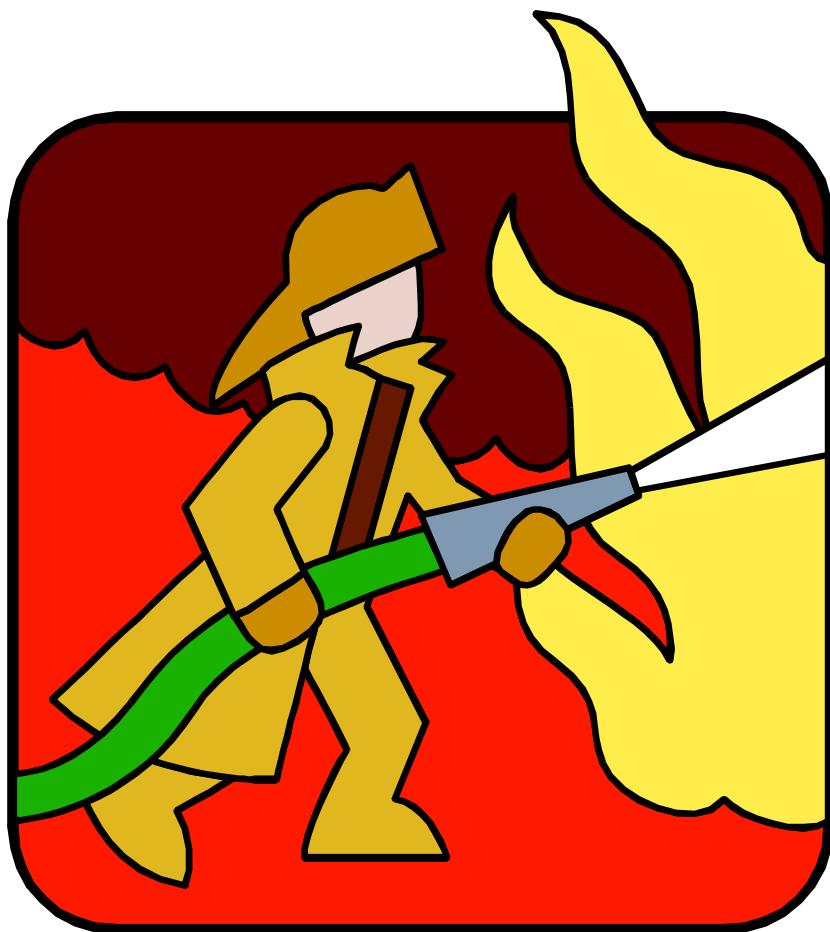# Fire Safety

Research on Ultra Fire-Resistant Materials

The objective of the Fire-Resistant Materials program is to eliminate burning cabin materials as a cause of death in aircraft accidents. Long-term activities include the synthesis of new, thermally stable, low fuel value organic and inorganic polymer systems. The synthesis effort is supported by fundamental research to understand polymer combustion and fire-resistance mechanisms using numerical and analytic modeling and the development of new characterization techniques. Aircraft materials which are targeted for upgraded fire resistance are (1) thermoset resins for interior decorative panels, secondary composites, and adhesives; (2) thermo-plastics for decorative facings, tele-communication equipment, passenger service units, molded seat parts, transparencies, and electrical wiring; (3) textile fibers for upholstery, carpets, decorative murals, tapestries; and (4) elastomers/rubber for seat cushions, pillows, and sealants. To date, significant progress has been made in achieving the interim goal of a 50% reduction in the heat release rate of burning cabin materials by the year 2002 and zero heat release rate cabin materials by 2010, with respect to the 1996 baseline for new aircraft.

Thermoset Resins

The flammability of organic polymer matrix, fiber-reinforced composites limits their use in commercial aircraft where fire hazard is an important design consideration because of restricted egress. At the present time, affordable, processable resins for fire-resistant aircraft interiors are unavailable since most organic polymers used for this purpose ignite and burn readily under fuel fire exposure conditions.

- Polybenzoxazine resins are a new, low-cost phenol-formaldehyde (phenolic) substitute for use in aircraft interior decorative panels. Polybenzoxazines have demonstrated an 80% lower heat release rate, lower toxicity, and better surface finish due to the absence of volatile reaction products. A patent has been filed on this technology (Case Western Reserve University).

- A zero heat release carbon-silicon resin has been synthesized which has a 97% char yield when burned. A patent has been filed on this technology (Dow Corning).

