \sim T_b$.

The third assumption is investigated only for a vaporizing droplet. For slow alterations of the boundary conditions, so that the temperature and composition profiles never differ appreciably from the steady state and the time derivatives in the conservation equations can be neglected, analytical expressions are obtained connecting time with droplet surface temperature and radius. Using these expressions, together with physical properties approximately valid for many hydrocarbons at atmospheric pressure, it is found that the unsteady period required for the droplet temperature to approach to within 0.1 per cent of its steady state value decreases significantly as T_∞ increases. Small droplet radius and high thermal conductivity of the gas favor short unsteady periods. As T_∞ increases there is also a decrease in the total vaporization time, but this decrease is not as fast as that for the initial period. For $\dfrac{T_\infty}{T_b}$ increasing from 1.5 to 10 the ratio unsteady period, total vaporization time decreases from about ½ to about ¼. If the steady-state conditions are assumed to hold throughout the droplet's history, then the total vaporization time is underestimated by about 20 per cent.

A rough comparison is made between calculated and experimental decreases of the radius of a burning droplet with time, with reasonable agreement. Finally, preignition times have been calculated on the assumption that these times are the same as the unsteady vaporization time. These vary between 1.1 and 0.6 times the experimental times quoted by Wise and Agoston,[1] as well as giving approximately the right dependence on droplet diameter. It is therefore suggested that unsteady vaporization composes the major part of the preignition period.

Reference

1. Wise, H. and Agoston, G. A. "Burning of a Liquid Droplet," *Advances in Chemistry Series, No. 20* American Chemical Society 116–135 (1958)

Subject Headings: *Droplets, vaporization and combustion of; Vaporization, of droplets; Combustion, of droplets.*

G. Dixon-Lewis

VI. Radiation

Rössler, F. (Forschungsinstitut St. Ludwig, Weil am Rhein, West Germany) "Temperature Measurements on a Sooty Flame," Optica Acta 7, 20–34 (1960)

Flame temperature measurement by optical methods offers the unique advantage that it may be carried out without any significant perturbation of the system under study. In the present paper, the author compares two experimental methods for the measurement of flame temperature of incandescent flames—one, the two-color technique, and two, the two-path method. Details of the experiment are presented, and the sources contributing to the experimental error are evaluated in some detail. It is shown that the two procedures yield the same flame temperature with a high degree of precision after suitable corrections are made to the experimental data.

211

However, in the presence of flames exhibiting continuous spectra due to incandescent particles, such as carbon or metallic oxides, some question arises whether such flames can be treated as black-body radiators. It has been known for quite some time that the measured color temperature of a Hefner candle is higher than the true temperature. The cause of this discrepancy is the variation of the emissivity of the carbon particle with wave length and with size distribution in the flame. For very small particles relative to the wave length Mie's theory [1] may be adequate to relate the particle absorptivity to wave length; for large masses of carbon, the emissivity is independent of wave length. However, the intermediate region is difficult to analyze theoretically. In addition, an interpretation of flame-temperature measurements by optical methods is complicated by the fact that the source of radiation is not restricted to an isothermal region. The magnitude of this perturbation in some simple models has been examined.[2] Both, the particle-size distribution and the nonisothermal region resolved by optical measurements and their effects on the experimental results are not considered specifically by the author of the paper under discussion.

References

1. Mie, G. *Annals of Physics*, **25**, 377 (1908)
2. Penner, S. S. *American Journal of Physics* **17**, 422, 491 (1949)

Subject Headings: *Flame, sooty, temperature measurement; Temperature, measurement of, in sooty flames.*

H. Wise

VII. Suppression of Combustion

Applied Physics Laboratory, The Johns Hopkins University "Flame Inhibition Research," Quarterly Progress Report (1 November 1960—31 January 1961)

This is the first quarterly report on a program of basic research on the inhibition of flames by volatile halides. The flame system methane-oxygen has been selected as the first one for study and hydrogen and deuterium bromides have been selected as the inhibitors. The approach to the problem is described.

The flame is to be stabilized on a flat flame burner at low pressures. Composition profiles of stable species are to be determined by the quartz probe technique developed in earlier work. An extension of this technique to the determination of atom and radical concentrations by the rapid mixing of probed samples with suitable scavengers is described. Temperature and aerodynamic profiles are to be determined by the usual methods. In addition, chemical kinetic studies of individual reactions which occur in the flame are planned.

To date only a few preliminary experiments have been performed. A methane-oxygen (7.8 per cent CH_4—92 per cent O_2) flame has been stabilized in a two-inch flat flame burner at 38 mm pressure with and without the addition of hydrogen bromide in amounts up to 0.005 mole fraction. Apparatus to probe the flame and to analyze the products on a Bendix time-of-flight spectrometer has been set up. A composition profile was determined for the uninhibited flame but with the

212

addition of 0.3 per cent hydrogen bromide difficulties associated with the determination of hydrogen bromide in the spectrometer were encountered. The work is continuing.

Subject Headings: *Flame, inhibition, by volatile halides; Inhibition, of flames.*

J. B. Levy

Aidun, A. R. (Syracuse University Research Institute) "Additives to Improve the Fire-Fighting Characteristics of Water," *Bureau of Yards and Docks, Department of the Navy Contract NBy 13027, Quarterly Progress Report No. 11* (April 1960)

In order to ensure adequate removal of smoke from the large-scale fire test apparatus described previously, exhaust facilities were modified to include four natural exhaust stacks in addition to the variable exhaust fan.

Most of the work reported deals with large-scale fire tests. Preliminary runs established the optimum operating conditions to be at a flow rate of 3.6 gallons of extinguishing solution per minute and a preburn time of 4 minutes. Two new viscosity additives, Dow Polyelectrolyte ET-460-4 and Carboxymethyl Cellulose (CMC), were tested under these conditions, except that for some experiments preburn times were varied to permit a more complete evaluation of the effect of the additives on extinguishment. Because of spraying difficulties encountered with these additives at viscosities higher than 7 centipoises, tests were conducted at a viscosity of 5.5 centipoises. Both additives showed ability to improve the effectiveness of water as a fire-fighting agent, but for reasons not yet completely understood the Dow product proved to be much more effective than CMC. This Dow product is said to be one of the more promising of the viscosity additives tested on the large-scale fire test apparatus to date.

The addition of opacifiers, aluminum powder and bronze powder, in various proportions to the Dow Polyelectrolyte solution improved further the extinguishing effectiveness, but not to the extent indicated in previous small-scale fire tests.[*] For these tests, the viscosity of the solution was first adjusted to 5.5 cps with the Dow additive and the opacifier particles (325 mesh) were suspended in the solution with 0.1 per cent detergent (Alkanol WXN). With the aluminum powder, optimum concentrations were found to lie between 0.1 and 0.2 per cent, the solution's effectiveness decreasing at higher concentrations. The bronze powder, owing to its greater density, has a lower coverage per unit weight and greater concentrations were therefore required to give the same effectiveness as the aluminum. The powder has to be added in concentrations greater than 0.2 per cent before any decrease in extinguishing time can be detected. Above this threshold extinguishing time decreases gradually as more powder is added and, at a concentration of 0.3 per cent (the maximum concentration experimented upon) extinguishing time was found to be half that obtained at 0.0 per cent powder concentration. It is realized that further tests at concentrations greater than 0.3 per cent will have to be conducted to fully evaluate the effectiveness of the bronze powder.

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

J. R. Jutras

[*] *Fire Research Abstracts and Reviews* 3, 91–94 (1961)

Barduhn, A. J., Patel, B. S., Meyer, W., and Smura, B. B. (Syracuse University, Syracuse, New York) "Adsorption of Halogenated Fire-Extinguishing Agents on Powders," *National Aeronautics and Space Administration Technical Report* R-51 (1960)

In an effort to develop new and improved fire-extinguishing agents, this study was undertaken with the primary purpose of determining the amount of halogenated hydrocarbon fire-extinguishing vapor that can be adsorbed on a variety of adsorbents and to determine the effectiveness of the combination of solid and adsorbed vapors in extinguishment of fires.

The study was made in two parts: first, an investigation into adsorption in an effort to determine which combination of halogenated hydrocarbons and solids showed promise from adsorption equilibrium considerations; and second, a comparison of the effectiveness of the adsorbed systems and the dry powder systems as fire-extinguishing agents.

