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# 12. FIRE SCIENCE

## 12.1 FIRE GRANTS

The CFR Grants Program was initiated in 1975 with funds from the plastics industry, and then in 1976 augmented by transfer of the fire program of the National Science Foundation's Research Applied to National Needs (RANN) project. This transfer was made with the understanding that the NSF funds would continue to be used for a grants program.

The NSF RANN program, developed and managed by Ralph Long, was focused around "Centers of Excellence." Primary among them were the Harvard University-Factory Mutual Insurance Corporation joint effort led by Professor Howard Emmons, Johns Hopkins Applied Physics Laboratory led by Professor Walter Berle, Princeton University led by Professor Irvin Glassman, University of California Berkeley led by Professor Patrick Pagni, and California Institute of Technology led by Professor Edward Zukoski. Each lead professor became an expert in the field of fire, and with his graduate students contributed major research papers, participated in the yearly CFR research conference, and in sessions

and publications of other technical societies. The graduate students frequently went on to become experts in fire protection, professors at other institutions or new staff members at CFR.

There were individual grants as well on specific research projects. These varied such that in any typical year, 20 percent to 30 percent of the program was in new grants.

Initially, the CFR program was administered by Clayton Huggett with yearly proposals from the principal investigators reviewed by CFR staff members with frequent review, evaluation and use of the results by CFR staff engaged in related research. Subsequently the program was managed by Robert Levine. Administrative matters were handled by Sonya Cherry of CFR who worked with the financial officers of the grantee organizations and the procurement staff at NBS. When questions arose about financial or administrative matters, Sonya Cherry's records and CFR procedures proved to be faultless. For these efforts, she received the Bronze Medal Award of the Department of Commerce in 1981.

The technical results of the program were outstanding. The Harvard-Factory Mutual Program, for instance, produced the first U.S. zone models of fire growth within a compartment (Harvard Fire Code V) and within a series of compartments (Harvard Fire Code VI). These became the bases for the Hazard software for the engineering design of fire safety systems for various occupancies. A series of research tasks described parts of the fire process in algorithms suitable for use in fire models. For instance, the California Institute of Technology developed a mathematical description of the buoyant plume and of buoyancy-affected flow in corridors.

For much of its life, this program was deprecated by other parts of NBS as a distraction from research to program management. However, they did not distract CFR personnel from research but put them into collaborative research relationships addressing the CFR program with outstanding peers.

***The grant program enlisted the support of the best brains in the country for fire research and trained a new generation of highly talented people for the fields of fire research and fire protection.***

When the Federal Emergency Management Agency (FEMA) was formed, support of grants for fire fighting science and technology was transferred to FEMA, which divided the work at the Applied Physics Laboratory (APL) into two programs. Both programs died because APL management could not cope with the financial problems created by FEMA's late contracting. However before this, APL in cooperation with Johns Hopkin's Medical School and Maryland's Medical Examiner performed pioneering work on toxicology of fire gases through studies of fire victims. The results led to the use of breathing apparatus by fire fighters during operations and overhaul of fire scenes.

The nature and scope of the Fire Grants program changed as its funding was reduced in parallel with CFR funding during the budget crises of the 1980s. Funding declined from \$2 million annually to \$1.34 million annually, and the decrease was exacerbated by the effects of inflation on research costs. The Centers of Excellence disappeared as their principal investigators retired. The Grants Program continues as external projects developed in cooperation with BFRL group leaders to complement the BFRL fire research program.

## **12.2 MEASURING THE TOXICITY OF FIRE SMOKE**

The creation of the NBS Center for Fire Research in 1975 made possible for the first time a technological assault

on the United States fire loss record, which was the worst in the industrialized world. From the outset, the new Program sought to maximize its impact by focusing on the factors giving rise to the most prevalent fire loss scenarios.

Early analyses of the causes of fire deaths had indicated that most fire fatalities resulted from smoke inhalation rather than burns. Scientists at NIST [1], elsewhere in the U.S. and overseas then began to identify the chemicals produced during the pyrolysis and burning of the materials that make up interior finish and common household furnishings. They soon discovered that literally hundreds of chemicals were produced, some of which were known to cause harm when inhaled. Toxicologists quickly began a variety of experiments using laboratory animals to determine the potential of fire smoke to cause incapacitation and death.

Much of this work was sponsored in the early 1970s by the National Science Foundation under the Research Applied to National Needs (RANN) program. This research grants program was transferred to the NBS in 1976. One of their four centers of excellence was at the University of Utah under the leadership of Professor Irving Einhorn. The Utah team found that smoke from a particular burning material produced smoke so toxic that even a small amount caused debilitation and death in lab mice. They dubbed the harmful component from this type of material a supertoxicant.



*Merritt Birky calibrating a combustible vapor detector.*

Almost immediately, fire toxicology research became directed at identifying any materials that produced supertoxicants (just as many other fire tests were designed to identify materials with unusually high flame spread rates, etc.) so that regulations could ban their use. Nearly 30 research groups worldwide developed apparatus for combusting small samples of materials and exposing the smoke to laboratory animals.

*Barbara Levin, leader of smoke toxicity research.*

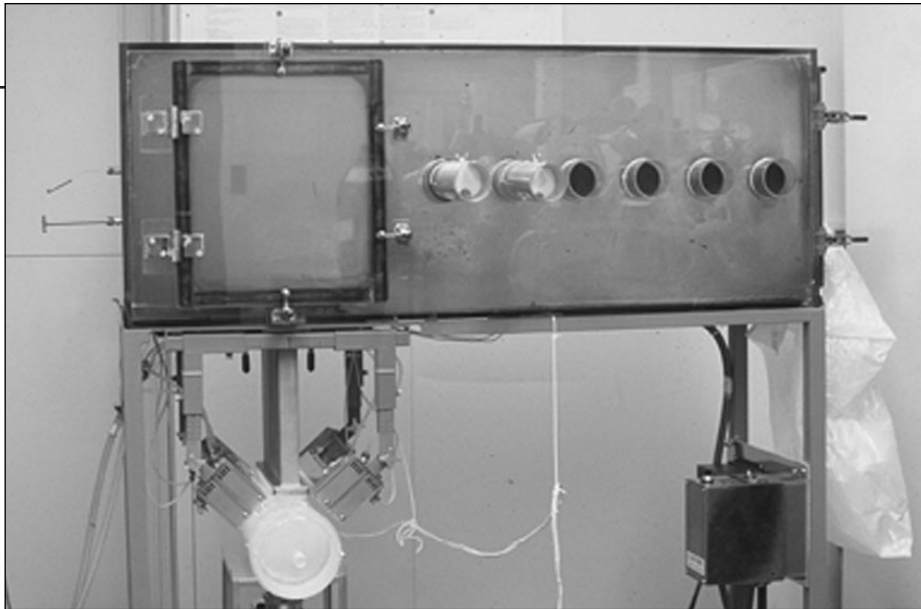


Realizing that the toxic potency of smoke was only one input to the calculation of fire hazard, NBS began to develop a test method that could be used to provide that input and to screen for materials whose smoke toxic potency merited special attention. The work was led initially by Merritt Birky, and upon his departure from NBS was completed under the leadership of Barbara Levin. The NBS Toxicity Test Method (alternately known as the Cup Furnace Method), published in 1982 [2], exposed rats to the smoke from test specimens that were pyrolyzed or autoignited.

Concurrently, the CFR was sponsoring research into combustion toxicity in Professor Yves Alarie's group at the University of Pittsburgh. They developed a test method [3] in which mice were exposed to the evolved gases from a specimen combusted in a tube furnace. Listing of data using this method was required in 1986 by the State of New York as a condition for allowing building materials to be sold in the State; the requirement has since been dropped.

The field of fire hazard analysis was advancing rapidly in the late 1970s and into the 1980s. In 1989, NBS released the first version of HAZARD I, a methodology for predicting the threats to life in a building fire [4]. New findings enhanced the quality of the toxic hazard component of overall fire hazard. The Southwest Research Institute under the sponsorship of the Vinyl Institute, published data showing that hydrogen chloride could be lost to wall deposition as the smoke moved further from the fire source. Autopsy evidence accumulated, showing that carbon monoxide and hydrogen cyanide levels in the blood of fire victims were frequently at lethal levels [5]. Yoshio Tsuchiya of the National Research Council of Canada proposed that the toxicity of fire smoke could be estimated by the sum of the contributions of all the gases in the smoke.

At NBS, Barbara Levin began a series of animal (rat) experiments to quantify Tsuchiya's hypothesis. As her results began to emerge [6,7], Richard Gann of NBS suggested that one need not consider all the gases, but rather that a small number,  $N$ , of these might well account for almost all of the lethal effect and that an animal check test would reveal the validity of this concept. The use of an "N-gas model," with input data based on Levin's experiments soon became the preferred input for fire hazard estimations [8]. Barbara Levin's pioneering research into the combined effects of



*NIST-developed apparatus for measuring the toxic potency of fire smoke. Now standardized as NFPA 269 and ASTM E1678, it is the only validated smoke toxicity test in the world.*

smoke components was also a bellwether in the wider field of combined physiological effects of mixed gases.