- Ethynyl polymers give off only 25 weight percent of combustible gases when burned (75% char yield). A patent has been filed on these materials (U. South Carolina).

- A low fuel value polymer is obtained from renewable sources by reacting silica sand or rice hulls with ethylene glycol (antifreeze) in the presence of an amine base to yield semi-inorganic monomers in essentially quantitative yield. Subsequent curing produces a variety of inexpensive silicon-containing polymers ranging from hard transparent films to low-density foams. A patent disclosure has been filed on this technology (U. of Michigan).

- Polycyanurate resins were prepared from polystyrene and evaluated for flammability along with commercial cyanate esters (Stockton College, the National Institute of Standards and Technology (NIST), and the FAA).

- Inorganic fire retardants based on zirconia and boron oxides are highly efficient, environmentally benign

additives which reduce the peak heat release rate by 60%-80% in commodity (nylon, PE, and polypropylene) and engineering (cyanate esters and ULTEM polyetherimides) polymers at low concentrations without increasing smoke or carbon monoxide. NIST is filing a patent on this technology (NIST).

Thermoplastics for Molded Parts

Commercial transport aircraft contain between 1500 and 2500 pounds of flammable plastics as seat trim, windows, window shades, wire insulation, and miscellaneous parts. At present these molded parts are not required to meet the heat release rate regulations imposed on large-area interior panels, stowage bins, ceilings, and partitions because of their small size. High-temperature plastics which pass the heat release rate test do not have the requisite toughness, durability, environmental resistance, and aesthetics to function effectively in aircraft interiors.

Nanocomposite technology is an entirely new generic approach to reducing the flammability of polymeric (plastic) materials using environmentally friendly, chemical-free additives. The fire-retardant effect of nanometer-sized clay particles in plastics was discovered by the FAA through a research grant to Cornell University. NIST has subsequently confirmed the effect in fire calorimeter testing. The approach is to disperse individual, nanometer-sized, layered silicates in a molten polymer to create a clay-plastic "nanocomposite." The clay particles are about the same size as the polymer molecules themselves (less than one millionth of an inch) so they become intimately mixed and chemically bonded. This has the overall effect of increasing the thermal stability and viscosity of the plastic

while reducing the transmission of fuel gases generated during burning.

The result is a 60% to 80% reduction in the rate of heat released from a burning plastic nanocomposite containing only 5% to 10% clay by weight. This extraordinarily high degree of fire-retardant efficiency comes with reduced smoke and toxic gas emissions and at no sacrifice in mechanical properties. Plastic nanocomposites have twice the stiffness and strength of the original material and a higher softening temperature (Cornell University and NIST).

Additional results on fire-resistant thermoplastics include

- Ultra high-modulus thermoplastic molecular composites have been tested which have low heat release rate and three times the strength and stiffness of high-temperature engineering plastics (MAXDEM, Inc.).

- New phosphineoxide-polyetherimide thermoplastics have significantly lower heat release rate when burned than commercial polyetherimides (ULTEM) currently used in aircraft interiors (Virginia Polytechnic and State University, Blacksburg).

- Polycarbodiimides are carbon-nitrogen backbone polymers, which can be flexible elastomers or rigid resins, have been prepared from inexpensive starting materials. Polymers depolymerize cleanly to monomers with extremely low fuel value upon heating to 200°C. Molecular modeling shows that thermal stability can be increased through stereochemistry (U. of Massachusetts, Amherst).

- Novel organic-inorganic interpenetrating networks (IPN's) have been synthesized by separately polymerizing organic and inorganic monomers in the same reaction mixture to give a co-continuous morphology. The reaction is solvent free and the inorganic (silica) phase is atomically dispersed so that the material is transparent, rigid, and has higher thermal stability than the organic phase alone (U. of Massachusetts, Amherst).

- Surface active flame retardants concentrate at a burning polymer surface using interfacial free energy as the driving force. Migration of surface active flame retardants from the bulk to the burning surface improves flame-retardant efficiency by reducing the loading level required for fire resistance (U. of Massachusetts, Amherst).

Rubber for Seat Cushions

Commercial transport aircraft contain between 1000 and 2500 pounds of flammable elastomers (rubber) which are foamed to make seat cushions and pillows or used at full density as sealants and gaskets. Foamed polyurethane rubber seat cushions are favored for their durability and recovery, but they are the primary fire load in aircraft interiors. In 1987 the FAA imposed regulations on the flammability of aircraft seat cushions to delay their involvement in cabin fires. Manufacturers responded to these regulations by wrapping the polyurethane seat cushion in a fire-resistant barrier fabric. Seat fire blocking allowed manufacturers to pass the FAA certification test, but the cushions burned vigorously when the fire-blocking layer was consumed after minutes of exposure to a fire.