Adsorption theories are discussed and data are presented for different vapor and solid combinations over two pressure ranges from 2 to 1000 mm of mercury pressure and from atmospheric to 250 psia pressure and temperatures from 30° to 75°C. Four Freons—Freon 12 (dichlorodifluoromethane), Freon 13 (chlorotrifluoromethane), Freon 13 B1 (bromotrifluoromethane), and Freon 22 (chlorodifluoromethane)—were studied with four solid adsorbents—carbon, silica gel, alumina, and molecular sieves (calcium aluminosilicate). The results generally were that the carbons absorbed 50 to 100 per cent and the silica gels 30 to 50 per cent of their own weight in Freon, and were superior to molecular sieves and alumina.

The fire extinguishing effect was determined by ability and time necessary to extinguish a 5 sq ft gasoline flame in air under an operator's manual control of the discharge of a commercially available extinguisher. The results indicate that bromotrifluoromethane adsorbed on carbon is the only successful adsorption type extinguishing agent and that it appeared to be about as effective as sodium bicarbonate powder expelled under nitrogen pressure. It was noted that the commercial extinguisher was not designed for adsorption type extinguishing agents and therefore the comparison tests are somewhat invalidated inasmuch as optimized discharge techniques were not employed for the adsorption type agents. Although the results of these tests were not rewarding, the authors felt adsorption type extinguishing agents which would be superior to existing extinguishing agents for specialized applications could be developed.

Subject Headings: *Extinguishment, agents, adsorbed on powders.*

D. Dembrow

Hough, R. L. (Wright Air Development Division, Wright-Patterson Air Force Base, Ohio) "Determination of a Standard Extinguishing Agent for Airborne Fixed Systems," *Wright Air Development Division Technical Report* 60–552 (October 1960)

The author presents a historical review of the development of airborne fixed fire-extinguishing systems, and reports the results of the following studies:

1) Flammability and flame speed determinations with propane and dibromodifluoromethane at elevated temperatures, up to 500°F.

ABSTRACTS AND REVIEWS

2) Determination of the influence of the system charge fill ratio and pressuriz-
ing characteristics on the extinguishing effect, using as extinguishing agents bromo-
trifluoromethane, bromochloromethane, bromochlorodifluoromethane, dibromodi-
fluoromethane, and trichlorofluoromethane.

3) Determination of the pressure-temperature relationships of selected charge
densities of the above agents to 500°F.

4) Investigation of the storage stabilities of these agents at elevated tem-
peratures, up to 500°F.

Discussion of the investigation results, and of possible mechanisms of ex-
tinguishment by chemical agents are included. In the discussion of extinguishing
mechanisms, a correlation is suggested between the agent dipole moment and its
effectiveness in inhibiting combustion.

This study was undertaken to determine if consideration of agents other than
bromochloromethane which is currently used by the Air Force, should be made
in order to meet the requirements of the new air-space environment, particularly
exposures to temperatures in the vicinity of 250°F as might be occasioned in the
atmospheric re-entry of a space vehicle. From the study it was concluded (con-
sidering the various requirements of system design, such as minimum pressure
vessel weight) that bromochloromethane should be continued as the Air Force
fixed fire-extinguishing systems agent with the provision that these systems,
charged with bromochloromethane, be protected from exposure to temperatures
exceeding 250°F, since above 250°F thermal decomposition of bromochloro-
methane occurs.

Subject Headings: *Extinguishment, agents, effectiveness of.*

J. E. Malcolm

Nagy, J., Murphy, E. M., and Mitchell, D. W. (U. S. Bureau of Mines, Pitts-
burgh, Pennsylvania) "Controlling Mine Fires with High-Expansion Foam,"
U. S. Bureau of Mines Report of Investigations 5632 (1960)

This report extends previous work by the authors and others on the control
of fires in coal mines by low density foam, prepared at a point remote from the
fire and pushed along the entry as a plug, to serve as a means of transporting
water to an otherwise inaccessible fire.

Sixteen fire tests were run in the Bureau of Mines Experimental Coal Mine,
the most significant using up to 12 tons of coal and transport distances up to
1010 feet. Supplementary foam transport tests without fire were run in an actual
mine.

Foam was prepared by blowing air at a velocity of 80 to 600 fpm through
a net or grid kept wet with foaming solution. Optimum rates were 100 to 200
linear feet per minute. The foam consisted of a mass of bubbles ¼" to 1½" in
diameter, having an initial "expansion" of 500, equivalent to a water content of
2 ounces per cubic foot. This is in marked contrast to foams used in controlling
fires in flammable liquids (National Fire Protection Association, Standard No. 11)
which have very small bubbles, expansions of from 3 to 30, and flow under the
influence of gravity. The foams used in the present tests would not flow, but were
pushed along the passage, completely filling it. The foam plug can turn corners
and accommodate itself to changes in cross section.

Initially the normal mine ventilating fan was used to provide air for foam

215

generation. This was later supplemented by a portable foam generator incorporating its own fan, as would be necessary in most actual fires. Recommended minimum capacity is 15,000 cfm at a differential pressure of 4″ water.

The extinguishing effect of the foam depends primarily on its water content, although restriction of access of air and retention of combustion products in the fire area also contribute. Effective foams had a water content of from 1.0 to 0.2 ounce per cubic foot when they reached the fire; a lesser water content was ineffective. A fire was considered controlled when it was possible for men to traverse the area without breathing apparatus or protective clothing, but deep-seated heat would cause rekindling unless water streams were used for final extinguishment.

Foams suffer both volume shrinkage and loss of water in travel along the entry, the rate of advance of the front of the plug decreasing exponentially with time. In one test, the rate decreased from the initial 160 fpm to 7 fpm at the end of 30 minutes, when the foam reached and controlled the fire 1010 feet away.

The fire tests employed ammonium lauryl sulfate, alkyl aryl sulfonate, or a mixture containing 83 per cent of the former, all at 0.4 per cent concentration. In laboratory tests the effect of water temperature, hardness and pH were determined. It was concluded that water having a hardness of over 500 ppm or a pH less than about 5 should be chemically treated.

Satisfactory foams retained 25 per cent of their initial water content after 15 minutes, roughly equivalent to the 3 minute "25 per cent time" designated as "optimum" in NFPA No. 11.

Conclusions

1) The foam plug method appears applicable when a fire has progressed beyond the stage where it can be attacked by water hoses, and before resorting to the more drastic steps of sealing and flooding.

2) While complete extinguishment cannot be expected, it is indicated that fires may be controlled to permit close approach and direct attack with hose streams.

3) Limitations of the method include the requirement of some fairly elaborate equipment, skilled operation, and proper evaluation of the effects of mine ventilation, water quality, the time that the fire has burned, and other factors.

Subject Headings: *Foam, for control of mine fires; Fires, coal mine, use of foams in control of; Mines, control of fires with foam.*

O. W. Johnson

Izumi, T. "Foaming Properties of the Lime Hydrolyzate of Keratin Protein," *Bulletin of the Fire Prevention Society of Japan* **10**, 21 (1961)

As the tenth report on a series of studies on air foam compounds, the author reports how the foaming property of keratin protein hydroylzed by $Ca(OH)_2$ depends on its composition, the temperature, and the time of hydrolization.

As the standards, the following data were adopted, following J. M. Perri.

Keratin powder	$= 20.0$ g
$Ca(OH)_2$	$= 11.25$ g
Water added	$= 250.0$ g
Temperature for hydrolyzation	$= 95-98\,°C$
Time for hydrolyzation	$= 5$ hr.

216

ABSTRACTS AND REVIEWS

The solution, after being hydrolyzed, was filtered and 1N HC1 was added to bring it to pH 7, the usual value for commercial solutions. Then it was tested after being diluted with 4 parts water.

The foaming capacity of this solution was measured by means of N. O. Clark's beating method which has been found to have an advantage over Perri's air bubbling method. The solution is contained in a cylinder and is beaten at its surface by a circular disk which vibrates up and down. The author improved Clark's apparatus by eliminating the perforations in the beating disk and by increasing the amplitude of vibration, because the AVF (air volume factor, i.e., the volume of air contained in the foam/the net volume of solution) of the foam produced by Clark's apparatus is not always consistent with that of the foam produced by an actual nozzle.

Results obtained are summarized as follows:

1) As the time of hydrolysis is increased, the foaming capacity increases during the first 3 hrs, but is kept constant after that and begins to decrease gradually after 10 hrs.
2) When the keratin component of the solution is increased from 10 to 40 g, the AVF increases proportionally, while the increase of $Ca(OH)_2$ from 2.5 to 11 g shows no remarkable change in the AVF.
3) When the time of hydrolysis is increased from 2 to 10 hrs, the metaprotein in the solution should decrease from 23.9 to 1.5 per cent. In spite of this, the AVF increases from 2.90 to 3.10. Thus, it is unreasonable to consider that the constituent which plays the most important role in foaming is metaprotein, the theory which has been devised by Perri *et al* using the results obtained by their air bubbling method.

