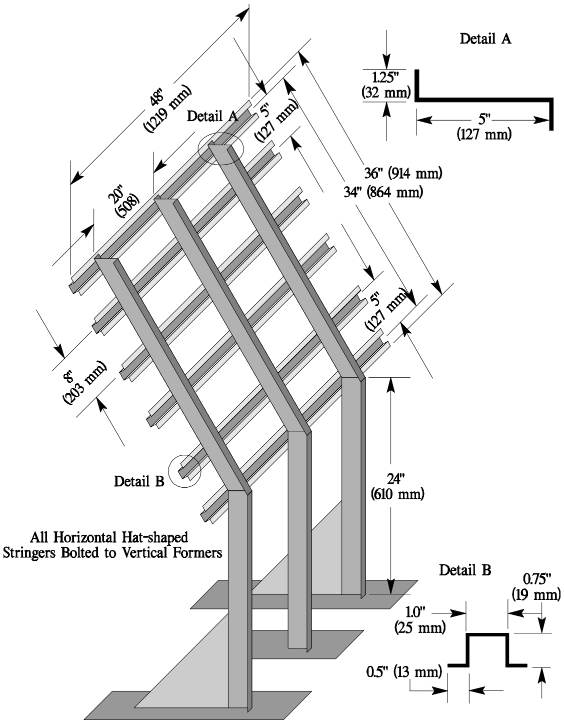
Fire Safety

Development of a Fire Test Method and Criteria for Thermal Acoustical Insulation Burnthrough Resistance

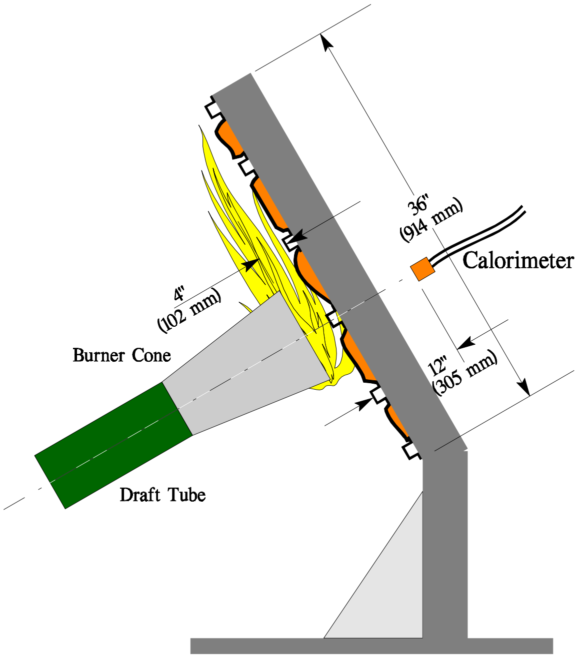
Fuselage burnthrough refers to the penetration of an external postcrash fuel fire into an aircraft cabin. The time to burnthrough is critical because, in survivable aircraft accidents accompanied by fire, ignition of the cabin materials may be caused by burnthrough from burning jet fuel external to the aircraft. Thermal acoustical insulation, typically comprised of fiberglass batting encased in either a polyvinyl fluoride (PVF) or polyester terephthalate (PET) moisture barrier, can offer additional protection if the material is not physically dislodged from the fuselage structure.

Full-scale testing using surplus aircraft has confirmed the burnthrough sequence of events as a large external fire penetrates into an aircraft cabin. In addition, full-scale tests conducted in a fuselage test rig have also highlighted the effectiveness of alternate insulation materials at significantly delaying or preventing the penetration of an external fuel fire into an aircraft cabin [reference DOT/FAA/AR-98/52 Full-Scale Test Evaluation of Aircraft Fuel Fire Burnthrough Resistance Improvements]. By delaying the burnthrough event, passengers can be afforded additional time to evacuate an aircraft, thus reducing fatalities. For this reason, a standardized laboratory test method was developed for evaluating the burnthrough resistance of thermal acoustic insulation blankets. Over 50 laboratory-scale tests were conducted in various-sized test rigs in an effort to establish a repeatable test condition that was representative of the threat likely to occur from a large external fuel fire. During the testing, it was determined that the method of attaching the insulation to the test rig structure played a key role in the effectiveness of the insulation material. In addition, the composition of the insulation bagging material, normally a thermoplastic film, may also be an important factor.

The fire threat was replicated in the lab using an oil-fired burner situated adjacent to a sample holder. This burner equipment is currently in use for other FAA test methods, such as the seat-fire blocking test and the cargo liner flame penetration resistance test. The test sample holder is oriented 30° with respect to vertical to better simulate the area of a fuselage that would likely be impacted during a postcrash fuel fire. The sample holder also incorporates three steel Z-frame vertical formers spaced 20 inches on center, typical of the construction used in large commercial aircraft fuselage. A total of six horizontal hat-shaped stringers were bolted into place as shown in figure below. This configuration allowed the



All Material 0.125" (3 mm) Thickness Except Center Vertical Former, 0.1875" (5 mm) Thick installation of two between-frame blankets that could be tested for burnthrough resistance. The test burner is aimed at the center of the test frame (below). Two heat flux transducers are mounted on the cold side of the sample holder to monitor the amount of radiant and convective heat flux passing through the test sample. A pass/fail criteria of 2.0 Btu/ft^2 sec on either transducer has been established.



In order to develop a test condition that was most representative of full-scale conditions, several tests were performed using Alclad aluminum skin identical to that used in the full-scale tests. During full-scale tests, the Alclad material failed in approximately 55 seconds, which was the target for the lab-scale testing device. During the baseline trials, the burner fuel flowrate, intake air velocity, and position respective to the test frame were modified in order to obtain the appropriate condition (Table below). By increasing the fuel flowrate to 6 gallons per hour and positioning the burner cone 4 inches from the sample holder frame, the proper 55-second burnthrough time was achieved. This condition produced a flame temperature and heat flux output of 1900°F and 13.5 Btu/ft^2 sec, respectively, measured at 4 inches from the burner cone exit plane.

After finalizing the fire exposure condition, trials were run using a combination of aluminum skin and thermal acoustic insulation. However, it became evident that the use of the aluminum skin created a cumbersome test, as it was difficult to quickly and realistically mount and remove the aluminum skin each time, so the configuration was simplified to involve the insulation materials only. Originally, to specify the burnthrough protection needed based on an analysis of past accidents, the pass/fail criteria was set at 5 minutes with the aluminum skin and insulation materials combination, but this was adjusted to 4 minutes in the