During this same time period, fire science was emerging as a disciplinary field. Practitioners at NBS and elsewhere soon realized that (a) complex commercial products might not behave in a manner that could be constructed from their component materials and (b) the combustion conditions in the cup furnace and most of the other toxicity measurement devices did not closely resemble the conditions under which products were exposed in most fatal fires. Fire incidence data showed that most fatalities resulted from fires that had passed beyond flashover, the point at which multiple fuels were involved and their combustion was ventilation limited [9]. The thermal input to the fuels was largely radiative.

Thus, NBS developed a next-generation bench-scale toxic potency measurement method [10]. The combustor was radiant, based on a 1990 design of

Arthur Grand of the Southwest Research Institute for the National Institute of Building Sciences. The rat exposure chamber was that of the cup furnace method. NBS staff under the leadership of Vytenis Babrauskas and Barbara Levin, developed a novel procedure for use of the apparatus.

Babrauskas next led development of a laboratory protocol to quantify the ability of bench-scale devices to reflect the potency of commercial products in real-scale fires. His team constructed five criteria for considering the accuracy of the bench-scale toxic potency data. They then showed that the radiant apparatus was superior to the Cone Calorimeter and the cup furnace in this respect, replicating the real-scale data within about a factor of three for the most conservative agreement criterion [11]. In 1997 under Gann's leadership, this method became the first (and still only) one adopted by U.S. national standards bodies as ASTM E1678 [12] and NFPA 269 [13]. Over twenty years after NBS began the enabling research, there was now a

method of known accuracy for obtaining lethal toxic potency data for fire hazard and risk analyses.

There was concurrent activity on smoke toxicity in the international arena, mostly taking place in ISO Committee TC92, Subcommittee 3 on Fire Threat to People and the Environment. The contentious issue was the drafting of a document on smoke incapacitation data for use in estimating the time available for escape. An extremely restrictive version of the document had been voted down as an ISO Standard in 1999, largely because of poor resolution over what was and was not known about the sublethal effects of fire effluent. This shortcoming triggered a major project under the Fire Protection Research Foundation to provide technical resolution. Led by NIST, the project's first report was issued in 2001[14]. Under the leadership of Gordon Hartzell, retired Director of the SwRI Department of Fire Technology, and Gann, the ISO document was heavily revised to reflect these latest findings and new fire hazard analyses. It was approved in 2001 as an ISO Technical Specification [15] and will again be considered as an International Standard in 2004.

***Today, fire smoke toxicity is routinely included in engineering estimations of fire hazard and risk. The drive to quantify and validate these data can largely be attributed to NBS/NIST metrology.***

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## 12.3 MEASUREMENT OF HEAT RELEASE RATE

Intuitively, the rate of heat release from an unwanted fire is a major indication of the threat of the fire to life safety and property. This indeed is true, and a reliable measurement of a fire's heat release rate was a goal of fire researchers at NBS and other fire laboratories at least as early as the 1960s. Traditionally, heat release measurements of burning materials were based on the temperature rise of ambient air as it passed over the burning object. Because the fraction of radiant emission varies with the type of material being burned, and because that energy does not all contribute to temperature rise of the air, there were large errors in the measurements. Attempts to account for the heat that was not captured by the air required siting numerous thermal sensors about the fire to intercept and detect the additional heat. This approach proved to be tedious, expensive, and prone to large errors, particularly when the burning "object" was large, such as a full-sized room filled with flammable furnishings and surface finishes.

During the 1970s a novel alternative technique for determining heat release rate was developed at NBS. It had distinct advantages over the traditional approach, but its widespread acceptance was hampered by uneasiness in the fire science community concerning

potential errors if the technique were used in less-than-ideal circumstances. In 1980, Clayton Huggett [1], fire scientist at NBS, published the seminal paper that convinced the fire science community that the new technique was scientifically sound and sufficiently accurate for fire research and testing. The technique now is used worldwide and forms the basis for several national and international standards.

The underlying principle of new heat release rate technique was “discovered” in the early 1970s. Faced with the challenge of measuring the heat release of combustible wall linings during full-scale room fire tests, William Parker, Huggett’s colleague at NBS, investigated an alternative approach based on a simple fact of physics: In addition to the release of heat, the fire process consumes oxygen. As part of his work on the ASTM E 84 tunnel test, Parker [2] explored the possibility of using a measure of the reduction of oxygen in fire exhaust gases as an indicator of the amount of heat released by the burning test specimens. Indeed, for well-defined materials with known chemical composition, heat release as well as oxygen consumed can be calculated from thermodynamic data. The problem with applying this approach to fires is that in most cases the chemical compositions of modern materials/composites/mixes that are likely to be involved in real fires are not known. In the process of examining data for complete combustion (combustion under stoichiometric/excess air conditions) of the polymeric materials with

which he was working, Parker found that although the heat released per unit mass of material consumed (i.e., the heat of combustion) varied greatly, the amount of heat released per unit volume of oxygen consumed was fairly constant, i.e., within  $\pm 15$  percent of the value for methane, 16.4 MJ/m<sup>3</sup> oxygen consumed.

This fortunate circumstance—that the heat release rate per unit volume of oxygen consumed is approximately the same for a range of materials used to construct buildings and furnishings—meant that the heat release rate of materials commonly found in fires could be estimated by capturing all of the products of combustion in an exhaust hood and measuring the flow rate of oxygen in that exhaust flow. The technique was dubbed oxygen consumption calorimetry, notwithstanding the absence of any actual calorimetric (heat) measurements.

Later in the decade, Huggett performed a detailed analysis of the critical assumption of constant proportionality of oxygen consumption to heat release. Parker’s assumption was based on enthalpy calculations for the complete combustion of chemical compounds to carbon dioxide, water, and other fully oxidized compounds. Indeed, a literature review by Huggett revealed that Parker’s findings were actually a rediscovery and extension of Thornton’s work [3], published in 1917, which found that the heat released per unit of oxygen consumed during the complete combustion of a

large number of organic gases and liquids was fairly constant. Nevertheless, since in real fires and fire experiments the oxygen supply is sometimes limited, incomplete combustion and partially oxidized products can be produced. Huggett’s paper examined in detail the assumption of constant heat release per unit of oxygen consumed under real fire conditions and assessed its effect on the accuracy of heat release rate determinations for fires.

Instead of expressing results on a per unit volume basis, as Parker did, Huggett expressed results in the more convenient and less ambiguous per unit mass of oxygen consumed. Huggett began by presenting values for the heat of combustion and heat of combustion per gram of oxygen consumed for typical organic liquid and gas fuels, assuming the products are CO<sub>2</sub>, H<sub>2</sub>O, HF, HCl, Br<sub>2</sub>, SO<sub>2</sub>, and N<sub>2</sub>. Notwithstanding large variations in the heat of combustion (up to a factor of 4) for this group of fuels, the heats of combustion per unit mass of oxygen consumed fell within  $\pm 3$  percent of their average value of 12.72 kJ/g (O<sub>2</sub>). Huggett explained that this near constancy was not surprising because the energetic processes are the result of breaking either carbon-carbon or carbon-hydrogen bonds, and these bonds have similar energetics.

An examination of the same data for typical synthetic polymers, some of which Parker did not consider, produced similar results; for this class of

materials the heats of combustion per unit mass of oxygen consumed fell within  $\pm 4$  percent of their average value of 13.03 kJ/g ( $O_2$ ). Fuels of natural origin (e.g., cellulose, cotton, newsprint, corrugated box, wood, etc.), that are likely to be found in large quantities in building fires, have heats of combustion per unit of oxygen consumed that range within  $\pm 5.3$  percent of their average of 13.21 kJ/g ( $O_2$ ).

The results presented so far assumed complete combustion. Huggett explored the effects of incomplete combustion on the assumption of constant heat release per unit of oxygen consumed. He did this by making several conservative but realistic assumptions concerning incompleteness of combustion for a range of materials likely to be found in a structural fire. For example, carbon monoxide often is present in a fire's combustion products, but usually at a very low level and rarely exceeds 10 percent of the carbon dioxide concentration produced by the fire. Huggett then calculated the heat of combustion per unit of oxygen consumed for the burning of cellulose in limited air, such that the carbon monoxide concentration was about 10 percent of the carbon dioxide concentration. The result was 13.37 kJ/g ( $O_2$ ) compared with 13.59 kJ/g ( $O_2$ ) for the excess air case. The difference was very small and, if necessary, could be corrected if the carbon monoxide concentration was measured.

Another consideration was that cellulosic fuels tend to form a carbonaceous

char that can affect heat release rate. By examining a hypothetical reaction that forces production of pure carbon, Huggett demonstrated that the effect was small; 13.91 kJ/g ( $O_2$ ) when pure carbon was produced versus 13.59 kJ/g ( $O_2$ ) when the reaction took place in excess air.