Subject Headings: *Foam, properties of keratin protein.*

T. Kinbara

VIII. Model Studies and Scaling Laws

Yokoi, S. (Building Research Institute, Ministry of Construction, Japan) "Study on the Prevention of Fire-Spread Caused by Hot Upward Current," *Report of the Building Research Institute No. 34* (1960)

This lengthy reports deals with the study of fire spread caused by upward flow of gases from burning structures. The work was performed and is presented in three parts: basic theory, temperatures above a burning house, and temperatures on upper parts of buildings caused by a hot gas flow from a lower vertical window. In the latter two parts considerable use was made of models, and a reasonably successful extrapolation to full-scale fires of the model information was accomplished. Full-scale fires were also employed.

Prior to a formulation of the equations governing temperature and velocity distributions above a point or line heat source, a series of experiments were performed. By use of a temperature compensated hot-wire anemometer and a copper constantan thermocouple connected to a recording potentiometer, velocity and temperature profiles above an alcohol lamp (point source) and at the mid-point of a vessel 1 cm wide and 100 cm long (line source) were obtained in five horizontal planes. Plotting of these data on reduced coordinates indicated that a simple

similarity law applied. The governing equations of momentum, continuity, energy, and state were formulated for the point and line heat sources. Since the flow is turbulent, two representations of the eddy viscosity are considered: the momentum transfer theory of Prandtl and the modified vorticity transfer theory advocated by Taylor. To effect a solution of the equations, it is assumed that the temperature and vertical velocity distributions can be represented as a product of elevation raised to a suitable power and the horizontal temperature distribution determined experimentally. Suitable manipulation of the equations yields the desired power for the elevation involved and plotting of the centerline values of temperature and velocity confirm these power values.

By employing the values obtained for the exponents of elevation and assuming that the horizontal distributions are represented by a product of an exponential function and a power series, consideration of the pertinent boundary conditions and judicious use of experimental information to evaluate the ratio of eddy diffusion to eddy viscosity allows satisfactory expression of the horizontal temperature and vertical profiles. To make the foregoing results more useful, a relation between burning rate of alcohol and centerline velocity and temperature was found experimentally. Hence, the temperature and velocity profiles could be expressed as a function of the heat liberated by the source.

A series of sixty tests was performed to determine the velocity variation along the axis of square, circular, and rectangular jets. The results for the circular jet agreed with those of previous investigators. In the case of the square and rectangular openings, it was found that the variation of velocity on the jet axis displayed a constancy at first. The velocity decrease then obeyed the law of the infinite line source, and finally conformed to that of a point source. In that the latter is the most stable pattern, the evolution is not unreasonable. The transition from one region to another for the rectangular jets was found to be a function of the ratio of the side lengths. Expressions describing the velocity variation on the axis for rectangular jets were obtained. Since the third velocity domain was similar to that above a circular jet, an equivalent circular jet could be defined for each rectangular jet.

Similarity relations for excess temperature and velocity above a finite heat source were found by consideration of the basic equations and applying techniques analogous to those for the point and line source. Experimental measurements above heat sources of a continuous (burning alcohol from a surface) and discontinuous (discrete heat sources arranged in a circular pattern) nature were made. The results showed that the temperature distribution obeyed two laws. In the region near the source, the center portion of the horizontal temperature profiles were flat and then fell to ambient. Further from the source the distributions approximated the Gaussian. Examination of the experimental data indicated that a minimum source size exists for similarity to prevail. Below this minimum heat release per unit area is a function of radius. The fact that above a certain diameter heat release per unit area is independent of size allows the experimental findings to be applied to full-scale fires.

Since most wooden houses are rectangular, the temperature field above a rectangular heat source was determined. In view of the findings for the velocity field, it was expected that three regions would be found. This was confirmed by experiment. The ratio of length to width will affect the temperature field strongly; the rate of decrease in the vertical direction being greater for narrow structure

than square. Temperature distributions above four sample structures of varying length to width ratios in the absence of winds were calculated during maximum fire intensity based on standard temperature-time curves and combustible concentrations for Japanese dwellings. Corrections are introduced for radiation loss due to entrained carbon particles.

In the light of the foregoing analysis and experimental findings, the problem of fire protection of television towers built in crowded areas is considered. While these structures have been built with due regard to earthquakes and typhoons, little attention has been paid to the structural weakening caused by building fires near their base. Calculations based on the prior work indicate that if combustible buildings are located within 60 meters of a tower base the possibility exists that tower members will be exposed to temperatures of approximately 1450°F. The subsequent reduction in strength will threaten collapse. Encasing of steel members in concrete is proposed as a protective device.

In examining the spread of fire from floor to floor, four full-scale tests were performed on three concrete fire-resistant buildings. During the tests, room temperatures were observed at various elevation and plan positions. Temperatures and velocities of out-flowing gases at the window openings were observed and the cracking and/or failure of various glazing materials, i.e., plain glass, wire-reinforced glass, etc., noted.

The room temperature rise was found to follow a standard time-temperature curve when the curve was suitably displaced with time. Flame ejected from a lower floor window was found to impinge on the windows of an upper story causing cracking and, in the case of the plain glass, failure. The lower edge of the upper window was approximately fifty centimeters above the lower windows. This vertical rise is less than the tentative standard of the Japanese Ministry of Construction. Temperature measurements of the ejected flames showed that windows with a horizontal length greater than height cause the upper portions of a building to be exposed to higher temperatures than will a window opening of opposite form, i.e., height greater than width. The outflow of gases from the window opening was found to vary with time (fire intensity) and reached values in excess of twenty-one feet per second in some tests. A temperature of about 900°F was found to cause plain glass in upper windows to rupture, thus facilitating fire spread. Wire reinforced glass maintained its integrity. A similarity between temperature profiles outside a window caused by a fire and that from an experimental finite-size heat source was found.

Subsequent to the full-size fire tests a theoretical treatment of outflow velocity from rectangular openings was made. The relation for efflux velocity could be expressed in terms of room temperature excess, i.e., amount above ambient, and position above the neutral plane, i.e., the location below which air flows into the room through the window rather than out. The analysis was based on the assumption of no vertical wall above the opening. The theoretical treatment was extended to determine the locus of points describing the maximum distance above the datum for each isovel, i.e., line of constant velocity.

Model tests substantiated the analysis for the case of no vertical walls above the aperture. However, a considerable variation from the predicted distributions were observed when a vertical wall was placed above the windows. A shift of the locus of maximum velocities toward the wall was observed, which was attributed to the asymmetric inflow of air. A method of extending the calculations to this case

219

was found and comparisons made with the results of the full-scale tests. The agreement was found to be excellent. The analysis predicted the effect of window aspect ratio previously observed.

Since in fire prevention work the important factor is the temperature contours outside a vertical opening and the effect upon the upper stories of a structure, work was undertaken to determine temperature profiles. The first phase of this work dealt with windows of similar shape but varying dimensions, i.e., aspect ratio constant. The second phase dealt with windows of constant height but varying width. It was found that the results obtained from the rectangular heat sources (horizontally oriented) yielded profiles similar to those of a vertical opening of the same width but twice the height. Although similar, the profiles were not identical.

A comparison of profiles obtained for openings with a wall above with those without walls indicated that the asymmetry caused the maximum temperature to bend in toward the building walls. Again the shorter and wider windows caused the upper wall to be exposed to higher temperatures. It was found that in the case of temperature profiles the work on models was directly applicable to full-scale fires with no need for modification as necessary in the velocity case. This unmodified extendability may be coincidental, i.e., the result of compensating errors. The results from these tests can only be applied to those cases where combustion in the room is complete. Incomplete combustion will result in a severe modification of the temperature profiles outside and above the windows, since flame and heat release will continue after efflux from the window.

The trend toward fireproof structures containing large windows has posed a problem insofar as fire spread is concerned. It has been recognized in Japan that spread of fire from floor to floor in a fire-resistant building is enhanced by the presence of large windows. Accordingly, the Ministry of Construction has set a tentative standard of 90 centimeters as the minimum vertical wall distance from the top of a lower window to the bottom of an upper story window. The results of this paper indicate that a standard dependent upon window size, room area, combustibles in the room, etc., is required rather than a fixed value.