The flammability of rubber depends on the chemical composition of the polymer from which it is made. Rubbers made from carbon-hydrogen-based (organic) polymers are the most flammable because of their high fuel value. Replacing carbon and hydrogen atoms in the polymer with inorganic atoms such as chlorine, silicon, nitrogen, sulfur, or phosphorus results in a semiorganic polymer with reduced flammability because of the lower fuel value or increased heat resistance. In the Fire-Resistant Materials research program we are focusing on semiorganic rubbers for seat cushions.

- Silphenylenes are hydrocarbon-silicon-oxygen backbone elastomers, which are crosslinkable and extremely heat resistant, have been synthesized. The silphenylene contains only 30% combustible material and can withstand temperatures of 600°C (1100°F). A patent is being filed on this composition of matter (U. of Massachusetts, Amherst).

- Polyphosphazenes are semiorganic rubbers based on a phosphorus-nitrogen backbone which contains an organic group that allows the material to be dissolved or crosslinked. Commercial production of polyphosphazene was recently discontinued despite the extremely low toxicity and ultra fire resistance of these foams because the process for making them was prohibitively expensive. We are pursuing a new low-cost, low-temperature, synthetic route to polyphosphazenes which eliminates a costly intermediate from the process and allows control over the molecular weight of the polymer. This new direct synthetic route has provided the first phosphazene copolymers

including an 80-20 urethane-phosphazene copolymer which does not ignite in a flame. A patent has been filed on this process (The Pennsylvania State University).

Fibers for Carpets and Textiles

Approximately 2000 pounds of combustible textile fibers are used in a modern commercial aircraft interior as seat upholstery, decorative textiles, wall coverings, carpeting, tapestries, blankets, curtains, and seat belts. Typical fabrics include wool, nylon/wool blends, and fire-retarded polyester, wool, and nylon. The chemical fire retardants added to these fibers reduce the propensity for small-scale ignition but increase the smoke density and toxic gas generation once the fibers catch fire and have little or no effect on heat release rate. Our research in fibers focuses on materials with unusually high thermal stability which have intrinsic fire resistance without the need for chemical additives. Current research includes the following.

- Zero heat release polyimide fibers are melt and solvent processable for spinning ultrahigh-strength thermally stable fibers and casting films. Fibers of this material exhibit the lowest (microscale) heat release rate of any polymer tested to date—ten times lower than aramid (Kevlar™) fibers and 150 times lower than nylon used in seat fabrics (U. of Akron).

- Substituted polyhydroxyamides generate flame-retardant compounds in a fire through a thermally activated chemical reaction which produces a zero heat release polymer (polybenzoxazole) during heating (U. of Massachusetts, Amherst).

Supporting Science and Technology

A microscale combustion calorimeter has been developed to measure flammability parameters of milligram polymer (plastic) samples under conditions which approximate aircraft cabin fires. The test takes only a few minutes to run and provides a quantitative measure of the aircraft fire hazard of research materials which are only available in milligram quantities from university and industrial polymer scientists. Quick feedback on flammability of new materials has helped guide the synthetic effort towards improved fire resistance. A sharp, quantitative, and reproducible heat release rate peak is obtained in the microscale heat release rate test. After normalizing the curves for the sample size, the results are independent of the physical form of the material (e.g., powder, film, fiber, etc.). The microscale heat release rate data are expressed in kilowatts per gram of original material.

The peak microscale heat release rate (HRR) measured on milligram samples of pure plastics in the microcalorimeter correlates extremely well (correlation coefficient = 0.95) with the heat release rate measured for 100-gram samples of the same material in a conventional fire calorimeter.

Full-scale fire tests at the FAA William J. Hughes Technical Center have shown that the heat release rate of interior materials measured in a fire calorimeter correlates with passenger escape time in a simulated postcrash fuel fire. The good correlation between fire- and microcalorimeter results shows that the microcalorimeter is also a good predictor of passenger escape time and, therefore, of full-scale fire hazard. A DOT/FAA patent has been filed on this invention (FAA and Galaxy Scientific Corporation).

The figure below shows microcalorimeter results for some of the new materials being developed in the program and how they compare materials currently being used in aircraft. It is clear that most of the new materials tested show significantly lower heat release rate when combusted than do the current (baseline) aircraft materials.