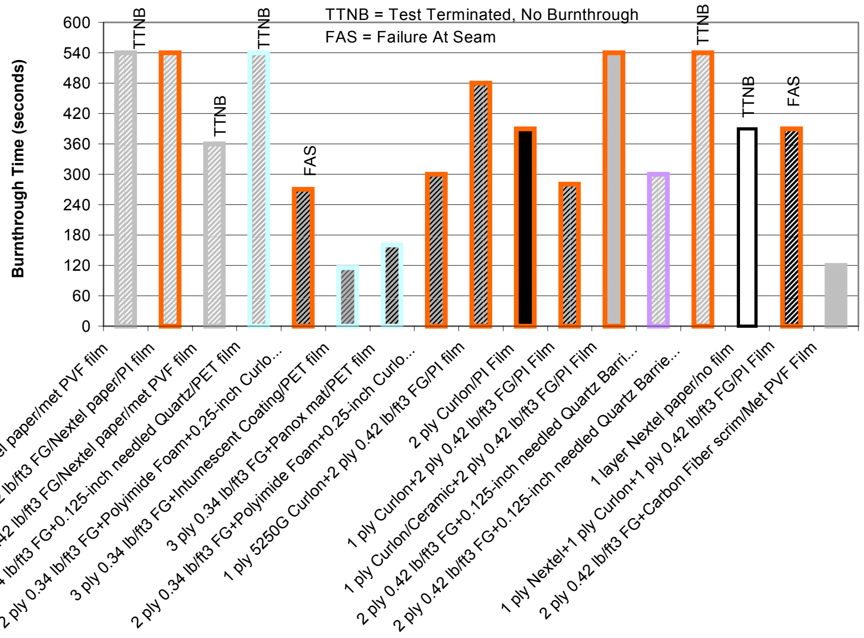
Test Date	Burner Fuel Flowrate (gal/hr)	Burner Air Velocity (ft/min)	Burner Distance (inches)	Skin Material	Skin Thickness (inches)	Burnthrough Time (seconds)
12/8/98	2	1800	5	5052 Aluminum	0.05	480 +
12/8/98	2	1800	2	5052 Aluminum	0.05	45 to 80
12/8/98	4	2000	4	5052 Aluminum	0.05	120
12/9/98	6	2200	4	5052 Aluminum	0.05	55
12/9/98	6	2200	4	5052 Aluminum	0.05	55

absence of the skin. The realistic test configuration further highlighted the importance of attachment of the insulation. As it appeared, some current original equipment manufacturer (OEM) designs allowed for easy flame penetration along the seam area where the two between-frame blankets join along the vertical former. As a result, a standardized attachment system was used to prevent early failure along the center vertical former. Future guidance material will be developed to evaluate OEM insulation attachment designs in order to prevent these types of failures in service.

Additional tests were run using a variety of insulation materials, in which the results correlated well with previous full-scale tests using identical materials (see figure below). This test method has been incorporated into a planned Notice of Proposed Rulemaking (NPRM) for new insulation flammability requirements, which is expected to be released in the latter part of 1999.

POC: Mr. Timothy Marker, AAR-422, (609) 485-6469.

Burnthrough Comparison Using 6 GPH Burner, 4 Inches from Sample Holder



Development of a Fire Test Method and Criteria for Thermal Acoustical Insulation Resistance to In-Flight Fire

Fiberglass bat-type insulation is used extensively throughout the fuselage of commercial aircraft. It serves two main purposes thermal and acoustical suppression. Fiberglass batting, using a very small fiber diameter, is a highly efficient thermal barrier and acoustic attenuator. Typically, the insulation blankets consist of fiberglass batting encapsulated in plastic moisture barrier film coverings. Film covering materials have consisted predominantly of polyethylene terephthalate (PET), polyvinyl fluoride (PVF), and to a lesser degree, polyimide.

Currently, a vertical Bunsen burner test is the only FAA requirement for all thermal acoustic insulation materials, including those used to insulate ductwork beneath floors, behind the sidewall, and in the cheek areas. Although these materials are required to meet this flammability test, some have been found to propagate fire under certain conditions. Several fire incidents/accidents between 1993 and 1995 focused attention on the flammability of the insulation materials. Following this, a series of tests were run which exposed the inability of the vertical Bunsen burner test method at discriminating between materials that allow flame propagation and materials that do not. A test originally developed by the aircraft manufacturers, involving the placement of flaming cotton swabs on the film surface, was evaluated and seemed to provide a more realistic assessment of the material performance [reference DOT/FAA/AR-97/58, Evaluation of Fire Test Methods for Aircraft Thermal Acoustical Insulation]. However, large-scale tests and in-service experience indicated that the cotton swab test was not severe enough, so research continued on the development of a more realistic test. After conducting a variety of mock-up tests in small-, intermediate-, and full-scale test rigs, the flame characteristics of the very thin film coverings were more fully understood, and a decision was made to use a radiant panel test apparatus for determining the fire resistance of insulation blankets.

The radiant panel test apparatus that has been proposed for evaluating the flammability of insulation blankets is shown in figure 1. This test equipment was originally used for measuring the critical radiant flux of horizontally mounted floor-covering systems according to ASTM E648, which exposed a test sample to a flaming ignition source in a graded radiant heat energy environment. The critical radiant heat flux can be described as the heat flux level below which flame spread will not occur. This test has been adapted for evaluation of the flammability of thermal acoustical insulation covering films, as it offers the possibility of recording flame propagation velocity, the time of ignition, and the burn length at different heat fluxes. The test also provides the level of incident radiant heat energy on the covering film at the most distant flameout point, which is the

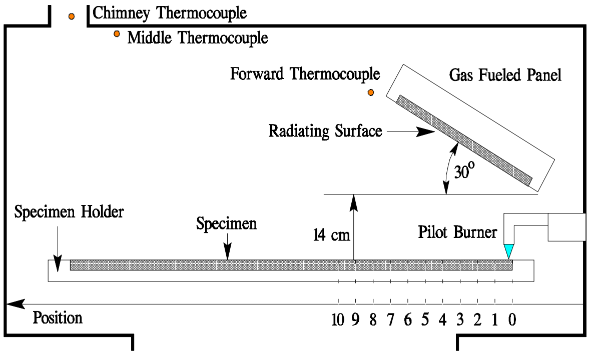


Figure 1. Radiant Panel Test Apparatus for Evaluating Flammability of Thermal Acoustical Insulation

critical heat flux measurement, in Btu/ft^{2}sec (kW/m^2). On August 12, 1999, the FAA issued an Airworthiness Directive requiring the replacement of metalized PET insulation blankets with materials shown compliant with the radiant panel test adopted by the FAA for evaluating the flammability performance of thermal acoustic insulation materials.

Prior to testing, the radiant panel was calibrated to determine the heat flux as a function of distance from the point of initiation of flaming ignition. This is referred to as the flux profile. The heat flux was measured using a 0 to 10-mV range heat flux transducer at 10 positions along the horizontal incident surface at a distance of 2 inches between each position (figure 2).

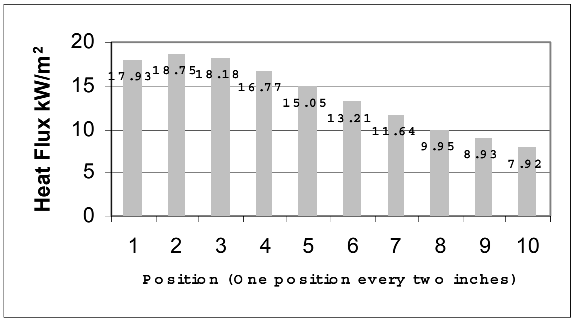


Figure 2. Flux Profile Curve of Incident Radiant Heat Energy Versus Position on the Specimen Surface

During the FAA's evaluation of the radiant panel test, a number of aircraft films were tested. The initial results in terms of burn length and critical heat flux are shown in figure 3. Overall, the results were consistent with what was observed during the mock-up intermediate- and full-scale fire tests. In addition, physical effects such as melting, contraction, and the behavior of the reinforcing scrim, which play an important role in the flammability of the thin films, can be readily observed and better understood. Finally, the test appears to be repeatable, which is an important consideration when the output is a proposed requirement.