The previous findings of this work and the results of other prior works were used to determine the distance required between vertical windows to prevent the spread of fire. To do this, a fire duration and burning rate were calculated for various conditions based on prior work. Temperatures during the period of maximum intensity were also based on prior experimental work. These quantities were used to determine the heat discharge from a window. Given the above quantities, calculation of the required height is possible. A distance based on a temperature of 900°F was used. Calculations indicated that for a room of 4m x 5m x 4m and combustibles loadings ranging from 25 to 200 kg/m^2, the tentative standard was insufficient for protection. The number of variables involved in these calculations make the preparation of standard charts impossible; hence, each case requires individual calculations.

Attachment of a projection above a window offers the attractive possibility of deflecting the outflow of hot gases from the building, thus allowing the needed vertical distance between windows to be diminished with a consequent greater architectural freedom. To investigate this effect quantitatively a model study was made. It was found that a substantial deflection of the hot gas outflow occurred and was especially pronounced close to the upper edge of the window. At greater

heights the size of the projection exerts lesser effect and all trajectories approach the situation of no projection. Again the effect of window aspect ratio is strongly felt. The case of two projections one above the other was also examined. The second projection was found to exert little effect. Temperature profiles were also obtained from the model fires and were found to fall between the limits with no projection and a vertical wall and no vertical wall. Hence, a temperature reduction on the building wall was obtained by use of a projection.

Calculations analogous to those previously outlined were performed for the vertical rise required between windows for fire prevention. A substantial reduction was found possible in all cases. Reduction ranged from 25 to 100 per cent.

Subject Headings: *Fire spread, prevention of; Convection, currents above fires; Temperature, distribution, in convection column above fire.*

H. N. McManus, Jr.

Langdon-Thomas, G. J. (Joint Fire Research Organization, Boreham Wood, England) "Fire and Space Separation," *The Builder* No. 6130, 887–893 (November 11, 1960)

This paper is concerned with the problem of designing new buildings in such a way as to prevent the spread of fire across the open space between the new building and any adjacent building. Such spread of fire is due to the transfer of heat from the fire to adjacent exposed combustible materials, raising their temperature sufficiently to cause ignition. The main mechanisms by which the heat can be transferred are (1) radiation, (2) convection, i.e., the flow of hot gases coming into direct contact with the exposed surface, and (3) flying brands.

The author points out that radiation is the most important of the three mechanisms, and the most dangerous, in so far as the adjacent combustible material may be raised to its ignition temperature by radiation without any visible effects to give warning. When considering the design of a new building, this problem of the spread of fire by radiation may be tackled in two ways:

1) By providing an imperforate barrier of sufficient fire resistance between the possible source of the fire and adjacent combustible material, and

2) By providing sufficient space between the source of the fire and adjacent combustible material so that ignition by radiation cannot take place.

This paper describes a procedure which may be followed by the building designer in order to determine a sufficient (although sometimes more than necessary) space separation to prevent the spread of fire by radiation. The procedure is based on experimental work and theoretical methods developed by the Joint Fire Research Organization and reported in a Fire Research Note.[1]

The design process is subdivided into four stages:

1) The determination of what part of the side of a building must be taken into account in the calculations.

2) The determination of the extent of the exposure hazard from the side of the building.

3) The determination of a minimum space separation based on the assessment of the risk determined by stage 2.

4) The location of any special area of exposure hazard which may call for a greater or lesser separation than has been obtained from stage 3, and the determination of the final distance of the building from the boundary.

221

In making calculations based on radiation hazard, any part of a wall which may contribute to the hazard is taken into account, and classified as an "opening." Thus, any part of the wall that does not possess the required fire resistance and any combustible material whether used as cladding or as an applied decoration to the external wall must be included in the calculations as an "opening", in addition to all doors and windows.

The four stages in the design process are followed through in detail in the paper, and all new concepts are clearly defined as they are introduced. Many numerical and diagrammatic illustrations are included, which clarify considerably the new ideas and methods of calculation employed. To simplify the calculations necessary in stages 3 and 4, tables worked out to cover a wide range of possible cases are included. In practically all cases the information and techniques presented in the paper should be adequate, but any special problems which are not covered can be resolved by reference to the detailed work on which the paper is based.[1]

With this method of calculation available, the building designer has two possible lines of approach (1) to vary the location of the building in relation to the boundary, and (2) to adjust the design (i.e., the area and arrangement of openings) of the new building to accord with a predetermined space separation that may be imposed by site conditions.

By using the methods presented at an early stage in the design of the building the designer can ensure that the necessary space separation need not be excessive.

Reference

1. Law, M. "Radiation from Fires and Building Separation," *Department of Scientific and Industrial Research and Fire Offices' Committee Joint Fire Research Organization, F. R. Note 437* (1960)

Subject Headings: *Fires, in buildings, spread of; Fires, spread of, between buildings.*

R. G. Siddall

Townsend, A. A. (University of Cambridge, Cambridge, England) "Temperature Fluctuations Over a Heated Horizontal Surface," *Journal of Fluid Mechanics* 5, 209–241 (1959)

Townsend studied experimentally the turbulent, convective motion over a heated horizontal surface. Distributions of mean temperatures, mean squares of the temperature fluctuation, the temperature gradient and the rate of change of temperature were measured. Also the statistical distributions of these quantities were measured for three different values of convective heat flux.

In this article Townsend exhibits his customary skill in selecting an interesting problem, in disentangling physical reality from a relatively complex maze of experimental results and in making meaningful comparisons with theoretical predictions. Of the many important applications of these studies of heat convection, Towsend elects to discuss a meteorological example that demonstrates the care that must be exercised in applying the results of convection experiments. He shows that the experimental results obtained here do not apply directly to natural convection in the atmosphere above the surface of the earth since there is nearly always a horizontal shearing motion superposed on the homogeneous natural convection.

In his experimental work, Townsend made an extremely interesting discovery.

When he measured at a point some distance above the surface, he observed periods of activity alternating with quiescent periods. The periods of activity were characterized by large fluctuations and the periods of quiescence by small ones. The frequency of occurrence of the active periods decreased with increasing distance from the surface and Townsend inferred that they probably occurred when rising columns of hot air passed through the point of observation. The quiescent periods occurred when the point of observation lay outside the columns and analysis of the statistical distributions showed that, during these periods, the distributions were nearly independent of height—they were not influenced by the conduction layer close to the surface of the body. The active period fluctuations, on the other hand, depended intimately on the layer.

Townsend concluded that the quiescent fluctuations were typical of the turbulent convection far from the surface while the active fluctuations were the manifestation of the convective processes arising near the rigid boundary. These processes may be described as the detachment of hot air from the top of the conduction layer (close to the rigid horizontal boundary) and the erosion of these rising columns by contact with the surrounding air which is in vigorous turbulent motion.

The experimental convection system was an open-topped box with bottom a horizontal and uniformly heated plate, 30 cm x 40 cm. The side walls were 56 cm high and are intended to ensure that convective transport of heat is as far as possible by turbulent transport and as little as possible by steady streaming motions. Outside of the box there was a gentle upward stream of air, and inside the box there were weak secondary air currents. However, Townsend succeeded in showing that these currents had negligible influence on the turbulent convection of heat within the box and that the experiment well approximated the ideal situation of convection over a single, infinite, horizontal surface in a perfect gas without other boundaries. The measurements were confined to the region within 8 cm of the horizontal plate and the important conduction layer close to the plate was only 0.3 cm thick. For these dimensions the side walls were shown to have little influence. Also great care was exercised in making the temperature measuring head so small that its influence on the flow and temperature distributions was negligible. The sensitive element was a short length (1–2 mm) of platinum wire, of diameter 2.5 microns, etched from Wollaston wire and supported by pieces of unetched wire of diameter 25 microns. In still air the time constant of such a wire is about 0.5 milliseconds. In order to obtain useful approximations to the mean values, it was necessary to take averages over periods of ten minutes, and this was done by converting the electrical output of the resistance thermometer into pulses whose repetition rate was a linear function of the wire resistance. Temperature gradients were measured with a thermometer head with two sensitive elements, each about 1.5 mm long and held parallel to each other with a horizontal separation of 0.212 cm.

In the experiment the boundary conditions were defined by the surface temperature of the horizontal plate and by the temperature at a point 40 cm above the surface of the plate, used as a reference temperature and as an approximation to the "temperature at infinity." Three values of heat flux were used, corresponding to temperature differences between plate and reference of approximately 20, 40, and 60°C. The heat flux was obtained from measurements of the mean temperature gradient near the surface.