Other partial oxidation reactions can occur and affect the heat release rate. Huggett argued that although their details are unknown, their effects could be assessed via representative examples; noting that the actual material in the example was not important since only the chemical bonds that were rearranged by the reaction significantly affected the results. He considered partial oxidation of propylene, polyacrylonitrile (produces hydrogen cyanide under some combustion conditions), and polytetrafluoroethylene and argued that under worst-case conditions the heats of combustion per unit oxygen consumed range from 10.76 kJ/g ( $O_2$ ) to 13.91 kJ/g ( $O_2$ ) and if present in small quantities would not introduce a significant error in heat release based on oxygen consumption. All these scenarios were considered 'limiting cases'; the effect in real fires usually would be less than presupposed in the analyses. In situations where large quantities of incomplete combustion products were produced, corrections could be made if these products were measured.

Huggett concluded that the assumption of constant heat release rate per unit mass of oxygen consumed would

be sufficiently accurate for most fire and fire-test applications. For fires burning conventional organic fuels, Huggett recommended the constant 13.1 kJ/g ( $O_2$ ), which should produce heat release rate results accurate to  $\pm 5$  percent or better. Ever since its publication, this value has been the accepted value for oxygen-consumption calorimetry when burning conventional materials.

Huggett examined other factors that influence the overall accuracy of oxygen consumption calorimetry. For example, dilution by products of combustion in the exhaust flow, where the oxygen concentration measurement is made, is a source of error because the number of moles of products is not the same as the number of moles of oxygen consumed. This 'dilution factor' is a function of the fuel's stoichiometry and can be taken into account if the stoichiometry is known. In general, however, this is not the case and the dilution factor must be estimated. Through analysis of 'limiting' cases, Huggett reasoned that if an appropriate dilution factor were not available, then assuming a value of 1.6 would lead to an error of less than six percent in the amount of oxygen consumed.

The paper by Huggett was published just as the rate of heat release was beginning to be recognized as the central property affecting fire growth [4]. The novel new technique was rapidly incorporated by Babrauskas and Twilley [5] in their invention of the



Vytenis Babrauskas, fire protection engineer and developer of the cone calorimeter, is collecting data critical to predicting the fire hazard of a product using a small sample of material. This test replaces time-consuming and expensive full-scale tests. ASTM and ISO adopted a voluntary fire hazard test method based on the instrument.

Cone Calorimeter, a bench-scale device now used worldwide for heat release rate measurements. It also became the technique used in fire calorimeters of larger (room) size at NIST and at most fire laboratories throughout the world. The oxygen-consumption technique forms the basis for several national (ASTM [6], NFPA [7]) and international (ISO [8]) standards.

Department of Commerce Medal Awardees received for this work include: the Bronze Medal to William Parker in 1976 for the concept of measurement of heat release rate; the Bronze Medal in 1984 to William Twilley for design and construction of the cone calorimeter; and the Bronze Medal in 1986 to Vytenis Babrauskas for the conception and standardization of the cone calorimeter. Babrauskas also received the NIST Rosa Award in 1992 for the contributions of heat release rate and the cone calorimeter to fire standards, worldwide.

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## 12.4 SMOLDERING COMBUSTION

Smoldering combustion has arisen as a fire safety issue in two principal contexts. The first is as a pathway for the initiation of destructive upholstered furniture and bed fires [1]. The threat here arises from the careless use of cigarettes whose own smoldering process can spread into soft furnishings with which they come into contact. The other context arose rather dramatically in the 1970s as a direct consequence of the increased use of thermal insulation materials in buildings to counter the rapidly rising cost of energy. Some of the most popular insulation materials were made from re-cycled newsprint that, if improperly formulated, could begin to smolder as a consequence of exposure to such heat sources as recessed light fixtures. In both of these areas, the life hazard was compounded by the possibility that the smoldering process would develop into a much more rapid flaming process. In both of the contexts, the goal of BFRL research has been to





Thomas Ohlemiller, chemical engineer, examines the results of an experiment to characterize the smoldering combustion of blown-in cellulosic insulation in attic spaces.

understand the basic mechanisms at work in this unique form of combustion so as to assure that test methods are soundly based.

The initial experimental and modeling studies were performed by grantees at MIT [2] and Princeton [3]. Simultaneous experiments at NIST established the fundamental role played by alkali metals as char oxidation catalysts in many practical materials. Thomas Ohlemiller moved to NIST and continued experimental and modeling studies of the variables, which influence smolder initiation [4], propagation rate and the transition from smoldering to flaming combus-

tion [5]. This background was useful when NIST began to study the role that cigarette design parameters [6] have in the initiation of smoldering in soft furnishings; that study is described in more detail under its own heading.

The understanding of smoldering combustion phenomena expressed in the referenced publications and others has helped substantially in the development of appropriate test methods to assess this hazard in various applications. Ohlemiller received the Bronze Medal Award of the Department of Commerce in 1986 for his studies of smoldering combustion.

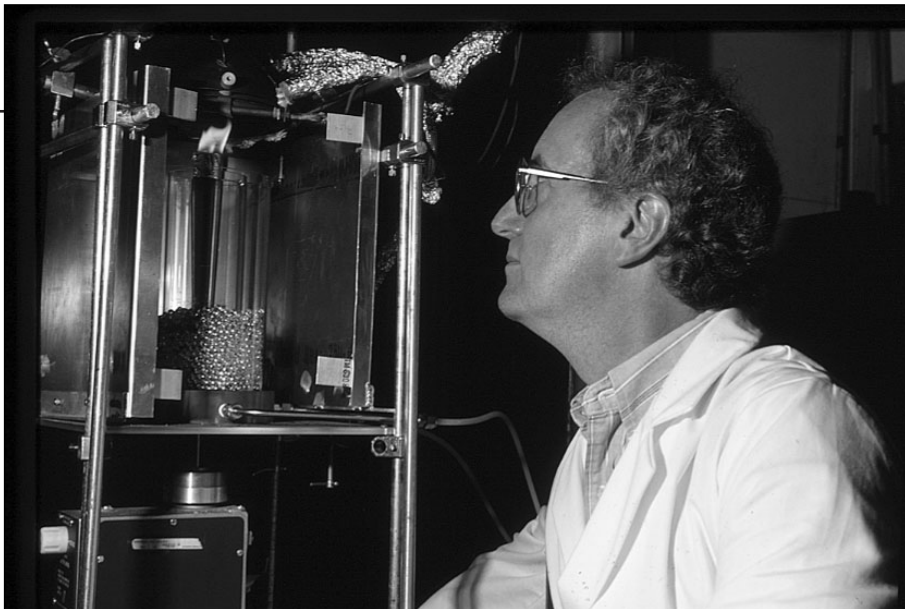
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## 12.5 ADVANCED FIRE MEASUREMENTS

The need for fire metrology has been driven from the earliest days of NBS by building codes, product performance, and fire fighting activities. The objective of our research has been to develop measurement methods for the performance of products and fire control technologies that allow extrapolation of the behavior of these products and technologies to actual building fires. Measurement advances at laboratory-, mid-, and full-scale all have been targeted since accurate predictions only can be achieved by a higher level of understanding of the dynamics of fire and more certain measurement methods.

Predicting how an object will respond in a real fire, how a fire will grow beyond the room of origin, or how well a suppression system will extinguish the flames hinges on the measurement of key properties in and around the fire under carefully controlled conditions. Because the dynamics of fire are strongly non-linear, different measurement methods have



*William Grosshandler, mechanical engineer, is using new test methods to quantify the impact of an electrically heated surface on the amount of a gaseous agent necessary to extinguish a burning plastic specimen.*

been developed to probe the multiple temporal and spatial scales that reveal the chemical and physical principles guiding fire behavior. Pioneering work was done by Ingberg [1] in the first quarter of the last century, with his measurement methods defining the concept of fire loading and endurance standards used in building codes throughout the world. The single most important characteristic of a fire is the rate of heat release. Huggett [2] developed a practical means to measure this parameter for fires at real scale, based upon the consumption of oxygen in the exhaust products. Oxygen calorimetry is now carried out routinely for fires of all materials, systems, and sizes as large as 10 MW.

Great attention has been paid to the design and scale of fire experiments. An important example is a multi-story house built within the large fire facility to duplicate a multi-fatality fire [3]. Measurements of CO in rooms remote from the fire revealed high levels, consistent with the cause of death but inconsistent with numerical predic-

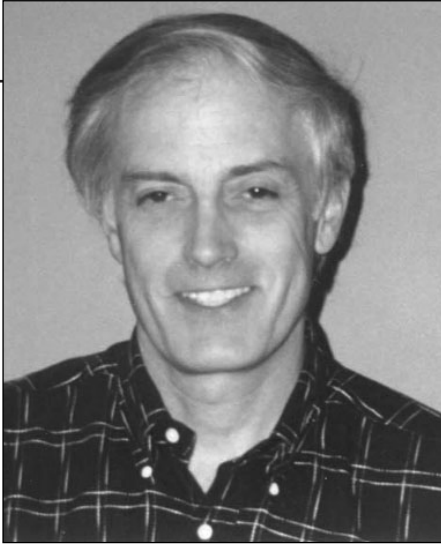
tions. These measurements led to a new research program focused on explaining this discrepancy.