A finalized test procedure has been adopted. During the test, a 10-inch wide by 40-inch long sample is clamped to a sliding platform with test samples typically consisting of two layers of fiberglass batting with film covering. After the temperatures within the test chamber stabilize, the sample is inserted into the test chamber via the sliding platform, and the chamber door is closed. Simultaneously, the pilot burner flame is brought into contact with the specimen. A burn length of less than a 2-inch radius is the proposed acceptance criteria. In effect, the proposed criteria prevents ignition under the specified in-flight fire exposure condition. This test method will also be included in a planned Notice of Proposed Rulemaking (NPRM), expected to be issued in the early part of 2000, which specifies new stringent flammability criteria for insulation blankets.

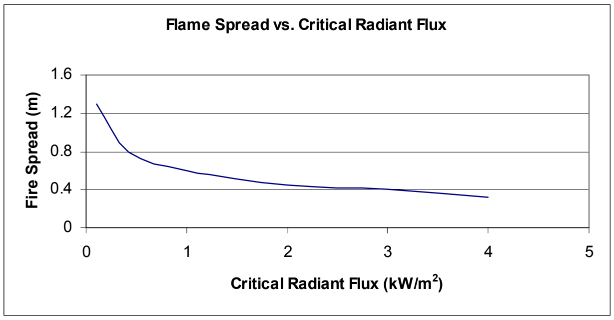


Figure 3. Relationship Between Flame Spread and Critical Radiant Heat Flux

POC: Mr. Timothy Marker AAR-421, (609) 485-6469.

Effectiveness of Flight Attendants Attempting to Extinguish Fires in an Accessible Cargo Compartment

Research was initiated at the request of an Aviation Rulemaking Advisory Committee (ARAC) subgroup to look at the issue of controlling fires in small accessible cargo compartments. These cargo compartments are designated as Class B compartments and rely on a crew member with hand-held fire extinguishers to control any fire. An in-flight cargo fire in a class B compartment on a B-747 led to the crash of the aircraft killing all 159 occupants. Subsequent full-scale testing in large cargo compartments led to an Airworthiness Directive that eliminated the traditional Class B compartment on transport category aircraft. The ARAC group was responsible for proposing new regulations for the class B cargo compartments on commuter-sized aircraft.

A Shorts 330 aircraft was used as the test article for the project. The test article was instrumented with thermocouples, smoke meters, gas analyzers, and video cameras. The Association of Flight Attendants (AFA) recruited volunteers from its membership to participate in the testing. The purpose of the testing was to determine what equipment and conditions were necessary for flight attendants to successfully extinguish the test fires based on their current level of training.

Some of the variables examined in the testing included the cargo compartment volume, the width of the cargo door opening, the quantity and type of extinguishers available, the presence of a clear aisle space inside the compartment, and the delay between the activation of the smoke detector and the start of the firefighting effort.

In addition to the fire tests, time trial tests were conducted to determine how long it would take the flight attendants to prepare emergency equipment to fight a fire. This involved opening and donning the protective breathing hoods and removing the fire extinguisher from its storage location and pulling the pin.

The study concluded that the test fires could not be extinguished in the size and configuration of compartments normally found on commuter aircraft with the quantity of fire extinguishers typically carried and that large quantities of smoke and gases filled the aircraft cabin when the cargo compartment door was opened to attempt to extinguish the fires.

In addition to the results of the fire tests, it was noted that there were numerous problems experienced by the flight attendants with the emergency equipment. Some of these were the inability to open the protective breathing hoods, poor visibility and hearing while wearing the hoods, and a lack of appreciation for how quickly visibility can deteriorate in a smoke-filled environment. The findings were published in Technical Note DOT/FAA/AR-TN99/29, Effectiveness of Flight Attendants Attempting to Extinguish Fires in an Accessible Cargo Compartment.

The results were made available to the ARAC group to support their recommended rule changes. A secondary benefit was the increased awareness of the importance of realistic training in the use of emergency equipment. The results of the test project was presented at the FAA Fire Safety and Research Conference in

Atlantic City, NJ, in November 1998 and at the Cabin Safety Symposium in Costa Mesa, CA, in January 1999. Airlines have made numerous requests for copies of videotape documenting the experiences encountered by the flight attendants in using the emergency equipment and in fighting the test fires. The airlines planned to use the video in their training programs.

POC: Dave Blake, AAR-422,
(609) 485-4525.

Protection of Oxygen Cylinders During a Cargo Compartment Fire

In the wake of the ValuJet fatal in-flight fire that was attributed to the improper packaging of solid oxygen generators, the shipment of all types of oxidizers including compressed gas cylinders has been closely regulated. Full-scale tests were conducted that highlighted the ability of gaseous oxygen to overtax the cargo compartment suppression system during a controlled, but deep-seated fire [reference DOT/FAA/AR-TN98/29, Oxygen Enhanced Fires in LD-3 Cargo Containers].

Further testing confirmed that the use of compressed gas shipping containers designed for protection against impact damage had the ability to delay the heating and subsequent overpressurization and release of oxygen from the cylinders during a controlled fire, which could otherwise lead to significant fire intensification [reference DOT/FAA/AR-TN98/30, Evaluation of Oxygen Cylinder Overpacks Exposed to Elevated Temperature]. A typical overpack is shown in figure 1.

Figure 1. Typical Oxygen Overpack

Tests showed that some common overpacks have the ability to protect the cylinders from pressure relief activation for nearly 60 minutes in a 400°F environment (cargo compartment temperature during a suppressed, deep-seated fire), while other types designed specifically for thermal protection can prevent rupture disc activation for even greater periods of time.

As a result of this research, a strawman thermal protection performance standard was developed and sent to the Research and Special Programs Administration (RSPA) for review. RSPA is the federal agency responsible for regulation of the shipment of hazardous materials.

The proposed standard specified two tests: a high-intensity open-flaming short duration exposure and a long duration nonflaming exposure at an elevated temperature of 400°F. The purpose of the combination exposures was to simulate the environment that could exist in a cargo compartment during a controlled fire. Realistically, once a fire originates, there is a period of delay between the actual fire event and the application of the suppressant. During this period, it is conceivable that a fire could build in intensity prior to the smoke detection system alerting the flight deck and subsequent arming of the suppression system and release of the agent. Subsequent to this, testing has shown that sustained temperatures of 400°F can exist inside the compartment, even though the fire is suppressed and fully under control.

In response to the proposed performance standard and NTSB recommendations, RSPA released a final rule on August 19, 1999, that impacted the shipment of compressed oxygen. The final rule references and describes the aforementioned FAA tests and reports. As stated in the final rule, the RSPA "believes that any increase in risk posed by the presence of a compressed oxygen cylinder in a cargo compartment can be significantly reduced, or even eliminated, if the oxygen cylinder is placed in an outer packaging or overpack that provides more thermal protection and flame resistance than the ATA 300 overpacks currently in use." Furthermore, working with the FAA, the RSPA "is developing proposed enhanced standards for outer packagings or overpacks to further protect cylinders from heat and fire. The RSPA anticipates publishing an NPRM later [in 1999] to invite comments on enhanced standards for these outer packagings or overpacks, including a proposed date for their implementation. At present, RSPA is considering a requirement that an oxygen cylinder may be carried in an inaccessible cargo compartment on an aircraft only when the cylinder is placed in an outer packaging or overpack meeting certain flame penetration resistance, thermal protection, and integrity standards. The flame penetration standards would likely be similar to those specified for class C cargo compartment liners in 14 CFR 25, appendix F, part III."