223

All results of the measurements were present in the non-dimensional form appropriate to the ideal system, with units the non-dimensional scales of length, velocity and logarithmic temperature that may be constructed from the thermometric conductivity, the gravitational acceleration and the buoyancy flux Q where $Q = H/\rho c_p T$ and H is the heat flux, ρ is the air density, c_p is the specific heat of the air at constant pressure and T is the absolute temperature of the air.

Using non-dimensional variables to plot experimental results the mean temperature distribution was indeed the same for all values of heat flux, up to a moderate distance above the surface, but not for large heights. In these variables the mean square of the temperature fluctuation was nearly independent of heat flux. It increased linearly from zero at the surface, then increased more slowly until it reached a maximum at some distance outside of the conduction layer and finally decreased according to a power law. Mean squares of the temperature gradients and of the time-rates-of-change of temperature varied in much the same fashion.

Study of the statistical distributions of the fluctuations showed two modes as discussed in the first part of this review: comparatively infrequent active periods during which temperature oscillated wildly alternately with extended periods of quiescence. The statistical distribution of the quiescent mode was roughly normal while the distribution of the active mode was far from normal and was easily distinguished from the first mode. The intensity of the active component decreased rapidly with distance from the plate and far away from the plate the distribution was principally that of the quiescent mode.

It appears probable that active regions are formed by more or less localized emission of heat from the conduction layer. These sources of heat persist for an appreciable length of time—of the order of twenty times the scale time in these experiments. A possible explanation is that, once a site is established it attracts to itself air heated by passage through the conduction layer which adds to the strength and stability of the up-draft.

Subject Headings: *Temperature, fluctuations, over heated surface; Convection, above heated surface.*

F. H. Wright

Schreiner, K. (Stuttgart-Bad Cannstatt, West Germany) "A Contribution to the Performance Calculation on Water-Spray Curtains," *VFDB Zeitschrift Forschung und Technik im Brandschutz* 9, 113–118 (1960)

This paper considers the possible use of a water-spray curtain as a means of preventing the spread of fire in mines by (1) direct flame propagation, (2) radiant energy transmission, or (3) flying burning debris. Schreiner determines physical characteristics desirable for such sprays.

In considering the transmission of radiant energy through a water-spray curtain, Schreiner follows the work of Thomas [1] where it was assumed that the radiation falls normally on the plane of the water-spray curtain, all reflected radiation can be neglected, and the Lambert-Beer law is valid. Correcting the coefficient of absorption for drop diameter, Schreiner calculates the radiant energy transmitted through the water curtain as a function of drop diameter and number density of drops. All numerical calculations are made assuming the radiant energy to be emitted from a plane surface, parallel to the spray curtain, infinite in extent

224

and heated to a temperature of $1000°C$. For a fixed volume of liquid per unit volume of the atmosphere and for a given spray curtain thickness, the smaller drops are more effective than the larger in preventing the transmission of radiant energy. However, since these finer sprays are more readily dispersed by lateral air motion than the coarser sprays, a fine spray pattern is not altogether desirable. Therefore, Schreiner recommends the use of a spray nozzle that will give a broad spectrum of drop sizes. Since he has represented all his plots in dimensionless units, his results are readily adaptable to numerical calculation involving other situations (i.e. different spray medium, other radiating fields).

In the latter part of his paper, Schreiner is concerned with the dynamics of sprays. He assumes the spray drops emerge from the spray nozzle with an initial velocity and fall vertically through a quiescent atmosphere. He subsequently develops an equation of motion containing the initial force, the gravitational force, and the resistive force due to the surrounding quiescent atmosphere. The resistive force is assumed to be directly proportional to the square of the particle drop velocity. This differential equation is integrated between the states corresponding to the initial velocity of the drop as it emerges from the spray nozzle and the terminal velocity corresponding to the point where the gravitational force balances the resistive force. Beyond this point, where the gravitational force balances the resistive force, the drop falls with a constant velocity. Schreiner shows that for small drops (0.2 cm diameter) the terminal velocity is reached in a very short fall (10 cm per initial velocity of 20 cm/sec).

Since a quiescent atmosphere does not generally correspond to reality, Schreiner considers the situation where the atmosphere is set in motion by the falling spray. Following the work of Radusch, Schreiner derives another set of equations based on the conservation momentum. From these relations he derives an expression for the time required for the falling drop to reach its terminal velocity. For a particle of 0.2 cm diameter and an initial velocity of 20 cm/sec this time, in the case of moving atmosphere, corresponds to about one-fifth the time required under quiescent conditions.

Considering all these results, Schreiner concludes that although a fine spray has the desirable properties for preventing the spread of fire, a coarse component to the spray is necessary to prevent lateral air motions from dispersing the water curtain. Schreiner has further substantiated these results by prior experimental work.

Reference

1. Thomas, P. H. "Absorption and Scattering of Radiation of Water Sprays of Large Drops," *British Journal of Applied Physics* 3, 385 (1952)

Subject Headings: *Water curtains, prevention of fire spread by; Fire spread, prevention of, by water curtains.*

<div align="right">H. E. Perlee</div>

Seekamp, H. (Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, Germany) "Investigations on the Effectiveness of Water Curtains," *VFDB Zeitschrift Forschung und Technik im Brandschutz* 9, 34–38 (1960)

The author presents experimental data and a technical discussion concerning the effect of water-spray curtains on the attenuation of heat transfer, primarily from the standpoint of thermal radiant energy transmission.

The study was motivated by the general practice of sectionalizing industrial activities in such a way that accidental fires may be limited in their scope. The author points out that in certain fabricating operations this sectionalization may not be practicable or compatible with the industrial process, if the means of accomplishment are limited to permanent walls, doors, or barricades. The proposed alternative is the use of fixed or portable water-spray devices to form a "fire curtain" at desired points.

The attenuation of radiation by a water-spray curtain could be expected only in certain discrete ranges of wavelengths of the emitted radiation. Physical effects of a fire producing radiation, such as strong indrafts, could perturb the spray curtain sufficiently to alter its effectiveness. It was presumed that the nozzle type, configuration, and resulting spray density would determine the spray effectiveness in absorbing radiant energy.

The study was undertaken to determine the general feasibility of the water-spray curtain, and to develop parameters of application.

Experimental Devices and Techniques

Two spray-curtain producing systems were used.

1) Nine spray nozzles at *ca.* 56 cm centers in a one-inch pipe 5 meters long (capable of producing a downward projected elliptical pattern), maximum dimensions 7 meters long (along axis parallel to the 5-meter pipe) and 2 meters wide (along axis perpendicular to the 5-meter pipe).

2) Seven nozzles, at *ca.* 76 cm centers along 5 meters of pipe, initially 1¼ inches in diameter reduced successively to 1 inch and ¾ inch diameter, each nozzle capable of producing a downward projected circular pattern of 6 meters, maximum diameter.

Within the limits of the experimental setup, little pattern change resulted from line-pressure change or change in elevation of the pipe above the spray-impinged floor. Favored pressure and elevations were 2½ atmospheres and 7½ meters respectively. The radiation source was composed of four oil burners operating vertically at ½ meter centers, giving an over-all flame-radiating area of *ca.* 2 meters by 2 meters. The oil consumption during operation was about 40 kg/hr. The burners were installed directly in front of a brick wall which acted as a wind screen, and to a certain extent as a refractory surface. The flame temperature was checked with a radiation pyrometer, and held within the temperature range of 1150° to 1200°C.

The radiant energy flux density was measured directly in watts/cm² by means of a device produced by Pyrowerk Hannover. The distance of the measuring device from the flame wall depended on the test configuration. With configuration (1), it varied from 3.5 to 4 meters, and with configuration (2) from 5.0 to 6.8 meters. In all cases it was centered on the line perpendicular to the flame vertical plane, midway. The test procedure was to first adjust the water nozzle height flow rate, etc., then turn off the water, start the burners, and allow to stabilize in ½ hour of operation (i.e., noted by obtaining a relatively constant reading of radiant energy flux density at the point of observation). After obtaining a base line radiant flux reading, the water-spray curtain was activated and the second flux reading was made. The rate of water application was also measured by total collection over a known period of time.

226

ABSTRACTS AND REVIEWS

Experimental Results

The experimental results are shown in the following table.