Measurements of the transformations that occur in solid and liquid fuels prior to and during combustion, such as in the recent work by Nyden [4], promise to reveal mechanisms that can be exploited to increase the fire resistance of materials. The quantity and type of smoke generated by these and other burning materials is the third characteristic (along with the rate of heat release and CO) of great importance. Optical and extractive methods have been developed to measure smoke levels, and these depend upon the precise measurements by Mulholland of the soot morphology and optical properties [5]. The smoke and CO levels are sensitive to the equivalence ratio (symbolized by the Greek letter  $\phi$ ). A unique instrument was developed by Babrauskas et al. [6] to directly measure  $\phi$  for the first time. Our understanding of the kinetics of soot formation have been greatly enhanced by the detailed spectroscopic

species profiles measured by Smyth [7] in a laminar methane flame.

The turbulence associated with jet flames and fire plumes of greater size controls the local mixing process and time available for chemical reactions. Small and large scale turbulent structures have been measured using Rayleigh scattering to explain lift-off and stabilization of hydrocarbon jet flames [8]. As fires get larger and buoyancy dominates, and as fuels become more complex, detailed species, temperature, and flow data become difficult to measure with certainty. Turbulent pool fires are an example of this class, which has been much studied. Hamins et al [9] describe their measurement methods and the data gathered in liquid pool fires of a variety of fuels and sizes. A fire within an enclosure is another class that presents a measurement challenge, especially as the fire becomes underventilated, when the flow through the doorway controls the fire. Steckler and Quinterre [10] quantified this flow in a full-scale room fire for the first time. While thermocouple measurements are straightforward to take, proper interpretation of the results and assessment of the measurement uncertainties are complicated in room fires. Blevins and Pitts [11] examined this problem and bracketed the magnitude of the uncertainty in temperature measurements for this situation.

Knowledge of the products of an incipient fire are key to early and certain fire detection. Traditional measurement methods have been used by



Kermit Smyth, leading researcher of chemical structure of flames.

Grosshandler et al [12] to characterize the content of the weak plumes that rise above small, growing fires. During the act of suppressing a fire, measurement of the details of the process are particularly challenging. In response to this challenge and with the desire to find suitable replacements for halon (halogenated hydrocarbon) 1301, several new measurement methods were developed that enabled the Department of Defense to select the best options for protecting military aircraft from in-flight fires [13].

Awards of the Department of Commerce for this work include: Bronze Medal to George Mulholland in 1985 for smoke particle generation and growth mechanisms; Bronze Medal to William Pitts in 1991 for turbulent combustion measurements; Silver Medal to Kermit Smyth in 1992 for measurements of the chemical structure of flames. Smyth also received the NBS Condon Award in 1987 for his seminal paper on the chemistry of molecular growth in flames.

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## 12.6 FIRE SAFE MATERIALS

In recent decades synthetic polymeric materials, because of their unique physical properties, have rapidly replaced more traditional materials such as steel and nonferrous metals as well as natural polymeric materials such as wood, cotton, and natural rubber. However, one weak aspect of synthetic polymeric materials compared with steel and other metals is that these materials are combustible under certain conditions. Thus the majority

of polymer-containing end products (for example, cables, TV sets, electric appliances, carpets, furniture) must pass some type of regulatory test to help assure public safety from fire. However, these traditional pass/fail tests have not provided any information regarding the relationship between flammability properties and the physical and chemical characteristics of polymeric materials. Such information is needed to develop more fire-safe materials, a need which has accelerated because of European environmental concerns about the use of halogenated flame retardants (because of potential formation of dioxins in the incineration of spent end products). The paper, *Effects of Weak Linkages on the Thermal and Oxidative Degradation of Poly(methyl methacrylate)* [1] is one of a series published on this topic by the members of the Materials Fire Research Group at NBS/NIST from 1985 to 1994 [2-11]. These papers represent a new approach that studies the effects of molecular-level structure of polymers on their thermal stability and flammability properties instead of a traditional global thermal-balance approach. This series of studies is built upon the pioneering work on thermal degradation of

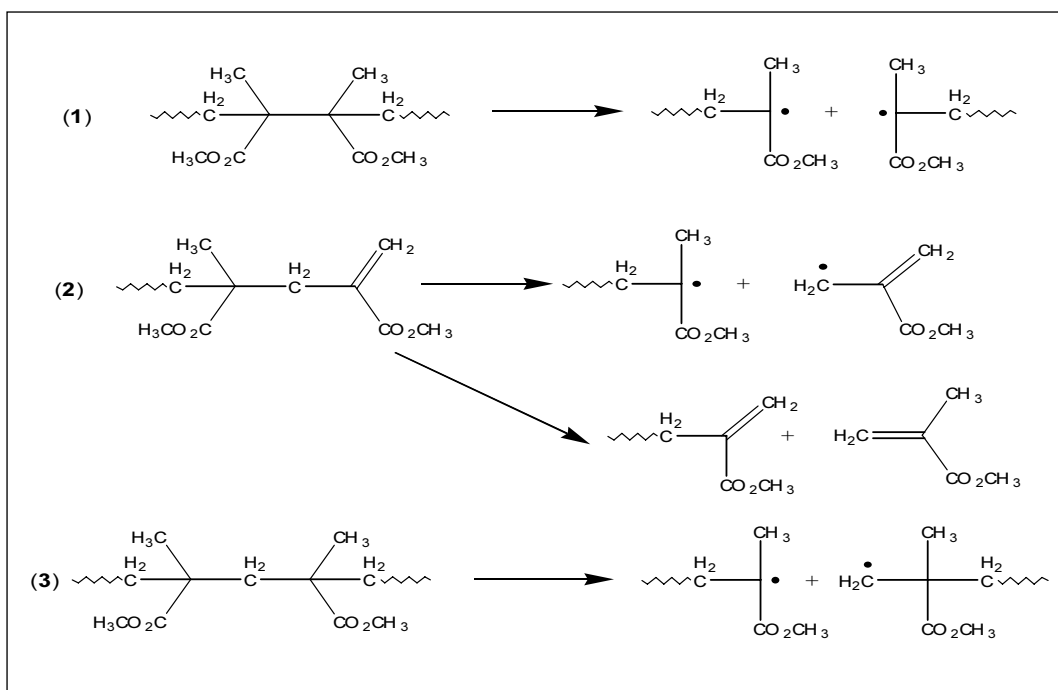
polymers conducted at NBS from the late 1940s to early 1970s [12].

Providing the technical basis for industrial clients to design less flammable materials requires unfolding the structural features that determine thermal stability. This paper [1] reports a study of the thermal and oxidative degradation mechanisms of an acrylic polymer in atmospheres of nitrogen and air by measuring the change in the sample mass while various specially polymerized samples were heated from 80 °C to 480 °C. Thermal degradation of the acrylic polymer, which was polymerized using a free-radical method, proceeds in three steps of mass loss: the first and easiest (see figure below) is initiated by scissions of head-to-head

linkages at about 160 °C (representing one type of defect at the polymer backbone); the second (scheme 2) by scissions at the chain-end initiation from vinylidene ends at around 270 °C; and the last (scheme 3) by random scission within the polymer chain (at the weakest bonds).

The first two mass loss steps were not observed with ionically polymerized samples, which indicates that the first two steps are caused by the defects in the polymer. Although the existence of head-to-head linkages could not be demonstrated, the vinylidene ends in the polymer were detected by the HNMR spectrum. No significant differences were seen in the thermal or oxidative degradation of the acrylic

Three proposed thermal degradation steps of PMMA.



polymer when it was polymerized with the free-radical method using two common initiators. It was found that gas-phase oxygen traps polymer radicals resulting from chain scissions at head-to-head linkages, and no mass loss was observed from this step in air. Similarly, oxygen traps radicals generated by end initiation, but mass loss is only delayed to slightly higher temperatures, presumably because of a slight gain in the thermal stability of the oxygen-trapped polymers compared with end initiation.

This series of studies involved not only experimental observations but also theoretical calculations in which kinetics equations were solved for each polymer chain. Detailed thermal degradation models were developed based on random initiation, depropagation of free radicals, and termination of free radicals; calculations were made with the assumption of steady-state free radical concentration [4] and without that assumption [5]. The kinetic rate constants for each reaction were derived by comparing experimentally measured molecular weights of polymer samples collected at various temperatures and exposure times with the theoretically calculated results [6]. The final paper of the series on thermal degradation investigated the behavior of primary radicals generated from random scissions by measuring evolved degradation products with a mass spectrometer [9].



*Fire Materials Research Group, 1994*

The influence on thermal stability by the above-discussed defects in the polymer have been studied and published [7,8,10]. The results show that a higher thermal stability increases pilot-ignition delay time and gasification rate of the polymer, but initial molecular weight does not affect ignition delay time. On the other hand, initial molecular weight of the polymer has significant effect on flame spread rate because low molecular weight materials will flow more readily when heated. The physical and chemical roles of the condensed phase in the burning process of polymeric materials were published as a summary of this series of studies [11].