POC: Mr. Timothy Marker, AAR-422, (609) 485-6469.

Development of a Hand-Held Fire Extinguisher Employing Dry Ice

A new type of fire extinguisher has been developed that produces a dry ice snow to extinguish fires. Carbon dioxide has long been employed as a firefighting agent for extinguishing flammable liquids. The only difference between existing carbon dioxide extinguishers and the new one is that the discharge horn has been replaced with a device called an Adiabatic Expansion Nozzle. The new nozzle is the same size as the discharge horn that it replaces, has no moving parts, and costs less than $5.00 to produce. The application for a patent has been submitted and is currently pending.

Conceptually, the device allows a multiple staged expansion of the carbon dioxide with several reversals in the direction of flow of the agent. In figure 1, liquid carbon dioxide emerges (flowing left to right) from the innermost tube (12) into a second tube (14) where expansion into gas

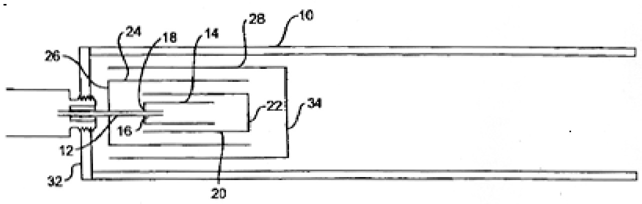


Figure 1. A Cross Sectional Drawing of the Nozzle.

occurs. End caps (18, 22, 26, and 34) force the flow of carbon dioxide to reverse direction as the carbon dioxide exits into subsequent larger tubes (20, 24, and 26). Spacers (not shown) are soldered between the tubes, holding the device together. As the high-pressure liquid carbon dioxide expands into a gas, the latent heat of vaporization cools the liquid subsequently entering the nozzle. Instead of the liquid expanding into a gas as happens with conventional carbon dioxide fire extinguishers, the liquid partially undergoes a phase change into the solid form of carbon dioxide, commonly known as dry ice.

Dry ice has several advantages over conventional carbon dioxide. First, the discharge pressure of the fire extinguisher is greatly reduced. This reduces the likelihood of blowing flaming material about or knocking over containers of flammable material, possibly causing the fire to spread. Second, the solid agent is extremely cold causing a reduction in the vapor pressure of the fuel, making it easier to fight the fuel fire. Third, dry ice remains on the site of the fire, making re-ignition less likely.

Limited testing at the William J. Hughes Technical Center has demonstrated that a 5-pound hand-held extinguisher equipped with the Adiabatic Expansion Nozzle puts out a standard Underwriter's Laboratory Class 1-B fire in approximately half the time compared to a conventional one. The extinguisher also operates at a lower flow rate, meaning that the time until the agent is exhausted is extended several seconds.

Above, a firefighter extinguishes a fuel pan fire using an extinguisher equipped with the Adiabatic Expansion Nozzle.

Somewhat different versions of the nozzle are useful for decreasing the exit velocity and temperature of fluorocarbon-based Halon replacement candidates. This means that agents previously considered only for total flood applications (e.g., engine nacelles) may also be used in a streaming mode (e.g., hand-held or manned apparatus), eliminating the need for two different agents depending on the application.

The invention was awarded the FAA 1999 Technology Transfer Award for Intellectual Property.

POC: Mr. Robert Filipczak, AAR-422, (609) 485-4529.

The Use of a Simulant for Certification Testing of a Halon 1301 System for Aircraft Cargo Compartments

The Federal Aviation Administration (FAA) requires certification tests of fire suppression systems to ensure proper operation of the system and an adequate concentration of extinguishing agent. Because Halon 1301 will continue to be the agent of choice in new fire suppression systems installed to meet the new cargo compartment rule, quantities of halon will be discharged into the atmosphere during certification testing.

To reduce atmospheric ozone depletion from future certification testing, the International Halon Replacement Working Group (IHRWG) formed a task group to evaluate zero ozone depletion agents as simulants for Halon 1301.

Published reports from the U.S. Department of the Navy and other entities identified two agents, Pentafluoroethane (HFC 125) and Sulfur Hexafluoride (SF_6), as excellent simulants for Halon 1301 fire protection systems used in shipboard machinery spaces and aircraft engine nacelles.

Agents Cylinders

On these merits, the FAA evaluated these agents with the intent of using one or both of them as a halon simulant for certifying aircraft cargo compartments. More than 50 discharge tests, in compartments with volume sizes of 300 ft^3 and 2000 ft^3, with HFC 125, SF_6, and Halon 1301 were conducted and compared on the basis of decay rate and volumetric concentration. The cargo bay leak rate was varied in the smaller compartment.

Results showed that for the first 5 minutes, after initiating the test, HFC 125 mimics very well the concentrations of Halon 1301, but after this period, the difference between these two agents increased significantly.

An average decay curve was generated from multiple tests and the six sampling probes that were located at different heights in the compartment. This exercise was conducted for all of the data that was collected during the tests at different leak rates. The decay rates were calculated and compared.

The maximum decay rate relative differences for HFC 125, when compared to halon, were 41.5% at a leak rate of 2 CFM, 15.6% at 11 CFM, 12.0% at 21 CFM, and 26.6% at 50 CFM. The relative difference between Halon 1301 and HFC 125, at 3% volumetric concentration (or at the end of the test in the case where 3% was not reached), ranged between 4.52% and 14.96%.

As shown in figure 2, HFC 125 achieved concentrations that resulted in differences that were on the unsafe side (i.e., indicative of a higher halon concentration) when compared to the baseline agent; this difference increased with time and as the leak rate of the compartment decreased.

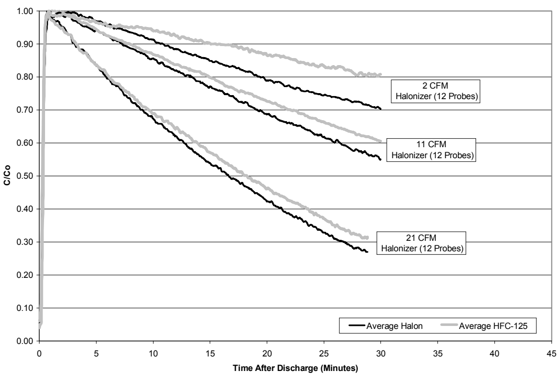


Figure 2. Halon 1301 VS HFC 125 Concentration Histories at Various Leak Rates

For these reasons HFC 125 was not deemed to be an adequate simulant for a cargo compartment fire suppression system using Halon 1301.

SF_6 did not match halon's initial concentration as well as HFC 125 during the total flood discharge, but as time passed, the concentration difference was much better than that of HFC 125. Once again, an average decay curve was generated from multiple tests. This exercise was conducted for all of the data that was collected during the tests at different leak rates. The decay rates were calculated and compared. With the exception of the decay rate calculated at 2 CFM, SF_6 had the lowest maximum relative difference when compared to the decay rate values obtained with HFC 125. SF_6 decay history at a 2-CFM leak rate did not follow a typical exponential decay, causing a higher difference. The maximum decay rate differences between SF_6 and Halon 1301 at different leak rates were 11.60% at a leak rate of 11 CFM, 1.60% at 21 CFM (with the gas probe at 22.5" from the floor), 0.40% at 21 CFM (with the gas probe at 45" from the floor), and 1.74% at 50 CFM. The relative difference between Halon 1301 and SF_6, at a 3% volumetric concentration (or at the end of the test in the case where 3% was not reached), ranged between 1.37% and 5.84%.