In addition to creating a metric for materials development (i.e., the microscale calorimeter), supporting science and technology provided the following technology base.

- Thermal degradation of polymers was modeled by computer to study the process which generates combustible fuel in a fire. The computer code (MD REACT) uses a commercial program (Discover 95, Molecular Simulations) to create the polymer chains for the model and then simulates the thermal degradation process at fire temperatures. This code will provide insight into the process and products of thermal degradation to allow the design of thermally stable, less toxic, fire-resistant polymers (NIST).

- A mechanistic fuel generation model was developed for polymers in fires which includes the competing processes of gasification and char formation. The simple analytic result provides the fuel generation rate of a burning polymer from conventional laboratory thermal analysis data (FAA William J. Hughes Technical Center).

- Molecular modeling of flammability utilizes computational quantum chemistry to predict the thermochemistry and kinetics of solid- and gas-phase combustion processes of burning polymers. Initial results for the effects of chain size and stereoregularity on the bond dissociation energy of novel polycarbodimides were obtained (U. of Massachusetts, Amherst).
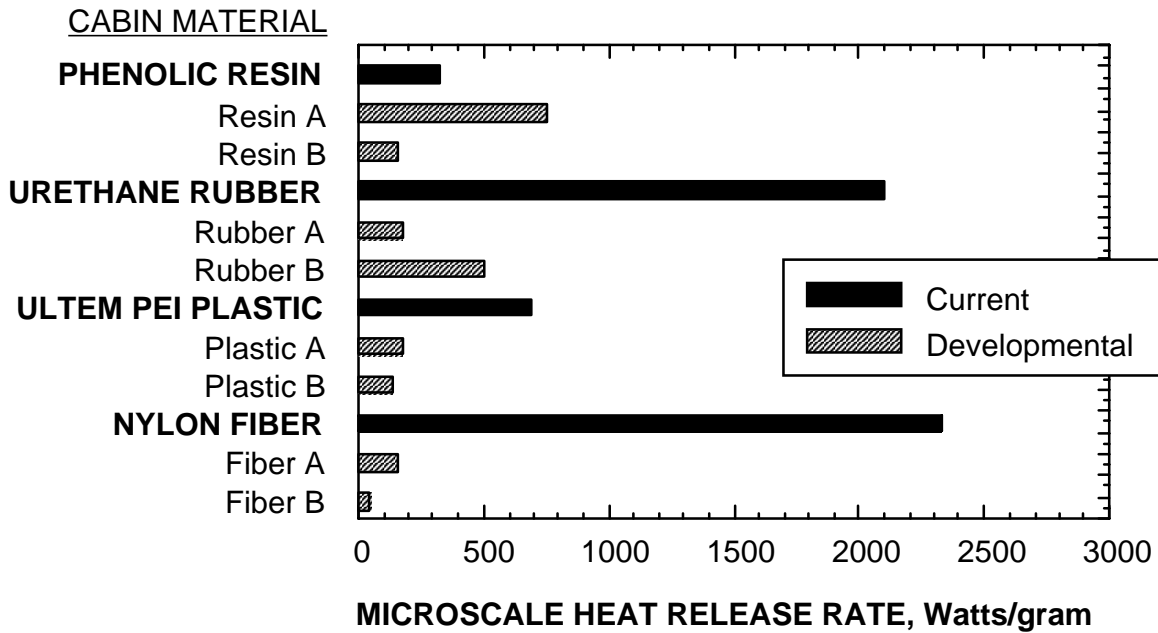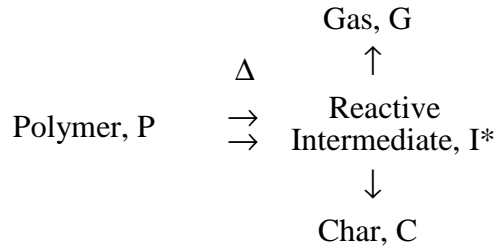
Heat Release Rate of Current and Developmental Aircraft Cabin Materials

- Atomistic models of polybenzoxazine have been developed and solved on a computer which provide insight into the high thermal stability and unusual volumetric expansion on polymerization (U. of Akron).

- Computational modeling of intumescence has shown the importance of bubble nucleation kinetics and thermal properties on the insulation value of this important commercial fireproofing technology (NIST).

- Thermomechanical stability of fire exposed resins and composites are studied using a new noncontact technique—ultrasonic spectroscopy. Results indicate surface embrittlement of the resin in a fire initiates surface cracks which mechanically destabilize the composite (U. of Massachusetts, Amherst).