The molecular-level study of the thermal degradation and flammability properties of polymers described above was pursued further by Marc Nyden and coworkers at NIST. They used molecular dynamic simulations of thermal degradation of polyethylene to identify factors that might be effective in reducing polymer flammability by promoting the formation of residual

char [13]. The results predicted that the formation of cross-linking, for example by exposure of polyethylene to ionizing radiation, enhanced further cross-linking when the polymer is burned. An increase in ignition delay time was observed for irradiated polyethylene samples compared to unexposed samples. A similar approach has been pursued by Charles Wilkie at Marquette University, Richard Lyon at the FAA Technical Center, and James McGrath at Virginia Polytechnic Institute and State University.

Because of the increasing demand for non-halogenated flame retardant additives for polymeric end products, this molecular-level study has been extended to include flame retardant mechanisms of polymers containing small quantities of inorganic flame retardant additives. As a result of advancements in nanoscale science and technology, molecular-level studies of the effects of trace additives in clay-polymer nanocomposites are demonstrating enhanced physical properties with simultaneous improvements in the



*Takashi Kashiwagi pioneered research in ignition and flame spread in microgravity and contributed significantly to understanding the combustion of polymeric materials and the mechanisms of flame retardants.*

flammability properties of polymers. This contrasts with the traditional approach that improves the flammability but often degrades mechanical properties.

The study described in this paper involved the synthesis of specific polymers, analytical characterization of the synthesized polymers, and careful thermogravimetric analysis. Two different groups, the Materials Fire Research Group at NIST and Department of Chemistry at Osaka University, contributed their own expertise to this highly collaborative undertaking. The group at Osaka University synthesized and characterized all polymer samples used in the study, while the group at NIST performed the thermogravimetric analyses.

Takashi Kashiwagi joined NBS in 1971 after he received his Ph.D. from Princeton University. He was a group leader from 1988 to 1998 in the Fire Science Division. He is currently a materials research engineer working on

improved fire-safe materials, as well as studying ignition and flame spread in a microgravity environment. He was a principal investigator of the ignition and flame spread experiment conducted on Space Shuttle flight STS-75. Atsushi Inaba received his Ph.D. in chemical engineering from Tokyo University in 1981 and was a guest scientist at NBS from May 1984 to March 1986. He is currently Director of the Research Planning Office of the National Institute for Resources and Environment in Japan. James E. Brown joined the Polymer Division of NBS in 1956 as a research chemist, moved to Fire Science Division in 1975, and retired in 1996. Koichi Hatada, a professor in the Department of Chemistry at Osaka University, was known internationally for his work on stereoregular and living polymerization and copolymerization. He retired from Osaka University in 1998 after serving as vice president of the University. Tatsuki Kitayama is a professor in the Chemistry Department of Osaka University. Eiji Masuda was a student under Professor Hatada and is currently a senior research scientist at Polyplastics Company in Japan.

Alexander Robertson received the NBS Rosa Award in 1978 for career contributions to standards for materials flammability test methods. Clayton Huggett received the Department of Commerce Silver Medal Award in 1978 for studies of flame inhibition, and William Bailey received the Bronze Medal Award for laboratory support of these and other fire studies. Takashi

Kashiwagi received the Department of Commerce Bronze Medal Award in 1982 for studies of radiant ignition, the Silver Medal Award in 1991 for characterization of flame spread, and the Gold Medal Award in 2000 for flame retardants principles and models. James Raines received the Bronze Medal in 1982 for laboratory automation support of these and other fire studies. Kashiwagi also received the NIST Applied Research Award in 1991 for studies of the thermal degradation of plastics. Marc Nyden received the Bronze Medal Award in 1993 for his studies of computational molecular dynamics. Jeffrey Gilman received the Bronze Medal Award in 1999 for his studies of nanocomposites.

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## 12.7 CARBON MONOXIDE FORMATION IN FIRES

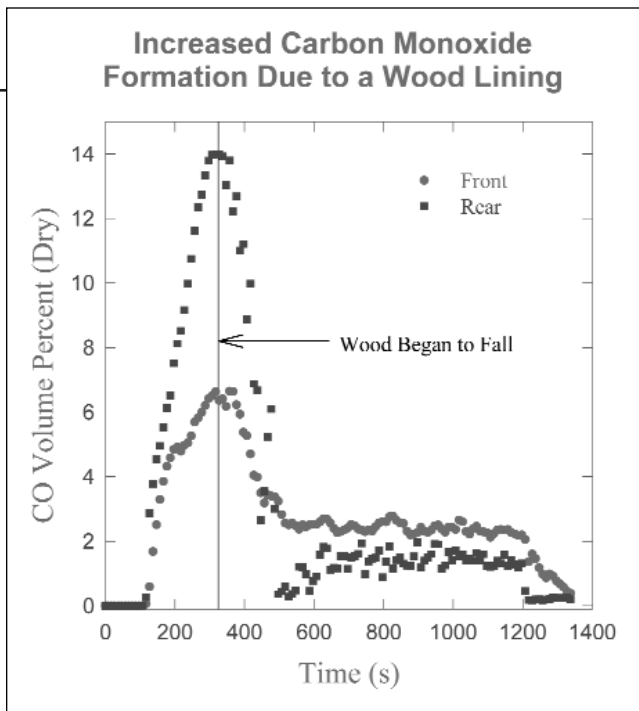
Fire safety research has been ongoing at NIST since its founding one hundred years ago. This research has traditionally been focused on understanding fire behavior and developing tests to improve fire safety. By the early 1970s the understanding of fire behavior had advanced sufficiently that the development of engineering models capable of predicting the behavior of fires in buildings could begin. By the late 1990s modeling capabilities had been developed to a point where governing bodies were willing to consider performance based codes, which require engineering estimates of fire safety, in lieu of existing prescriptive codes.

Major components of fire safety engineering are human behavior and safety. Even though fire was a serious problem claiming thousands of lives each year, the causes of fire deaths were not well characterized during the first half of the last century. By the 1970s studies were indicating that most fire deaths were the result of smoke inhalation and not burns. The vast majority of victims of smoke inhalation were found to have carbon monoxide (a molecular species known to induce hypoxia) levels in their blood streams sufficient to cause incapacitation and/or death. Even though these studies suggested that the formation of carbon monoxide was responsible for a significant fraction of fire deaths, very

little was known concerning the amounts formed or the physical mechanisms responsible for its generation. As a result, it was nearly impossible to model the effects of a fire on potential victims.

Recognizing the importance of carbon monoxide formation in fires, CFR initiated a long-term project aimed at identifying the mechanisms of carbon monoxide formation in fires and developing methodologies for predicting the levels generated [1, 2]. The principal investigator was William M. Pitts who worked with a number of BFRL staff including Nelson Bryner, Erik Johnsson, George Mulholland, and William Davis.

The starting point for the project was seminal research carried out at Harvard University and the California Institute of Technology under Center for Fire Research sponsorship. By using hoods to capture the products of combustion generated by fires burning in open laboratories, these researchers demonstrated that high levels of carbon monoxide were formed when the amount of air entrained by a fire plume located beneath a layer of combustion gases was insufficient to consume all of the fuel present. Such burning is referred to as being under-ventilated. Even more significant was the observation that concentrations of the major species of combustion (including carbon monoxide) in the hoods were strongly correlated with the ratio of the masses of products derived from fuel and air present in



The plot shows the dramatic increases in carbon monoxide levels due to the presence of wood in the upper layer of an underventilated enclosure fire. When the wood weakens and falls to the floor of the enclosure, the carbon monoxide levels return to those typical of fires without wood present.

the hood normalized by the fuel-to-air ratio required to fully convert the fuel to water and carbon dioxide. This normalized ratio is known as the global equivalence ratio (GER), and the existence of the correlations is referred to as the GER concept. Interestingly, when the yields of carbon monoxide were expressed on a mass generated per mass of fuel consumed basis, the results were found to be nearly fuel independent. An initial survey of real-scale fire tests results carried out as part of the Building and Fire Research Laboratory project showed that observed yields of carbon monoxide in underventilated fires were roughly in line with those found during the hood experiments.

The NIST research program was designed to confirm the applicability of the GER concept for the production of

thermodynamic and kinetic investigations in order to better understand the chemical nature of the upper layers formed during fires in enclosures. These studies indicated that the upper-layer combustion products formed during underventilated burning are predominately determined by kinetics and are far from thermodynamic equilibrium. The gases only start to approach thermodynamic equilibrium for temperatures in excess of 1100 °C. The calculated reaction behaviors were also consistent with the experimental observation that the composition in the hood experiments varied somewhat with the temperature of the gases.

The experiments that identified the GER concept are highly idealized models for enclosure fires. In order to verify that the GER concept was appropriate for more realistic en-

closure fires as well as to identify other mechanisms capable of generating carbon monoxide in enclosure fires. A concurrent research program at the Virginia Polytechnic Institute and State University funded by the Building and Fire Research Laboratory had similar goals.

One of the first steps in the BFRL project was to perform fundamental

sure fires, a series of natural gas fueled fires were carried out in both a 40 percent-scale and a full-scale model of an enclosure widely used in fire testing. The full-scale room had dimensions of 2.4 m wide, 2.4 m high, 3.7 m long and contained a single doorway centered in one of the short walls.