On a positive note, the difference that exists between the concentrations of SF_6 and Halon 1301 are on the safe side. This conservative difference indicates that the simulant concentration in the compartment may be lower than what the halon concentration would be during the certification tests, providing a margin of safety. Figures 2, 3, and 4 provide a qualitative comparison between the evaluated agents.

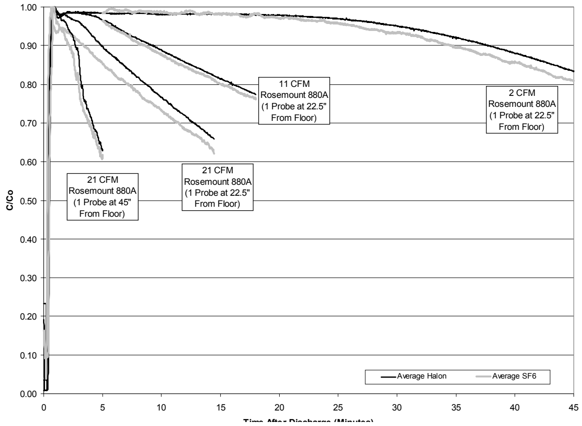


Figure 3. Halon 1301 VS SF6 Concentration Histories at Various Leak Rates

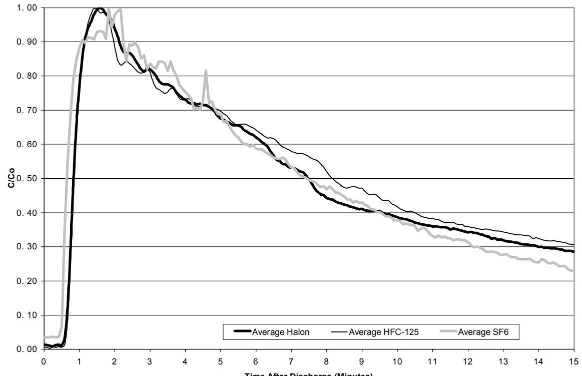


Figure 4. Agent Concentration Histories at 50-CFM Leak Rate

Figure 5 illustrates the concentration history of SF_6 and Halon 1301 after the metering system was activated. The discharge flow and pressure of the metered system were arbitrarily selected; the main purpose of this setup was to compare the concentrations of the agents rather than to optimize the system. Qualitatively, the graph shows that SF_6 mimics very well the injected concentration levels of Halon 1301 using this specific metering system. The maximum average concentration relative differences between these two agents, at two distinct leak rates, are 8.18% at 11 CFM and 7.38% at 21 CFM.

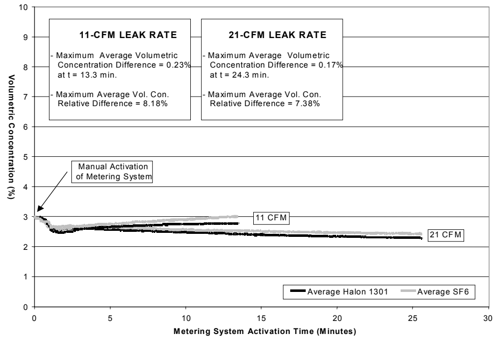


Figure 5. Agent Concentration History With Metering System Activated

In summary, these tests have shown that SF_6, based on equal initial volumetric concentrations, is the best of the two identified Halon 1301 simulants when used in certification testing of the aircraft cargo compartment fire suppression system. Results showed that SF_6 and Halon 1301 had similar decay rates and volumetric concentrations when submitted to various leak rates, cargo sizes, and metering. SF_6 is an excellent simulant when considering aircraft cargo leakage rate and the integration of a suppression system with a metering system.

The IHRWG task members will carefully review these results in order to address any unforeseen issue and finalize the work. After completion, the task group will issue a recommendation to the FAA certification officials. Once implemented, this simulant will reduce the atmospheric ozone depletion caused by the use of halon during cargo compartment certification tests.

POC: John Reinhardt, AAR-422,
(609) 485-5034.

Impact of Mass Loading and Environmental Heating or Cooling on Fuel Tank Vapor Concentration

In response to the TWA 800 accident, the NTSB “has recommended maintaining sufficient amount of fuel in the Center Wing Tanks (CWTs) of transport aircraft to limit the liquid fuel temperature rise and evaporation, thus keeping the vapor fuel/air ratio below the explosive limit.” While considering the reduction of the fuel/air ratio by means of increasing the mass loading (and thus reducing the vaporization of fuel due to heating), it is still necessary to look at all possible methods of reducing the fuel/air ratio. At the other end of the spectrum, by reducing the mass loading, there is more depletion of the lightweight, volatile hydrocarbon components of the fuel vapor, or the light ends, thus reducing the mass of the fuel vapors.

Experiments were conducted to examine the effect of the reduction of the mass loading on the ullage vapor concentration. Knowing that the effect would be seen at a relatively low mass loading, the tests used values below 6 kg/m^3. In addition, tests were conducted to evaluate the lag time (time needed to reach fuel vapor concentration equilibrium at a given fuel temperature) and the effects of cold tank walls on vapor concentration within the tank.

The test setup, shown in figure 1, consisted of the 88.21 ft^3 fuel tank, 14 K-type thermocouples, a 150,000-Btu kerosene heater, and a total hydrocarbon analyzer. The tank was constructed of ¼-inch aluminum. The 14 thermocouples were used to monitor ullage, wall, and fuel temperature within the tank and heating air in and out under the tank.

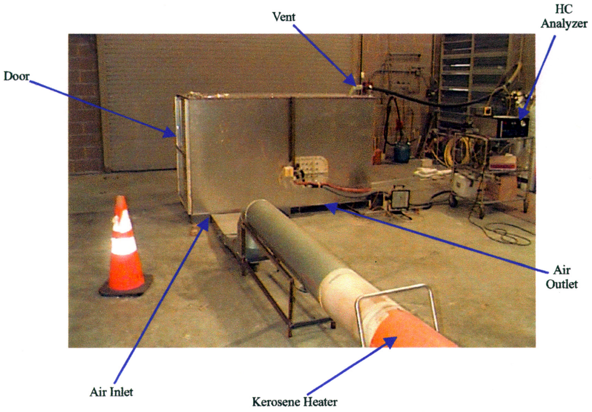


Figure 1. Test Setup

The simulated fuel tank was approximately 1/20 the volume of a typical B-747 CWT. From these tests, it has been determined that the CWT would have to be nearly empty (a mass loading between 0.15 and 0.08 kg/m^3) in order to have a substantial effect on the flammability of the vapor (Figure 2).

Again, it should be noted that the effect was said to be substantial if the resulting decrease in the maximum hydrocarbon count was a minimum of 20% of the average of all tests conducted with larger mass loadings. It has also been learned that while the distribution of the fuel has no effect on the maximum flammability (fuel vapor concentration) that is reached, it does have a very significant effect on how long it takes to reach the final value. The less dispersed the liquid fuel is the longer it will take the vapor to reach its maximum flammability point. In addition, it was determined that residual amounts of fuel on the side walls of the tank had little to no effect on either the maximum flammability point that was reached or the time that was necessary to reach this point.