TABLE 1

TEST VALUES

| Nozzle type (Thickness of Curtain) | Spraying height m | Water per nozzle 1/s | Distance radiation measuring point m | Test no. | Radiation flow density at measuring point Watts/cm² | | Decrease per cent |
					Without water curtain	With water curtain	
	2.5	0.12	3.5	1	0.61	0.51	16
				2	0.64	0.50	22
	5.0	0.12	3.5	3	0.58	0.46	20
A (2 m)	7.2	0.11	4.0	4	0.25	0.20	20
				5	0.42	0.37	12
	2.5	0.20	3.9	6	0.66	0.58	12
				7	0.72	0.61	15
	2.5	0.16	5.0	8	0.37	0.33	12
B (6 m)		0.21	5.0	9	0.44	0.36	18
	5.0	0.16	6.8	10	0.26	0.23	10
				11	0.25	0.22	12

It was not possible to establish dependencies between the three variables (tube height above the floor, thickness or depth of the water curtain, and the water rate) and the effectiveness of the curtain. It was reasoned that the maximum mean decrement of radiant-energy transmission which could be expected would be about 20 per cent, taking 99 per cent confidence limits, and using the results reported as random samples.

Results of experiments were cited wherein the radiation exposure times for ignition of a strip of newspaper in cases where exposure was preceded by operation of the water curtain in close proximity to the paper sample were compared to those in which no water-curtain operation was made. In the case of no water-curtain pre-exposure, $2\frac{1}{2}$ minutes exposure to radiation sufficed for ignition; in the case of pre-exposure to the water curtain, 10 minutes exposure to the radiation was required to effect ignition. These results point out that in addition to attenuation of radiant energy, other beneficial effects of the water curtain, such as increasing the moisture concentration in exposed combustibles, and convection cooling, may be realized, thus justifying the selection of the upper value of 20 per cent as the mean decrement of radiant-energy transmission for further analysis of the use of water curtains.

In the evaluation of the test results the author used material presented by McGuire,[1] wherein the radiation intensity was presented essentially as:

$$I = \epsilon \sigma T^4 \Phi = \epsilon \sigma \tau^4 \frac{1}{\pi} \int_0^{s'} d\omega \cos \theta$$

I = intensity of radiation at receiver
ϵ = emissivity, or black body constant, taken as unity by the author
σ = Stephan-Boltzman constant $= 1.37 \times 10^{-12}$ cal cm^{-2} sec^{-1} °K^{-4}

227

T = temperature of radiating body, °Kelvin
Φ = configuration factor
s' = limit to indicate solid angle subtended by whole of radiation is considered
θ = angle of incidence of radiation falling on irradiated surface
dω = solid angle subtended at the radiator by the elemental receiving area

For a scheme as shown, indicating parallel surfaces
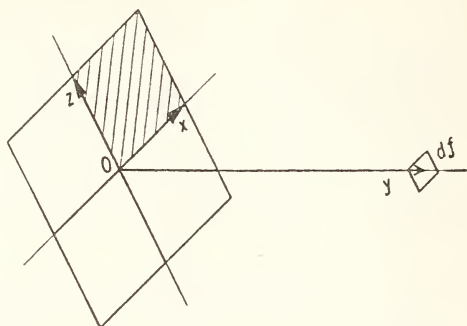
the configuration factor Φ was taken from McGuire (*op. cit.*)

$$\Phi = \frac{2}{\pi} \left(\frac{X}{\sqrt{x^2+y^2}} \text{ arctg} \frac{Z}{\sqrt{x^2+y^2}} + \frac{Z}{\sqrt{z^2+y^2}} \text{ arctg} \frac{X}{\sqrt{z^2+y^2}} \right)$$

To avoid ignition on surface element df it was pointed out that the value of I could not exceed a critical value, taken as 0.6 cal cm^{-2} sec^{-1} for wood fiberboards, thus $I_{cr} = 0.6$ cal cm^{-2} sec^{-1} was taken as an upper limit. A temperature of 1273°K was assumed as the radiating surface temperature (1000°C, 1832°F is generally accepted as typical of free air burning wood or petroleum). Then assuming a 20 per cent decrement in radiant energy transfer by interposition of a water curtain between source and receiver,

$$I = 0.8 \ \sigma \ T^4 \ \Phi = 2.88 \ \Phi \text{ cal cm}^{-2} \text{ sec}^{-1}$$

where $I_{cr} = 0.6$ cal cm^{-2} sec^{-1}

$$\Phi_{cr} = \frac{0.6 \text{ cal cm}^{-2} \text{ sec}^{-1}}{2.88 \text{ cal cm}^{-2} \text{ sec}^{-1}} = 0.208$$

i.e., where $\Phi = 0.208$ is not exceeded, angle exposures with the water curtain interposed will remain within danger limits.

Further, where $\Phi = 0.208$, or

$$0.208 = \frac{2}{\pi} \left(\frac{X}{\sqrt{x^2+y^2}} \text{ arctg} \frac{Z}{\sqrt{x^2+y^2}} + \frac{Z}{\sqrt{z^2+y^2}} \text{ arctg} \frac{X}{\sqrt{z^2+y^2}} \right)$$

the relation between x and Z can be determined with the aid of the McGuire table, since y is given by the water-screen thickness.

It was stated that relationships and curves for other thicknesses of the curtain could be obtained through extension or contraction of the origin of coordinates, and a series of curves were presented based on $I_{cr} = 0.6$ cal cm^{-2} sec^{-1} for opening dimensions of 0.5 x 0.5 meters to 17 x 100 meters wide, showing the limiting values

228

of these openings using selected water-screen thicknesses up to 12 meters. For example, at 12 meters screen thickness, the maximum permissible opening to keep under $I_{cr} = 0.6$ cal cm^{-2} sec^{-1} indicated by the plots would be 5.02 meters high x 100 meters wide, or intermediate values terminating at 16.5 meters high by 8 meters wide. Examples were given on the use of the plot.

Another plot was presented which correlated water-curtain thickness per unit height of opening *vs.* opening width per unit opening height for three values of I_{cr} 0.6, 0.8, and 1.0 cal cm^{-2} sec^{-1}. This plot was presented in view of different critical radiation intensity values for differing fuels, and release of toxic fumes in some materials at radiation intensities above 1 cal cm^{-2} sec^{-1}.

In conclusion, the author pointed out the necessity of refining the basic data presented on the radiation attenuation by water droplets, particularly with respect to character of the water droplets (density in space dispersion, and size) and the inherent effect of curtain thickness of radiation attenuation. Laboratory-scale study was suggested. In the interim, the author recommended that the tabulated relationships should be applied only with some tempered judgment, since it could not be stated that the proposed methods would be effective in preventing ignition in all cases.

Reference

1. McGuire, J. H. "Heat Transfer by Radiation," *Fire Research Special Report No. 2* London (1953 reprint 1955)

Subject Headings: *Water curtains, prevention of fire spread by; Fire spread, prevention of, by water curtains.*

J. E. Malcolm

X. Meteorological Interactions

Countryman, C. M. (Pacific Southwest Forest and Range Experiment Station, U. S. Forest Service) **and Schroeder, M. J.** (U. S. Weather Bureau) "Prescribed Burn Fireclimate Survey," *U. S. Forest Service Pacific Southwest Forest and Range Experiment Station Technical Papers 29 (December 1958), 31 (April 1959), 34 (July 1959), 35 (July 1959)*

Application of available knowledge of behavior of wildland fires "is frequently hampered by lack of information about behavior of fireclimate in specific places—how wind, temperature, humidity, and fuel moisture are affected by topography, water bodies, season, and the fire itself." Since existing weather stations are widely spaced, gather only momentary samples of weather, and provide no information on the effect of the fire on weather pattern, the Pacific Southwest Forest and Range Experiment Station has started studies to establish "some of the principles controlling local fireclimate patterns and the effect of fire on these patterns." One part of the study program is to make short-time surveys around prescribed or planned fires set by forest land managers for brush clearing, logging slash disposal, etc. These studies, as represented by the present series of four made in 1957, explore fireclimate patterns and provide details of some of their phases.

Weather observations were begun three to eight days before each fire started and continued until it was out. The planned fire areas were about one-half to two miles in breadth and length. Along the previously prepared fire lines surrounding each area, the investigators set up five or six continuous recorders of wind speed and direction and one to three recorders of temperature and relative humidity. In addition they intermittently measured these weather elements with hand-held instruments at 11 to 18 other important points of topography or exposure. Each report includes a diagram of the area giving significant topographical features and locations of the different types of instruments. Each report briefly describes the general weather pattern of California and vicinity during the period studied including pressure distribution, air masses, and winds aloft. Sample charts of significant features of the weather in the burn area and photographs of the fuels, slopes, and fire are included.