Measurements made in the 40 percent-scale model revealed that the composition of combustion gases and temperatures in the upper layer of the fire varied somewhat with location, but that the composition was still strongly correlated with a global equivalence ratio based on the fuel release rate and the amount of air entering the doorway. This finding confirmed that the mechanism for carbon monoxide formation identified in the hood experiments was also important in enclosure fires. However, the experimental results, along with field modeling of the flows in the enclosure, also showed that a fraction of the air passing through the doorway could enter the upper layer of the room directly without being entrained into the fire plume. For a fuel rich upper layer the detailed chemical kinetic modeling indicated that this air would react with fuel to generate primarily carbon monoxide. Thus direct entrainment of air into a rich, high temperature upper layer provides an additional mechanism for carbon monoxide formation in enclosure fires.

Somewhat surprisingly, much higher levels of carbon monoxide were observed during burns in the full-scale



enclosure than in the reduced-scale enclosure. Analysis showed that these higher levels were due to the higher temperatures present in the upper layer of the full-scale facility. These temperatures were sufficiently high for the underventilated fire gases to begin to react and approach thermodynamic equilibrium. This leads to increases in carbon monoxide since this species is thermodynamically favored at high temperatures. The upper-layer temperatures for which increased carbon monoxide formation was observed were consistent with the predictions of the detailed chemical kinetic modeling.

Comparison with a number of real-scale tests carried out at the Center for Fire Research indicated that the three mechanisms discussed above were sufficient to explain the formation of carbon monoxide for many fires. However, it was recognized that for several large fires in which wood was burned the levels of carbon monoxide were considerably higher than predicted based on these mechanisms alone. Since wood contains a significant fraction of oxygen and is known to generate carbon monoxide when heated to high temperatures in anaerobic environments, it was postulated that high concentrations of carbon monoxide in fires can be generated when wood is located in high temperature fire environments where oxygen is unavailable. In order to test this hypothesis, underventilated natural gas fires were burned in both enclosures in which the upper walls and ceilings were lined

with plywood. Observed upper-layer concentrations of carbon monoxide were as much as six times higher than when wood was absent, thus confirming the hypothesis and providing a fourth mechanism for generating carbon monoxide in enclosure fire environments.

Based upon the understanding developed during the research program, an algorithm was developed that allows fire safety engineers to determine whether carbon monoxide is likely to be formed during an enclosure fire and to estimate the amounts generated. The four formation mechanisms identified during the investigation are incorporated: 1) quenching of a turbulent fire plume upon entering a rich upper layer, 2) mixing of oxygen directly into a rich, high-temperature upper layer with subsequent reaction, 3) pyrolysis of wood in high-temperature, vitiated environments, and 4) approach to full-equilibrium combustion product concentrations in a rich, high-temperature upper layer.

The results of this research not only provided an understanding and predictive method for the generation of carbon monoxide in enclosure fires, but also had an impact on the study of fire toxicity in general. Prior to this work it



*A scale model experiment used to investigate carbon monoxide formation during underventilated burning within an enclosure.*

had been common for fire researchers to assess the potential of a particular fuel to generate toxic products by burning or pyrolyzing small samples and either identifying the products generated or monitoring the response of animals, such as rats, to the products. However, the results of this research showed that the amount of carbon monoxide, which is often the dominant toxic species present, generated is determined primarily by the ventilation and flow conditions under which real-scale burning is occurring and is much less dependent on fuel-to-fuel variations. This topic remains as active area of research, but many researchers have concluded that small-scale testing is only appropriate when

it is suspected that unusually toxic species may be generated by a particular fuel.

The significance of this research was recognized in 1996 when Pitts was awarded the Department of Commerce's Silver Medal "for ground breaking research in predicting the yields of carbon monoxide from fire and propelling a new era in real-scale fire research."

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## 12.8 LESS FIRE-PRONE CIGARETTES

On September 30, 1984 the landmark Cigarette Safety Act of 1984 (PL. 98-567) was signed into law. It had long been known that cigarette-initiated fires were the largest single cause of fire deaths in the United States: 1570 in 1984, along with 7000 serious injuries, 390 million of destroyed property, and a total cost of about \$4 billion. Patents for less fire-prone cigarettes dated back

to the turn of the century, but legislation to control the ignition strength of cigarettes had been thwarted by a powerful industry lobby. Rather, a mandatory standard for the cigarette resistance of mattresses and voluntary standards for upholstered furniture had become effective in the 1970s. Much of the developmental work for these standards was done in the Center for Fire Research by John Krasny and Joseph Loftus under the leadership of James Winger. They acquired detailed knowledge of cigarettes and furnishings. Now, this would be put to use in examining the cigarette.

The 1984 Act established a Technical Study Group on Cigarette and Little Cigar Fire Safety (TSG), which was directed to determine the technical and commercial feasibility, economic impact, and other consequences of developing cigarettes and little cigars that will have a minimum propensity to ignite upholstered furniture or mattresses. Such activities were to include identification of the different physical characteristics of cigarettes and little cigars which have an impact on the ignition of upholstered furniture and mattresses, an analysis of the feasibility of altering any pertinent characteristics to reduce ignition propensity, and an analysis of the possible costs and benefits, both to the industry and the public, associated with any such product modification. The TSG was composed of five representatives of Federal agencies, four representatives of the cigarette manufacturing industry, two members from the furniture manufac-

turing industry, two members from public health organizations, and two members from fire safety organizations. Richard Gann of the NBS Center for Fire Research was chosen to chair the TSG.

Over the next three years, most of the research was performed at NBS in the Center for Fire Research and the Center for Building Technology under the overall leadership of Gann: [1-7]. A team led by Robert Levine showed that it is possible to use laboratory-scale tests to produce cigarette ignition propensity data that correlated well with full-scale chairs of the same materials.

- Thomas Ohlemiller, Richard Harris, and co-workers identified certain properties of cigarettes that can be varied to reduce the likelihood of igniting a fire.
- Rosalie Ruegg's team of Steven Weber, Barbara Lippiatt, and Sieglinde Fuller, all from the Center for Building Technology showed that the cost of modifying cigarettes to lower ignition propensity is modest and is far outweighed by the societal benefits of fewer fires, injuries, and deaths.

Other projects were performed by the Consumer Product Safety Commission and the National Fire Protection Association.

As a result of this work, The TSG concluded that it was technically feasible to develop cigarettes with a significantly reduced propensity to ignite uphol-

stered furniture and mattresses and to do so with minimal economic impact, presuming the modified cigarettes were commercially feasible. The TSG also identified five additional pieces of technical work needed to support a safety standard for less fire-prone cigarettes.

The Congress responded with a second piece of legislation, the Fire Safe Cigarette Act of 1990 (P.L. 101-352). It created a Technical Advisory Group (TAG) with the same composition as the TSG. Again, Gann was chosen as the Chair. This Act specifically charged the NIST Center for Fire Research to develop a standard test method for cigarette ignition propensity, compile performance data for cigarettes using this method, and conduct research to develop predictive capability. The Consumer Product Safety Commission and the Department of Health and Human Services were also assigned tasks.

The NIST research was again successful, generating the products directed by the Act:

- A team of Kay Villa, Emil Braun, Richard Harris, Randy Lawson and Richard Gann, led by Thomas Ohlemiller and supported by Keith Eberhardt of the NIST Statistical Engineering Division, developed two methods for measuring the ignition propensity of a cigarette type: [8,9]
  - The Mock-up Ignition Method measures whether a cigarette causes ignition by transferring enough heat to a fabric/foam simulation of a piece of furni-

ture (substrate). A lit cigarette is placed on one of three different mock-ups. Ignition (failure) is defined as the char propagating 10 mm away from the tobacco column. The procedure is repeated a set number of times and the percent of failures is calculated.

- The Cigarette Extinction Method measures whether a cigarette, when placed on a heat-absorbing substrate, burns long and strong enough to cause ignition had it been dropped on a piece of furniture. A lit cigarette is placed on one of three substrates consisting of a fixed number of pieces of common filter paper. Failure is defined as the cigarette burning its full length. The procedure is repeated a set number of times and the percent failures is calculated. [While the metric in this test is the cessation of burning, it is not a test for "self-extinguishing" cigarettes. Some cigarette designs that pass this procedure have also performed well in the Mock-up Test, burning their full length without causing an ignition.]

The two methods produce similar results. Both were subjected to an interlaboratory evaluation to measure their reproducibility.

- Test data on 20 commercial cigarettes and 5 experimental cigarettes using the two methods. These data indicated that the best selling cigarettes were potent igniters of fur-

nishing and that a few specialty cigarettes had somewhat improved performance, while far better performance was technically possible. The data also provided a reference assessment of the 1993 marketplace for future use [8].

- Henri Mitler and George Walton created computer models of a multi-layer cushion subjected to a stationary heat source, a model of a burning cigarette lying on such a cushion and a protocol for using the two together [10].