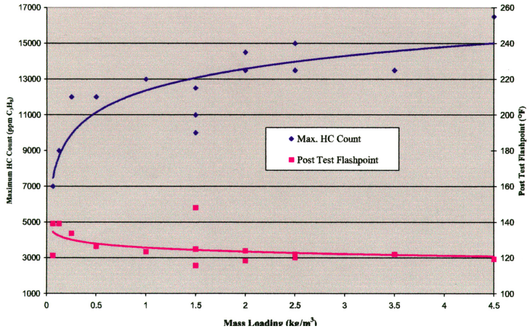


Figure 2. Maximum Hydrocarbon Count (ppm C_3H_8) and Posttest Flashpoint (°F) as a Function of Mass Loading

The results of this study are documented in Technical Note DOT/FAA/AR-TN99/65, “Mass Loading Effects on the Fuel Vapor Concentrations of an Aircraft Fuel Tank Ullage.”

POC: Mr. Richard Hill, AAR-422, (609) 485-5997.

Smart Polymers

Organic polymers (plastics and resins) exhibit a wide range of fire performance from highly flammable to noncombustible. Within this range of fire performance are categories such as flame resistant and fire resistant which are loosely defined by the results of standardized tests. Flame-resistant materials are typically commodity plastics and resins (e.g., polyethylene, polystyrene, polycarbonate, ABS, epoxy) to which flame-retardant chemicals have been added to achieve self-extinguishing behavior in a small Bunsen burner flame test.

Fire resistance is a much more severe requirement for materials and use of these materials results in a higher level of safety. Fire-resistant materials not only resisting ignition from a small heat source or flame, but if ignited in a fire environment such as a postcrash aircraft cabin, burn slowly (or not at all) to allow passengers sufficient time for escape. Fire resistance is quantified by measuring the rate at which heat is released in a fire calorimeter by the burning material. Over the past two decades fire science and engineering has advanced considerably and the relationship between the heat release rate of a burning material and its hazard in a fire is now well established, largely through the pioneering efforts of the FAA Airport and Aircraft Safety Research and Development Division's Fire Safety Section. In fact, the FAA was the first to adopt heat release rate of burning materials as a federal fire safety regulation for public transportation.

To date fire resistance has been achieved only by char-forming polymers with high thermal decomposition temperatures, T_p. Some drawbacks to the use of these high-temperature plastics for fire resistance are the dark color they impart to the finished product, their tendency to crack during use, and the need for very high molding temperatures (several hundred degrees) to soften and flow the material. In addition, thermally stable polymers are relatively expensive because of the high cost of the starting materials and synthesis procedures. Thus, while heat-resistant plastics are relatively fire safe their high cost, difficult processing characteristics, and poor durability have limited their commercial use in public transportation.

A simple burning model (see Solid-State Thermochemistry of Flaming Combustion on page 67) predicts that the fire hazard or heat release rate of a combustible materials is given by

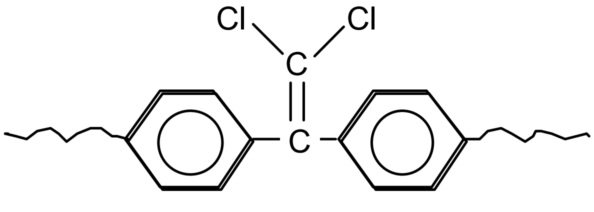
$$\text{Fire Hazard} \propto \frac{h_c(1-\mu)}{T_p^2} \qquad (1)$$

where h_c is the effective heat of combustion of the fuel gases, T_p is the polymer decomposition temperature, and μ is the fraction of polymer mass converted to char in a fire. Equation 1 shows how and to what extent fire resistance can be improved by raising the decomposition temperature to provide more heat resistance, lowering the amount of heat given off during burning, and increasing the amount of carbonization (charring) of the plastic to reduce the amount of volatile fuel. Until recently, there has been no way to optimize all of these fire parameters in a single material so that the potential order-of-magnitude reduction in fire hazard as predicted by Equation 1 has remained elusive. Our current approach has been to achieve the desired result using two materials.

We use molecular engineering to design "smart" polymers that are tough and flexible under normal use conditions but transform themselves into noncombustible materials with high μ, T_p, and low h_c in a fire. Under normal use and processing conditions these polymers have the desirable attributes of commodity plastics and resins in that they are readily soluble in common solvents, easy to mold, flexible, and impact resistant. When heated in a fire, however, they convert to thermally stable, high-char yield materials with the evolution of noncombustible gases, resulting in a material with an order-of-magnitude lower fire hazard than commodity versions of the same polymers. Two different smart polymers have been designed, synthesized, and tested to date: chloral-based polymers and polyhydroxyamides.

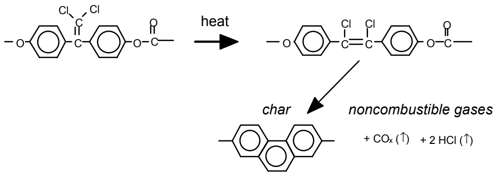
Chloral Polymers

The first type is based on a new, low-cost chemical 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (bisphenol-C, BPC) which is linked together to make long chain polymers containing predominantly the "smart" bisphenylchloroethylene group.



The Bisphenylchloroethylene (BPC) Group is the Backbone of Chloral Polymers

When heated in a fire to about 450-500°C (842-932°F) the BPC group spontaneously transforms into noncombustible carbon dioxide and hydrogen chloride gases and a noncombustible solid char. A possible mechanism for the BPC transformation is shown below for a BPC polycarbonate. While the exact mechanism is the subject of current research efforts, preliminary combustion measurements confirm the low heat of combustion of the product gases ($h_c \approx 3$ kJ/g) and the near quantitative char yield based on the chemical structure of the polymer.



Possible Fire-Resistance Mechanism of Chloral Polycarbonate

A wide variety of common polymers are based on bisphenol-A including epoxies, polycarbonate, polyarylates, polysulfones, etc., and bisphenol-C is a "drop-in" replacement for bisphenol-A in many of the synthesis procedures. Preliminary microcalorimeter screening of gram quantities of a few polymers we have synthesized using bisphenol-C (BPC) in place of conventional bisphenol-A (BPA) confirms that an order-of-magnitude increase in fire safety can be achieved (see table 1). The efficacy of chloral-based polymers containing a predominance of the thermally stable bisarydichloroethylene chemical group on heat release rate derives from the unique combination of a high decomposition temperature ($T_p \approx 500$°C), high char yield ($\mu > 0.5$), and extremely low effective heat of combustion of the fuel gases ($h_c \approx 3$ kJ/g) during the burning process of polymers. Compared to the bisphenol-A polymer analogs with $T_p \approx 400 \pm 50$°C, $h_c \approx 30 \pm 5$ kJ/g, and $\mu \approx 0.2 \pm 0.2$, we expect a factor of about 20 reduction in fire hazard for polymers containing a preponderance of the BPC group.