Paper 29 concerns an area of light grass, scattered clumps of brush 2 to 4 feet tall, and an open stand of oak trees in the lower foothills of the Sierra Nevada northeast of Fresno, California. The westerly slopes are moderate but become steep on the east side of the area. At 11:00 a.m. just before starting the fire, the temperature was 84°, the relative humidity was 22 per cent. Wind in the vicinity, but removed from the fire influence, was westerly 6 to 10 miles per hour.

Fires were first set along the upper side of the area and were allowed to back slowly down the slope a considerable distance from the automatic wind recorders before the lower side of the area was set. Although a hot moving front did not pass the observation stations, the fire did appear to affect the wind pattern. The authors were "looking particularly for effects of fire on the wind patterns on the lee side of the fire." Several abrupt and progressive changes in direction from station to station along the fire line are described in relation to the heat developing at different times and places at considerable distance inside of the line. "One surprising phenomenon observed in the survey was an increase in wind speed on the lee side of the fire near the head of one small canyon. This is an area where indrafts have usually been thought to decrease prevailing wind speed or to change its direction. This apparent effect of fire must have further investigation and study."

Paper 31 describes a burn mostly in dense brush 6 to 8 feet tall on a steep east-facing slope in the lower foothills of the Sierra Nevada near Sonora, California. Observations before the fire showed the wind pattern to be expected. The general wind flow caused by pressure patterns and large-scale thermal effects was westerly. The local circulation from local heating and cooling was most evident at times and places where effect of the general circulation was least. The combined pattern for five different times of day are illustrated. The authors were particularly interested in the air flow on the lee side of the ridge. Changes in weather in the area during general changes in the synoptic weather pattern in the week before the fire are described.

The authors prepared a forecast of detailed wind directions and speeds and temperature and humidity for the day of the burn. The forecast was well verified by the actual weather. Fire behavior also followed the pattern expected. Firing began about 8:00 a.m. at a place where difficulty in holding the line was expected and continued later around the perimeter until noon. A large "firewhirl" was observed developing and moving out of an area where the survey had shown probable existence of eddies. From another sector in light fuel one spot fire

started 1,500 to 2,000 feet across a reservoir from the nearest fire. The authors suggest that warm air flowing above cool air at a water surface or in a canyon may carry sparks farther than normal. A general conclusion of the study was that the fireclimate had far more effect on fire behavior than the fire had on the fireclimate.

Paper 34 describes a prescribed burn north of San Francisco 60 miles from the ocean on an east-facing and moderately steep slope ranging from 1,100 to 2,200 feet in elevation covered with a moderate to dense stand of brush. The survey on five days before the fire showed that instead of up-slope winds during the day and down-slope at night, the up-slope winds in the burn area changed to down-slope about noon and increased in speed to 6:00 p.m. Another pattern occurred on the higher more exposed points and in the southeasterly draining valley. Aided by the survey results, the authors prepared a detailed forecast for the day of the fire which was well verified by actual weather.

The firing followed a plan prepared before the wind survey and apparently based on up-slope spread of the fire. The sets on the westerly edge ran rapidly down-slope with the westerly wind. Spot fires also started across the drainage to the east and were concentrated about one-third the way up the slope. As suggested by the spot fire in Paper 31, cooler air in the valley bottom may have influenced the warmer air from the fire to carry farther than expected.

Paper 35 describes a burn 70 miles west of Sacramento, California, on a steep northeast-facing slope covered with a heavy stand of brush. The well-defined canyon opened "into a relatively broad valley—topographic features supposedly ideal for the normal mountain wind pattern" of up-slope, up-canyon and down-slope, down-canyon winds. The survey wind records averaged over periods of an hour or more indicated this pattern, but major variations occurred during short periods and the directions were highly variable. Neither of two attempts eight days apart were successful in burning the area. Although fuel was dry and humidity was low the second time, wind direction and poor fuel arrangement nullified those factors. The smoke did verify the air-flow pattern previously observed. "The observations suggested that air movement in the canyon might occur in layers—each layer moving in a different direction."

The surveys indicate a "need for more complete measurements of environmental factors in field research in fireclimate patterns and fire behavior."

Subject Headings: *Weather, effect of, on prescribed burns; Fire climate.*

<div align="right">W. G. Morris</div>

XI. Operational Research Principles Applied to Fire Research

Bruneton, M. (National Federation of Military Firemen of France and the French Union, Fire Services of Alpes-Maritimes, France) "The Struggle against Forest Fires," *Courrier de la Normalisation* **24**, 550–557 (1957)

The stated purpose of this report is to improve public understanding of the resources for fighting forest fires and the conditions under which they are applied.

France has two distinct regions related to forest fires: (1) the littoral of the Mediterranean near Italy and the littoral of the Atlantic near Spain—dry

climate, strong winds, and predominantly coniferous forests produce fearful fires; (2) the remainder of France—fires are not feared except in the pine plantations or in autumn and spring.

Forest-fire fuel characteristics of conifers and broadleafed undergrowth, wind, temperature, relative humidity, and terrain are briefly discussed to explain how they affect fire behavior. One statement that may be questioned is that the shrubs and plants in the undergrowth evaporate volatile oils which, during the hot hours of summer, need only a spark to ignite them.

The number of fires and area burned by causes are listed for each of the four years 1953–57. For the average year, 2,095 fires burned about 66,000 acres. Causes and their percentage of the total number were: negligence 33, railroad 8, malevolence 3, lightning 2, other causes 7, and unknown causes 47. (In the United States, policy usually requires that practically every fire be assigned to its probable cause class.) The average damage size was 32 acres, but "malevolence" and "other" averaged 42 acres while "railroad" and "lightning" averaged 12 acres or less.

Tactics of attacking fires are briefly discussed according to four classes based on light or strong wind and rough or smooth terrain. Except in the rougher terrain, the usual road network allows use of tank trucks with power pumps. Tank and pump capacity are given for three sizes of vehicles ranging from the small jeep with 65 gallons to a large truck with about 800 gallons. Bulldozers, etc., are used for large fire lines when the terrain permits. Helicopters are used for observation and radios for communication. Hand tools such as green branches, rakes, fire bats, shovels, etc., are used in places inaccessible to power equipment. Authority for using backfiring tactics is restricted to experienced men.

The organization of men for fire fighting is described. By law the mayor of a parish is primarily responsible for assembling and equipping fire fighters. If several parishes are involved, the prefect assumes co-ordinating supervision. In some localities fire-fighting crews are retained all the year. In others crews are assembled only when needed.

The conditions, organization, equipment, and methods resemble closely those found in several parts of the United States.

Subject Headings: *Forest fires, occurrence and organization of tactics, in France.*
W. G. Morris

XII. Instrumentation

This paper makes very good use of the rapidly expanding field of gas chromatography. A technique is described for the quantitive measurement of oxidation products from a mixture of n-pentane-air in the temperature range of 400° to 800°C.

ABSTRACTS AND REVIEWS

The gaseous mixture under consideration was passed through a vycor glass annular reactor. Oxidation products were allowed to flow through a liquid air-cooled collector, and noncondensibles were vented. Using helium as the carrier gas, the system was purged after effluent had flowed at a known rate for five minutes. When the liquid air trap was removed from the collector, helium swept the vaporizing liquid through an 8 ft column packed with a carefully chosen substrate. Gas samples were taken from the noncondensible stream and run through a 15 ft column containing a different substrate. Among the noncondensibles were hydrogen, oxygen, nitrogen, methane, and carbon monoxide. All of the above gases were quantitively determined except hydrogen. The latter has a thermal conductivity too near that of helium for very small concentrations to be detected. Formaldehyde, peroxide, and acid analyses were accomplished by use of conventional chemical methods.

To identify the products, the authors used several methods including the Bendix time-of-flight mass spectrometer. Infrared spectrophotometry in combination with the chromatographic column was employed to identify seven of the compounds. The instrument was placed on the downstream side of the column, and sample was passed directly into the spectrophotometer. Relative retention time (based on n-pentane=1) was another of the criteria used to identify or confirm the presence of a suspected component.

In evaluating the results quantitatively, the authors analyzed known volumes of pure compounds under the same or similar conditions as the effluent gases from the reactor. Component peak areas were related to component concentration by a comparison with calculated calibration factors derived from the pure compound results. Concentrations were calculated by weight ratio, and areas were estimated as the product of peak height and peak width at half height. Where the base line undulated, the areas were measured by planimeter.