In March 1994, the crew of the CBS News Magazine, 60 Minutes, visited NIST. While there was concern among NIST management that the institution would be harmed by the team of reporter Mike Wallace and producer Lowell Bergman, this turned out not to be the case. Michael Smith, the BFRL technician who had done the lion's share of the testing of the commercial cigarettes, was filmed for the show and Dick Gann was interviewed about the NIST research. The segment "Up in Smoke" aired on March 27, 1994, marking the first time NIST had been featured on the show.

During the course of the filming, Mike Wallace (who generally struck fear in the subjects of his interviews) asked Michael Smith about the difficulties of giving up smoking. Smith suggested that Mike Wallace should keep the discussions to technical topics, and Wallace apologized for the intrusion.

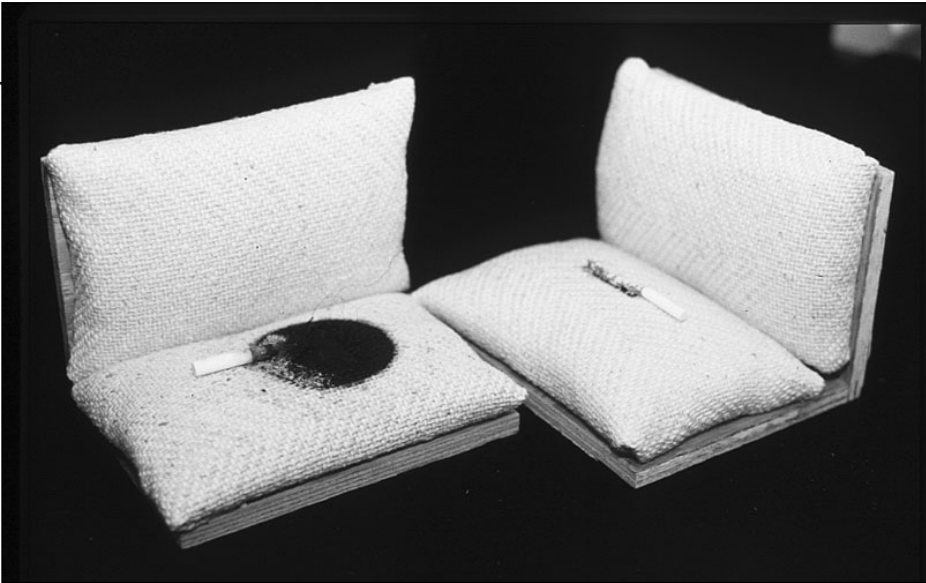


*Michael Smith, physical science technician (back to camera), demonstrates the NIST test for measuring the ignition strength of cigarettes (later ASTM E2187) for Richard Gann, chief, Fire Science Division and Mike Wallace of 60 Minutes.*

For his leadership in response to both of these Acts, Gann was awarded the Department of Commerce Silver Medal. Both test methods are currently being processed by ASTM Committee E5 on Fire Standards. Based on these results, legislation to develop a National standard for less fire-prone cigarettes has been introduced in the Congress, but a law has not yet emerged. Meanwhile, there has been activity in several state legislatures, and in June 2000, the State of New York enacted the first bill directing the development of a cigarette fire safety standard by January 2003. That regulation uses ASTM E-2187-02b, Standard Test Method for Measurement of the Ignition Strength of Cigarettes, which is the result of the NIST work. In December 2002 the team of Richard Gann, Emil Braun, Keith Eberhardt, John Krasny, Randy Lawson, and Tom Ohlemiller were honored with ASTM's Simon H.

Ingberg Award for the research leading to the Standard.

On January 11, 2000, a major manufacturer of cigarettes announced that it would soon be test marketing a modification of one of their cigarettes that would make them less likely to start a fire. The cigarette design evolved from one of the patented ideas tested (with positive results) under the Cigarette Safety Act of 1984, entailing adding circumferential bands of low air permeability paper to the paper that wraps the tobacco column. The manufacturer's ignition propensity test data, using the Mock-up Ignition test Method, indicated this design would be distinctly less likely to start a fire. The public safety community anticipated the potential for a significant reduction in life loss and injury; the regulatory community anticipated the existence of a product that would make a less fire-prone cigarette standard feasible.



Demonstration of the results of NIST research on the cigarette properties that affect the propensity of a cigarette to ignite a chair or bed. The cigarette on the left could have led to a serious fire. The cigarette on the right has properties that make it unlikely to ignite upholstered furniture.

In May 2000, soon after the test marketing of the modified cigarettes began, the Federal Trade Commission requested that the NIST Building and Fire Research Laboratory conduct tests to determine whether and to what extent this cigarette does reduce the risk of ignition. While NIST does not routinely perform product tests, it recognized the important role of the Federal Trade Commission in assuring the public of the veracity of product claims and the high potential for less fire-prone cigarettes to reduce fire deaths and injuries and agreed to measure the ignition propensity of these test cigarettes relative to the performance of the unmodified product. The NIST tests show that the banded cigarette does have a lower relative ignition propensity than its conventional counterpart and performs far better than the best selling cigarettes from 1993 [11]. That cigarette is now in commercial production.

Thus, NIST research has paved the way for reducing the single most frequent cause of fatal fires. As governing

bodies proceed toward cigarette safety standards, NIST continues to provide them with guidance on the technology to make such standards effective.

John Krasny received the Bronze Medal Award of the Department of Commerce in 1980 for his studies of self-extinguishing cigarettes, and Joseph Loftus, also in 1980, received the Bronze Medal for his studies of cigarette ignition resistance of materials. Richard Gann received the Silver Medal Award of the Department of Commerce in 1994 for his leadership of the studies of cigarette ignition propensity.

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## 12.9 ALTERNATIVE FIRE SUPPRESSANTS

The ability to control fire is universally and exclusively human. While about 400,000 years ago homo erectus had learned how to "capture" and use fire, their effort was directed at keeping the fire from going out. The first formal requirement for fire suppression appeared in ancient Rome, the first water pump and hose was implemented in 1725, and the automatic sprinkler was invented in 1812. Today, the application of chemicals, manually and by mechanical devices, to control fires has become a mainstay of safety in modern society.

Carbon tetrachloride, first mass produced early in the 20th century, was the first "clean" agent, i.e., unlike water it caused no damage to a building or its contents and left no residue itself. It was also the first halon. However, concerns soon arose about its toxic effects on firefighters and others at the fire scene. The same held true for other early halons.

In 1948, the U.S. Army commissioned a search for a fire suppressant of high efficiency but low toxicity. Two compounds emerged and became commercial successes. Halon 1301 (CF<sub>3</sub>Br) found widespread use as a total flooding agent and halon 1211 (CF<sub>2</sub>ClBr) became the predominant streaming agent. By the 1980s, most computer rooms, nearly all commercial and military aircraft, and numerous museums were typical of the high value properties protected by these halon systems.

The National Bureau of Standards became involved in fire suppression during this period. Beginning in the early 1960s, Carroll Creitz developed new ways of studying inhibited flames and proposed a mechanism for the effectiveness of halogenated flame inhibitors [1,2]. In the mid 1970s, the Center for Fire Research (CFR) hired Richard Gann, who had done research on halogenated fire suppression with the Naval Research Laboratory, and Gary Mallard, who had done similar research with the Bureau of Mines. Together, they began looking for halons that might be more effective than halon 1301.

In the 1970s, it was found that when these halons were released into the atmosphere, they would rise to the stratosphere where they would deplete the earth's delicate protective ozone layer. Under the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer and its subsequent amendments, production of halons 1301 and 1211 was restricted,

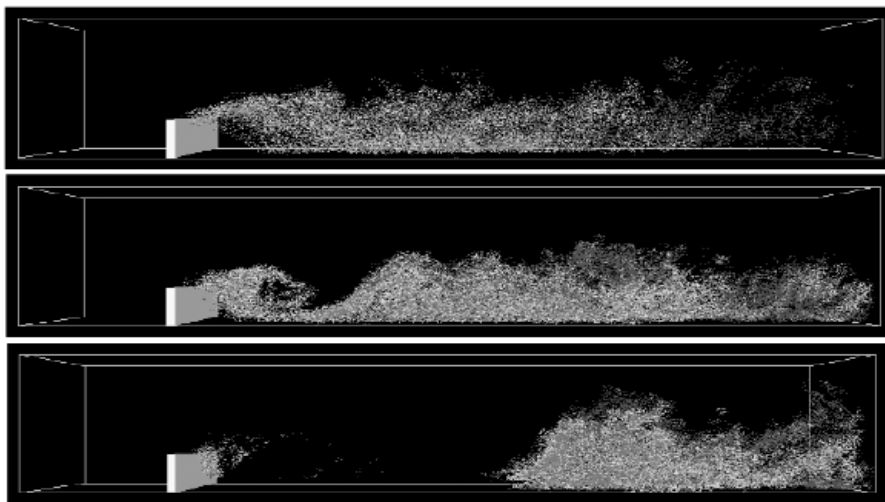
and in January 1994, nearly all production ceased.