- An integral method of nonisothermal kinetic analysis provides a new, semi-exact solution of the mass loss integral which is useful for extracting flammability parameters from laboratory thermal analysis data (FAA William J. Hughes Technical Center).

- In situ flame chemistry by remote laser spectroscopy has been successful at identifying flame species in burning polymers to study the chemical reactions which lead to combustion inhibition and toxic byproducts in flame-retarded polymers. A patent is being filed on this technology (U. South Carolina).

- Fire calorimetry of flame-retardant polymers showed that fire retarded (FR) polymers ignited and burned readily under aircraft cabin fire exposure conditions with increased smoke and toxic gas production compared to the original (non-FR) material—validating the FAA's focus on inherently fire-resistant polymers and composites (Omega Point Labs).

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

A Simple Fuel Generation Model for Burning Plastics

A molecular basis for polymer burning was developed from thermal degradation kinetics and compared to experimental data for flaming heat release rate in fires. The solid-state fuel generation rate in fires has been derived [1] from the polymer thermal degradation scheme

$$\text{Polymer, P} \quad \begin{matrix} & & \text{Gas, G} \\ & & \uparrow \\ \Delta & \rightarrow & \text{Reactive} \\ & \rightarrow & \text{Intermediate, I*} \\ & & \downarrow \\ & & \text{Char, C} \end{matrix}$$

assuming that the majority of pyrolysis gases, G, and 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 1-4. 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 $dT/dt = \beta$ is

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

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

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

The pyrolysis zone thickness for steady burning of a polymer of thermal conductivity κ at net surface heat flux $\dot{q}_{net}$ is

$$\delta = \frac{e\kappa}{\dot{q}_{net}} \frac{RT_p^2}{E_a} \qquad (7)$$

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 is

$$\dot{q}_c(W/m^2) = -\chi h_c^\circ \frac{\dot{m}}{S} = \chi\rho\delta\left[h_c^\circ \frac{-\dot{m}}{m_o}\right] \qquad (8)$$

or with Equation 6

$$\dot{q}_c = \chi\rho\delta \dot{Q}_c \qquad (9)$$

Equation 9 states that the ratio of the steady-state macroscopic heat release rate to the peak kinetic heat release rate for comparable temperature histories is in the range

$$\frac{\dot{q}_c}{\dot{Q}_c} = \chi\rho\delta \approx 0.4 \pm 0.2 \text{ kg/m}^2 \qquad (10)$$

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/m³, and the pyrolysis zone thickness, $\delta =$

0.5 ± 0.2 mm at $\dot{q}_{net} = 50$ kW/m^2 from Equation 7.

The heating rate at the surface of a steadily burning polymer is

$$\beta \;=\; \left.\frac{d\mathrm{T}}{d\mathrm{t}}\right|_{x=0} \;=\; \frac{\dot{q}_{net}^2}{\kappa\rho c_p\!\left(T_p - T_o\right)} \qquad (11)$$

with $c_p = c(T_p)$ the polymer heat capacity at the peak pyrolysis temperature. Substituting Equation 11 along with Equations 6 and 7 into Equation 9 recovers the continuum result for thermal diffusion limited steady burning

$$\dot{q}_c(\mathrm{W/m}^2) \;=\; \chi\, h_c^o\, \frac{\dot{m}}{S} \;=\; \chi\, \frac{h_c^o}{h_g}\, \dot{q}_{net} \quad (12)$$

with the heat of gasification defined $h_g \equiv c_p(T_p - T_o)/(1-\mu) = \dot{q}_{net}/(mY/S)$.

In principle the macroscopic heat release rate at any net surface heat flux $\dot{q}_{net}$ is now calculable from the pyrolysis kinetic parameters and heat of combustion of the volatiles using Equations 6, 7, 9, and 11. However, these kinetic and combustion parameters are rarely known with any certainty, particularly at the surface heating rates in a fire.

Consequently, our approach [2] was to measure the kinetic heat release rate directly using pyrolysis-combustion flow calorimetry (PCFC). In the PCFC test, a 1- to 3-milligram polymer sample is pyrolyzed by heating in an inert environment to a maximum temperature $T_{max} = 923$ K at a linear heating rate $\beta \approx 8$ K/s (calculated from Equation 11) to approximate the rapid, anaerobic heating of a polymer surface in a fire or fire calorimeter at $\dot{q}_{net} = 50$ kW/m^2.