The factor of 20 reduction in heat release rate predicted by equation 1 is approached but fuel-containing linkages from the polymerization reaction (e.g., ester, triazine, carbonate, phenoxy) reduce the performance somewhat. These levels of fire performance have never been achieved in commercial engineering polymers

Table 1. Reduction in Heat Release Rate of Polymers by Replacing BPA With BPC

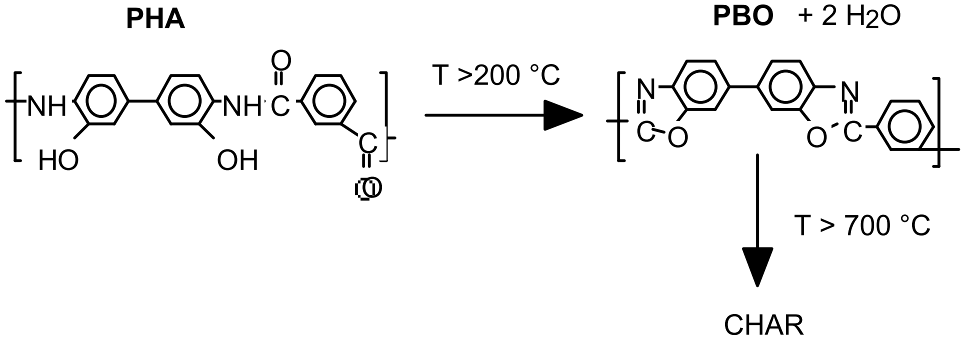
Polymer	Heat Release Rate Reduction
THERMOPLASTICS	
Polyarylate	14X
Polycarbonate	17X
THERMOSETS	
Epoxy	8X

Polyhydroxyamides

A second polymer which exhibits smart behavior by transforming to a fire-resistant material *in situ* is polyhydroxyamide (PHA). When heated, the linear PHA polymer converts to polybenzoxazole (PBO) with the evolution of water as shown below. PBO has excellent thermal and oxidative stability but is only soluble in strong mineral acids and doesn't melt so it is difficult or impossible to use for fabricating aircraft interior parts. Polyhydroxyamides (PHA) are PBO precursors which are soluble in common solvents and are easy to process into films and fibers. When heated in a fire, polyhydroxyamide generates PBO and water *in situ* by a cyclization reaction (see figure below). Further heating above 700°C results in predominantly char formation.

This work was awarded an FAA in a 1999 Technology Transfer Award.

POC: Mr. Richard Lyon, AAR-422, (609) 485-6076.



Fire-Resistance Mechanism of Polyhydroxyamides

Heats of Combustion of High-Temperature Polymers

Commercial passenger aircraft cabins contain several tons of combustible plastics, thermoset resins, and elastomers in sidewall panels, ceilings, seat parts, foamed cushions, carpets, etc. The potential fire load represented by these interior materials is their heat of combustion. Using full- and bench-scale fire testing the Federal Aviation Administration (FAA) determined that the fire hazard in an aircraft cabin is not only a function of the effective heat of combustion of the cabin materials but also the rate at which this heat is released by the burning material in a fire. Consequently, FAA regulations were developed for both effective heat of combustion and heat release rate of large area cabin materials. In the FAA test, convected heat released during flaming combustion is calculated from the temperature rise of an air stream flowing past a standard-sized sample of the burning material. Bench-scale fire calorimeters have since been developed which use the oxygen consumption principle to determine the chemical heat release rate of burning materials. The oxygen consumption principle is based on the observation that combustion of a wide range of organic compounds and common polymers produces 13.1 ± 0.7 kJ of heat per gram of diatomic oxygen consumed independent of the chemical composition of the organic material. The oxygen consumption principle has recently been adopted by the FAA for measuring non-flaming heat release rate of milligram-sized samples in a microscale combustion flow calorimeter.

In the FAA's Fire-Resistant Materials program we are developing and evaluating new polymers with extremely low heat release rates in fires. Typically these materials tend to be char-forming, thermally stable polymers containing a high degree of chemical bond unsaturation, aromaticity, and the heteroatoms nitrogen, sulfur, silicon, phosphorus, and oxygen. The objective of the present work was to measure and document the heats of combustion of some commercial, precommercial, and research polymers for use in calculating their heat release rate in flaming and nonflaming combustion. The accuracy of the universal value of 13.1 kJ of heat per gram of O_2 for combustion of thermally stable, char-forming polymers would be examined. The heats of complete combustion of 49 polymers were measured by the standard experimental procedure for determining gross calorific value using adiabatic oxygen bomb calorimetry and compared to the results of two different thermochemical calculations of the heat of combustion based on (1) oxygen consumption and (2) group additivity of the heats of formation of products and reactants.

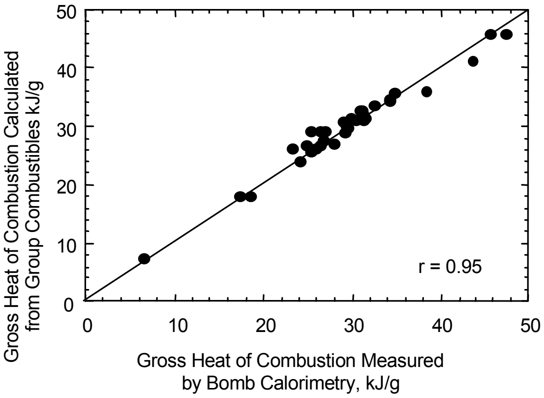


Figure 1. Heats of Combustion Calculated From Group Contributions Versus Experimental Heats of Combustion For 38 Polymers. Line is Y = X.

The heats of combustion of 49 polymers of known chemical composition were measured and calculated. The agreement between experimental values for the gross heat of combustion and thermochemical calculations of this quantity from heats of formation (figure 1) and oxygen consumption (figure 2) was 4.2 and 4.4 percent, respectively, for these calculation methods.

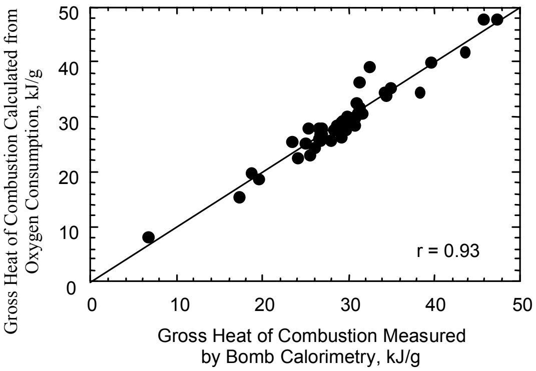


Figure 2. Heats of Combustion Calculated From Oxygen Consumption Versus Experimental Heats of Combustion for 49 Polymers. Line is Y = X

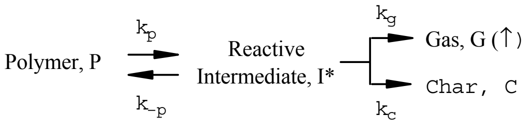
The value E = 13.10 ± 0.78 kJ/g-O_2 (n = 48) for the net heat released by combustion per unit weight of diatomic oxygen consumed was obtained in the present study of high temperature, heteroatomic polymers. This value of E for thermally stable polymers is statistically indistinguishable from the universal value E = 13.1 kJ/g-O_2 used for calculating heat release rates of burning materials from oxygen consumption calorimetry.

This work was reported in “Heats of Combustion of High-Temperature Polymers,” DOT/FAA/AR-TN97/8, September 1998, and has been submitted for publication in the Journal of Fire and Materials. In addition, the data has been incorporated into the new revision of the Fire Protection Handbook, National Fire Protection Association (NFPA), Boston, MA.

POC: Mr. Richard Lyon, AAR-422, (609) 485-6076.