In 1989, the newly organized industry/government Halon Alternatives Research Consortium commissioned a team led by Gann to formulate a comprehensive plan to identify new, environmentally safe fire suppressants. The first two projects were funded at NBS by the Air Force. Led by Gann, a team from CFR, the Center for Chemical Technology (CCT), and the Materials Science and Engineering Laboratory, developed a set of tools to screen possible candidates [3]. A second team, lead by William Pitts of the CFR with staff from the CCT, scoped the world of chemicals to be examined [4]. Little further public research was done, as companies began to market as fire suppressants chemicals that had emerged from the search for alternate refrigerants, a far larger market. Many users of the halons converted to these other suppressants or ceased providing fire protection altogether.

However, the Department of Defense (DoD) was faced with a critical problem. Fires and explosions were (and continue to be) among the greatest threats to the safety of personnel and the survivability of military aircraft, ships, and land vehicles in peacetime and during combat operations. For these, halon 1301 had become the fire suppressant of choice. In 1992, the DoD initiated a massive program to identify the optimal commercially available replacements for all their ozone-depleting substances, including

the halons. A large team of staff from the Building and Fire Research Laboratory and other NIST Laboratories, led by Gann, played a major role in the search for alternatives to halon 1301 for aircraft applications, establishing new science and engineering in a broad range of topics: [5,6]

- Thermodynamic properties of alternate agents: Jiann Yang, Brett Breuel
- Fluid dynamics of agent discharge: William Pitts, Jiann Yang, Grzegorz Gmurczyk, Leonard Cooper, William Grosshandler, Carole Womeldorf, Michelle King, Thomas Cleary; Marcia Huber, William Cleveland, Cary Presser (Chemical Science and Technology Laboratory, CSTL)
- Flame suppressant effectiveness: Anthony Hamins, Grzegorz Gmurczyk, William Grosshandler, Isaura Vazquez, Thomas Cleary, and Cary Presser
- Flame inhibition chemistry and the search for additional fire fighting chemicals: Marc Nyden, Gregory Linteris; Donald Burgess; Wing Tsang, Michael Zachariah (CSTL)
- Agent stability under storage and discharge residue: Richard Peacock, Thomas Cleary, Richard Harris
- Corrosion of metals: Richard Ricker and Mark Stoudt (Materials Science and Engineering Laboratory, MSEL)
- Elastomer seal compatibility: Gregory McKenna and William Waldron (MSEL)
- Human exposure and environmental impact: Emil Braun, Richard Peacock, Glenn Forney, George



*The Transient Application, Recirculating Fire (TARPF) Facility was the first laboratory-scale apparatus that enabled measuring the effectiveness of new fire suppressants in the complex environment of aircraft engine nacelles. The picture shows the progression from stable flame to one that is about to be extinguished.*

- Mulholland, Barbara Levin
- Suppression of high-speed flames and quasi-detonations: Grzegorz Gmurczyk, William Grosshandler
- Photodegradation of  $CF_3I$ : Marc Nyden
- Effects of suppressants on metal fires: Thomas Ohlemiller, John Shields
- Suppression of engine nacelle fires: Anthony Hamins, Thomas Cleary, Kevin McGrattan, Glenn Forney, William Grosshandler; Cary Presser
- Prediction of HF formation during suppression: Gregory Linteris
- Real-time suppressant concentration measurement; William Pitts, George Mulholland, Bret Breuel, Eric Johnsson, Richard Harris
- Identification of a halon 1301 simulant for use in engine nacelle certification tests: Carole Womeldorf, William Grosshandler

William Grosshandler was awarded the Department of Commerce Silver Medal in 1995 for his prime research role in this program.

The outcome of this work was the military's concurrence on the NIST rec-

ommendation of  $C_2HF_5$  as the optimal commercially available chemical to replace halon 1301 for use in engine nacelles and dry bays. Unfortunately, this chemical is about 2-3 times less efficient than halon 1301, requiring significant and costly modification of the aircraft for its implementation. [However, recent re-engineering of the Navy's F/A-18 C/D aircraft has made  $C_2HF_5$  the leading halon 1301 replacement contender for that use.]

In 1997, the DoD initiated the Next Generation Fire Suppression Technology Program (NGP) to develop retrofitable, economically feasible, environmentally acceptable, and user-safe processes, techniques, and fluids that met the operational requirements satisfied by halon 1301 systems. The new technologies would be of low mass and volume and compatible with the host weapons system design. Any new chemicals would have high suppression efficiency and perform well in evaluations of ozone depletion potential, global warming potential, atmospheric lifetime, reignition quenching, residue level, electrical conductivity,

corrosivity to metals, polymeric materials compatibility, long-term storage stability, toxicity of the chemical and its combustion and decomposition products, speed of dispersion, and occupational safety requirements. Again, Gann was appointed to lead the program.

In the first four years of the NGP, now focused on aircraft applications, about one fourth of the research was performed at NIST, mostly within BFRL with contributions from CSTL and PL. The NIST findings have led to new insights into the fire suppression process, accurate metrics for the performance of potential fire suppressant chemicals, and identification of candidate suppressants: [7,8]

- Screening tests for fire suppression efficiency: [9,10] Jiann Yang, Michelle Donnelly, William Grosshandler
- Screening protocol for agent toxicity, environmental impact, and materials compatibility: [11] Marc Nyden
- Measurements of environmental impact of suppressants: [12] Robert Huie (CSTL)
- New fire suppressant chemicals: [13-16] Gregory Linteris, Valeri Babushok, William Pitts, Linda Blevins, Jiann Yang; Wing Tsang, Marcia Huber (CSTL)
- Real-time measurement of suppressant concentration: [17] George Mulholland, Erik Johnsson; Gerald Fraser (PL)

As the research continues for new suppressants and more efficient methods

of delivering them to the fire, the NIST approach has made its mark on the entire NGP:

- use of sound science, archival and new, in planning the research and interpreting the results,
- bringing the full suite of expertise at NIST to bear on the problem,
- close collaboration with outside experts in the contributing disciplines, and
- detailed documentation of the findings and the processes that led to them.

Jiann Yang received the Department of Commerce Bronze Medal Award in 2000 for his studies of the suppression effectiveness of liquid agents.

Driven by a continuing sequence of new demands, research on fire suppressants has continued for over a century. It is likely that new criteria will continue to arise, and the NIST findings of this century will become the basis for the investigations of the next.

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## 12.10 FURNITURE FLAMMABILITY

Upholstered furniture fires have, for decades, shown up in U. S. fire statistics as one of the leading causes of fire deaths. These fires typically start through the careless use of smoking materials, particularly cigarettes, but,



*A furniture mock-up subjected to the California Technical Bulletin 113 gas flame igniter that was developed at NIST. To the left of the burner are two heat flux gages measuring the energy feedback from the flames.*

in recent years, children playing with matches have also been shown to be significant contributors. There are thus two major modes of ignition: smoldering, through contact with cigarettes, or flaming, through direct small flame contact. Either mode of ignition may eventually lead to a large flaming fire that poses a major life hazard. BFRL research on furniture flammability has largely been in support of the development of both voluntary and governmentally-mandated tests to establish the degree of hazard and to enable the development of lesser hazard designs. An implicit goal has been the development of an understanding of the ignition and burning processes as a means of assuring that meaningful measurements are at the heart of test methods.

The above goals have led in several directions. The cigarette smoldering ignition mode [1], for example, led to fundamental experimental and modeling studies of smolder initiation and propagation in upholstered furniture material composites (e.g., fabric over

polyurethane foam) and to development of test methods to establish the ignition propensity of both furniture materials and, separately, cigarettes themselves. The fundamental smoldering combustion studies and the cigarette ignition propensity studies are treated separately under appropriate headings in this history. The study of the tendency of various furniture material combinations to ignite to smoldering as a result of cigarette contact led to a test method that has been the basis for a voluntary industry standard for more than two decades.

The other major thrust that emerged from the above goals focused on measuring the flaming fire behavior of furniture and predicting this behavior from small-scale tests. Both of these were very much tied up with the development of techniques to measure the rate of heat release from a fire by measuring its oxygen consumption. Heat release rate emerged clearly as the most meaningful measure of the size of any fire; oxygen consumption

was the only truly practical and accurate means to measure this variable. It was applied to full-size chairs and sofas in the context of a furniture calorimeter developed at NIST [2]. It was applied to small samples of materials taken from furniture in the context of the Cone Calorimeter, also developed at NIST [3]. Efforts to use the small scale results to predict the full-scale behavior have met with limited success and efforts along these lines continue to this day [4]. The challenge lies in the extremely complex behavior of the burning furniture. The most recent efforts focus on bed fires that present very similar problems and challenges (with some unique slants) [6].

Throughout these studies, NIST/BFRL has worked interactively with the Consumer Products Safety Commission, which has regulatory authority in the area of furniture flammability. Each advance in testing methodology has supported CPSC

efforts to implement improved flammability standards for the upholstery and bedding industries. In a similar manner, BFRL interacted with the California Bureau of Home Furnishings, which has regulatory authority in that state, to enable them to put implement more effective test methods [5]. This agency has been a strong advocate for fire safety and the impact of their testing philosophy has reached well beyond the state of California.

James Winger received the Silver Medal Award of the Department of Commerce in 1978 for his early studies of the flammability of furniture and fabrics.

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