The well-known difficulty of surface conditions affecting reproducibility in oxidation reactions of this type was eliminated by coating the reactor with nitric acid and then heating the vessel to 1000° C. This procedure rendered the surface fairly stable and it gave reproducible results for the rich pentane-air mixtures. From a plot of per cent pentane reacted *versus* temperature resulted the familiar curve illustrating the negative temperature coefficient. This is thought to be a positive indication of the two-stage character of many hydrocarbon oxidation reactions.

A surprising result was the presence of a high concentration of the compound 2-methyl tetrahydrofuran. This product accounted for as much as 20 per cent of the carbon content of the n-pentane reacted. The authors tentatively believe that the high surface-to-volume ratio and nitric acid pretreatment of the tube are responsible for formation of this product. Several good graphs of product concentration variation with reactor wall-temperature are presented. Curves for all identifiable components are shown and discussed.

The method of sampling employed in this work, utilizing the gas chromatographic technique, is a vast improvement over previous methods. It eliminates the transferring of samples to the chromatograph, while at the same time it allows samples to be taken for conventional analysis. Most of the products condensed in the collector can be analyzed in a single-stage process by increasing the column temperature in a specified manner.

Thus far in its development, this technique offers the following features:

233

(1) a method of obtaining a reproducible surface, (2) variation of product distribution with reactor temperature, and (3) confirmation or determination of certain suspected and some unsuspected compounds in the reaction product mixture. No mechanism for the reaction is offered. Though there is more work to be done before this major objective is attained, the paper offers encouragement to kineticists who are constantly searching for a better scheme to assist them.

Subject Headings: *Chromatography, in analysis of combustion products; Pentane, analysis of combustion, by gas chromatography.*

C. O'Neal, Jr.

Pengelly, A. E. (The United Steel Companies Ltd., Moorgate, Rotherham, England) "Apparatus for the Measurement of Gas Velocity in Furnaces and Models," *Journal of Scientific Instruments* 37, 339–346 (1960)

The author describes the design of Pitot-static tubes and a pressure recording device for use in industrial furnaces and model furnaces. The tubes are based on the National Physical Laboratory Pitot-static tube described in reference 1 and range in size from 3 mm outside diameter uncooled devices to 19 mm outside diameter water-cooled probes.

The relationship between the pressure difference, ΔP, measured with the Pitot tube and the dynamic pressure of the gas, $\frac{1}{2}\rho V^2$, is $\sqrt{\frac{1}{2}\rho V^2/\Delta P} = k$. The value of k is a function of the Reynolds number and probe design. For the NPL design, k is unity for Reynolds numbers greater than 4000 or for speeds above 20 ft/sec for probes of the order of $\frac{1}{2}$-inch diameter. For lower Reynolds numbers, $0.96 < k < 1.05$ and the value depends in detail on probe design. The author reviews briefly the literature concerning the values of k and describes the calibration of a probe in a furnace.

The recording device described in the paper is based on the use of commercially available differential transformers which are controlled by flexible diaphragms. The pressures to be measured are applied to either side of the diaphragms and the resulting displacement is indicated by the change in mutual inductance. A description is given of a novel 1000 cps oscillator which is used to drive the transformers.

The equipment is said to be capable of measuring pressure differences as low as 0.003 mm w.g. when special precautions are taken to isolate the sensing device. This corresponds to gas speeds of about 20 cm/sec at 20°C or about 60 cm/sec at 1500°C.

The title of the paper is somewhat inappropriate in that the instrumentation described is a differential pressure-sensing device and does not measure the velocity directly. A separate determination of the density is required to convert the recorded pressure signals to velocities. The author also omits any discussion of the effects of pressure or temperature fluctuations in the flow on his device.

Reference

1. Goldstein, S. *Modern Developments in Fluid Dynamics* 1, 248 ff. Oxford: Clarendon Press (1938)

Subject Headings: *Velocity, measurement of, in furnaces and models.*

E. E. Zukoski

ABSTRACTS AND REVIEWS

Seekamp, H. (Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, Germany) "Testing of Treatments for Reducing the Flammability of Wood," *Handbuch der Werkstoffprüfing* 3, 99–107 (1957)

Flameproofing of wooden materials can be attained via at least three methods. First, cover the wood with a protective layer; second, use material that will conduct, melt and dissociate without flaming; and lastly, coat with substances producing inert gases at higher temperatures which in effect dilute the concentration of the ignitable gaseous substances streaming from the material during burning. The mechanism of the surface combustion reactions are often altered considerably by any of the above protective methods, resulting in the formation of outer protective char layers, thereby protecting the inner layers.

In addition to studying the observed effects of outer layers and impregnating materials, it is useful to study the nature of the products formed by these protective substances. Contrasting studies of protected and untreated woods give a measure of the effect of various materials through observed differences in the various parameters of burning characteristics.

The paper divides its detailed discussions into several sections. Among these are descriptions and specifications of testing materials and test methods, treatment of test bodies and samples, measurements and observations, interpretation of test results and a summary of the most common test methods other than those described in detail here.

It is pointed out that the measurement or evaluation of a particular property such as ignition point or flare point, for example, is quite difficult. This is one good reason to try and develop standard testing procedures for all these tests. The author discusses apparatus designed for a standard or regulated procedure for each test. The methods outlined include studies of the steps leading to inflammation and loss of material strength during the course of burning through the sample, the duration of afterglow, the extinguishment of self-sustained burning, the spread of the flame front at the surface, the true burning rate as determined by weight loss with time, the loss of weight as a function of flame intensity and the length of time necessary for the sample to reach maximum weight loss.

Included is a discussion of all results obtained and their interpretation with reference to the various burning characteristics mentioned above.

Subject Headings: *Wood, flameproofing of.*

P. Breisacher

INDEX OF AUTHORS

INDEX OF SUBJECTS

Volume 3

CUMULATIVE INDEX AUTHORS

Affens, W. A., 202
Aidun, A. R., 91, 93, 213
Akita, K., 202, 207
Alumbaugh, R. L., 94
Applied Physics Laboratory The Johns
        Hopkins University, 212
Ashton, L. A., 56

Barduhn, A. J., 214
Beech, J. A., 232
Beer, J. M., 39
Beers, F. D., 105
Bennett, W. D., 64
Berendsen, R., 76
Berl, W. G., 113
Berlad, A. L., 208
Biswas, A. B., 61
Bonnetain, L., 83
Broido, A., 107, 193
Brown, K. C., 36
Bruce, H. D., 54, 95, 96
Bruneton, M., 231
Bruszak, A. E., 33
Burgess, D. S., 20, 159, 177
Busch, A. M., 51

Cadenhead, D. A., 27
Calcote, H. F., 35
Campbell, J. A., 51
Carhart, H. W., 202
Christiansen, W. H., 111
Clarke, S. H., 67
Coleman, E. H., 22
Colson, D., 105
Countryman, C. M., 103, 229
Cousins, E. W., 88
Cramer, O. P., 65

Dacey, J. R., 27
Deo, A. V., 61
Dixon-Lewis, G., 44
Dobbins, R. A., 99
Dodd, K. N., 60
Dorsett, H. G., Jr., 205
Drubel, R. B., 52
Duval, X., 83

Emmons, H. W., 102
Engibous, D. L., 50
Essenhigh, R. H., 36, 39, 206

Fahnestock, G. R., 58
Fons, W. L., 54, 95, 96
Foster, C., 78
Friedman, R., 128, 133

Gharpurey, M. K., 61
Gibbs, G. J., 35
Gifford, F., Jr., 63
Grognard, M., 86
Gross, D., 151
Grove, C. S., Jr., 91
Grumer, J., 159, 177
Guise, A. B., 87

Haggerty, W., 133
Harker, H., 80
Harrison, W. J., 109
Hase, R., 84
Hay, J. S., 62
Hering, H., 81
Higgins, H. G., 26
Hill, E. L., 106
Hinkley, P. L., 40
Hough, R. L., 214
Hunter, J. J., 66

Inami, S. H., 30
Izumi, T., 216

Jablonski, E. J., 49
Jacobson, M., 205
Johnson, J. E., 202

Kaesche-Krischer, D., 39
Kaskan, W. E., 209
Keraudy, S., 81
Kinbara, T., 1, 202
Knewstubb, P. F., 34
Kollman, F., 19
Kubala, T. A., 159
Kulkarni, S. B., 61

Volume 3

CUMULATIVE INDEX OF SUBJECTS

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