Solid-State Thermochemistry of Flaming Combustion

The solid-state fuel generation rate of polymers in fires can be described by the thermal degradation scheme



wherein pyrolysis gases G and solid char C are produced anaerobically from the reactive intermediate I* in a single step via parallel reactions. The system of rate equations for the species at time, t, is

$$\frac{dP}{dt} = -k_p P + k_{-p} I^* \qquad (1)$$

$$\frac{dI^*}{dt} = k_p P - \left(k_{-p} + k_g + k_c\right) I^* \qquad (2)$$

$$\frac{dG}{dt} = k_g I^* \qquad (3)$$

$$\frac{dC}{dt} = k_c I^* \qquad (4)$$

The stationary-state assumption $dI^*/dt \approx 0$ eliminates I* from equations 1through 4. Defining an initial mass, $m_O = P + G + C + I^* \approx P + G + C$, and a sensible mass, $m = P + C + I^* \approx P + C$, the maximum fractional mass loss rate at a constant heating rate $\Delta T/\Delta t = \beta$ is

$$\frac{-\dot{m}_{max}}{m_o} = \frac{\beta(1-\mu)E_a}{eRT_p^2} \quad (5)$$

where E_a is the global molar activation energy of pyrolysis, $\mu = C(\infty)/m_o$ is the equilibrium char fraction, T_p is the temperature at peak mass loss rate, R is the universal gas constant, and e is the natural number 2.718. Multiplying equation 5 by the heat of complete combustion of the pyrolysis gases h_c^o gives the *peak kinetic heat release rate*

$$\dot{Q}_c^{max}(\mathrm{W/kg}) = h_c^o\frac{-\dot{m}_{max}}{m_o} = \frac{h_c^o\beta(1-\mu)E_a}{eRT_p^2} \quad (6)$$

A rate-independent material flammability parameter emerges from this analysis when the peak kinetic heat release rate $\dot{Q}_c^{max}$ (equation 6) is normalized for heating rate.

$$\eta_c = \frac{\dot{Q}_c^{max}}{\beta} = \frac{h_c^o(1-\mu)E_a}{eRT_p^2} \quad (7)$$

The thermokinetic flammability parameter η_c has the units and significance of a heat [release] capacity (J/g-K) when the linear heating rate is β(K/s) and it contains only material properties.

To relate $\dot{Q}_c^{max}$ to the macroscopic heat release rate per unit area of flaming surface requires a characteristic dimension. If the characteristic dimension is the pyrolysis zone thickness δ, then the areal density of pyrolyzing polymer of bulk density ρ and surface area S is $m_o/S = \rho\delta$ so that the macroscopic heat release rate per unit area of burning surface at temperature $T_s = T_p$ is

$$\dot{q}_c(\mathrm{W/m^2}) = -\chi h_c^o\left[\frac{\dot{m}}{S}\right]_{T_s=T_p} = \chi\rho\delta\left[h_c^o\frac{-\dot{m}_{max}}{m_o}\right] \quad (8)$$

with χ the combustion efficiency in the flame. Substituting equation 6 into equation 8

$$\dot{q}_c = \chi\rho\delta\,\dot{Q}_c^{max} \quad (9)$$

At a net incident heat flux $\dot{q}_{net} = 50\ \mathrm{kW/m^2}$ the pyrolysis zone thickness is

$$\delta = \frac{\kappa}{\dot{q}_{net}}\frac{eRT_p^2}{E_a} \approx 0.3\ \mathrm{mm} \quad (10)$$

for typical $T_s = T_p = 750$ K, $E_a = 200$ kJ/mol, and $\kappa(T_p) \approx 0.2$ W/m-K. The surface heating rate in a fire at $\dot{q}_{net} = 50$ kw/m^2 is

$$\beta = \left.\frac{dT}{dt}\right|_{x=0} \approx \frac{1}{2}\frac{\dot{q}_{net}^2}{\kappa\rho c(T_p-T_o)} \approx \frac{\dot{q}_{net}^2}{\kappa\rho h_g} \approx 5\ \mathrm{K/s} \quad (11)$$

with c the polymer heat capacity at the pyrolysis temperature and h_g the enthalpy of gasification. From equation 9 the ratio of the macroscopic/microscopic heat release rates is the effective areal density

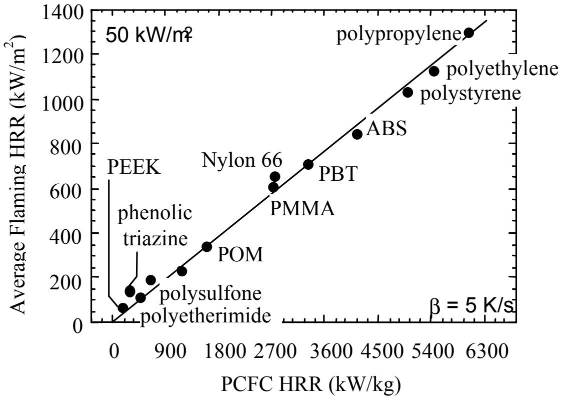
$$\frac{\dot{q}_c}{\dot{Q}_c^{max}} = \chi\rho\delta \approx 0.2 \pm 0.1\ \mathrm{kg/m^2} \quad (12)$$

which is calculated at $\dot{q}_{net} = 50\ \mathrm{kW/m^2}$ using typical values for the gas phase combustion efficiency in a fire $\chi = 0.7 \pm 0.2$, the polymer density $\rho = 1000 \pm 100$ kg/m^3, and $\delta = 0.3 \pm 0.1$ mm (equation 10). Substituting equations 6, 10, and 11 into equation 9 recovers the energy balance for thermal diffusion-limited steady burning

$$\dot{q}_c(\mathrm{W/m^2}) \;=\; \chi\, h_c^o \frac{\dot{m}}{S} \;=\; \chi \frac{h_c^o}{L_g}\dot{q}_{net} \qquad (13)$$

when the latent heat of gasification is defined $L_g \equiv h_g/(1-\mu)$ as obtained from a mass balance at the polymer-flame interface. Since χ lies in the relatively narrow range χ = 0.5-0.9 for well ventilated flaming combustion, it is the dimensionless combustibility ratio or heat release parameter, $h_c^o/L_g = (1-\mu)h_c^o/h_g$, which is the dominant material burning parameter since it can vary by orders of magnitude for polymer solids with typical h_c^o = 5-40 kJ/g, $h_g \approx 3$ kJ/g, and μ = 0-0.9.

The figure below shows the proportionality between the average heat release rate in flaming combustion measured on a cone calorimeter at an external radiant flux of $\dot{q}_{net}$ = 50 kW/m^2 and the kinetic heat release rate $\dot{Q}_c^{max}$ measured directly in the FAA's microscale heat release rate calorimeter at a comparable heating rate (β = 4.3 K/s). The correlation is seen to be very good and the reciprocal slope of the best fit line gives an effective areal density $\chi\rho\delta$ = 0.2 kg/m^2 in agreement with equation 12.



Macroscopic Versus Kinetic Heat Release Rate for Commercial Polymers

This work was reported in "Solid-State Thermochemistry of Flaming Combustion," DOT/FAA/AR-99/56, July 1999, and will be published as a chapter by the same name in the upcoming book Fire Retardancy of Polymeric Materials, A. Grand and C.A. Wilke, Eds., Marcel Dekker, Inc., NY, NY.

POC: Mr. Richard Lyon, AAR-422,
(609) 485-6076.