The pyrolysis gases are swept from the small-volume pyrolysis chamber of the PCFC by flowing nitrogen and mixed with excess oxygen prior to entering a 900°C furnace to effect complete combustion. Combustion products are scrubbed from the gas stream prior to entering an oxygen analyzer. Heat release rate is calculated from oxygen consumption and the measured flow rate of the gas stream.

Results of these PCFC tests are compared to literature values for average macroscopic heat release rate at $\dot{q}_{net} = 50$ kW/m^2 in a cone calorimeter in the figure below.
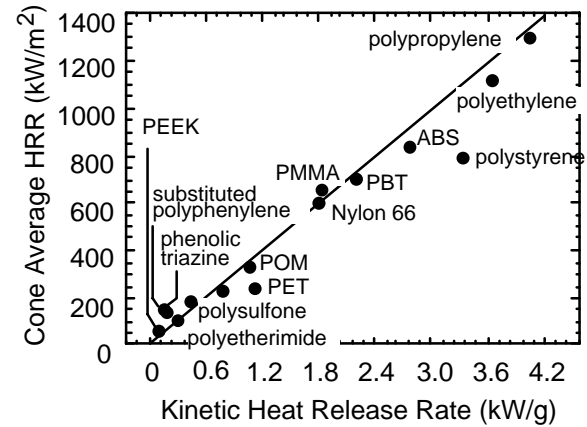
Macroscopic Versus Kinetic Heat Release Rate For Some Polymers

Proportionality is observed between the macroscopic and kinetic heat release rates with slope $\dot{q}_c/\dot{Q}_c = 0.33$ kg/m^2, which is within the range of predicted values using Equation 10.

We conclude that steady polymer burning is a thermal diffusion controlled kinetic process in which the rates of the solid-state reactions (pyrolysis) and gas phase reactions (combustion) are rapid in comparison to the rate of heat transfer at the flaming surface. The pyrolysis zone depth is determined by the coupling between thermal diffusion and pyrolysis kinetics and effectively correlates

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the molecular and macroscopic heat release rates.

REFERENCES

1. R. E. Lyon, Polymeric Degeneration and Stabilization, <u>61</u> (2), 201-210 (1998).

2. R. N. Walters and R. E. Lyon, Proceedings of the 42nd International SAMPE Symposium, <u>42</u> (2), 1335-1344 (1997)

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

A Flammability Test Method for Thermal Acoustical Insulation

An aircraft thermal acoustical insulation blanket is typically comprised of a fiberglass core encapsulated by a film cover or bag. Blankets of various thicknesses are placed against the aircraft skin throughout the aircraft interior circumference. Their function is to reduce noise and act as a thermal barrier, depending on the location of the blankets. The two principle reasons that films are used as coverings on the aircraft blankets are for containment of the fiberglass (keeping the batting in place) and resistance to moisture permeation. Selection of films is based on durability, fire resistance, weight, and installation considerations.

Between 1993 and 1995, a number of cabin
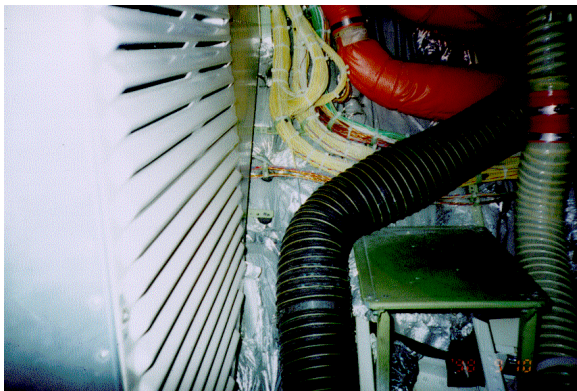
fires involving flame propagation on thermal
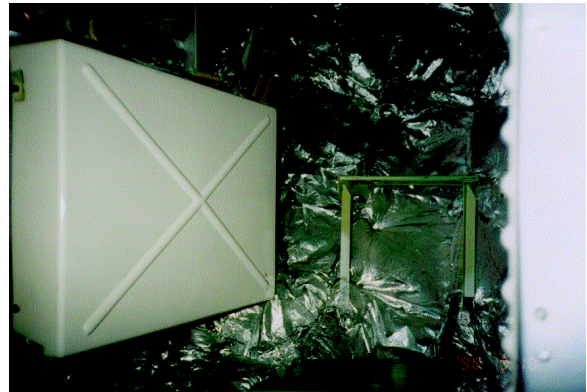
acoustical insulation blankets were reported. As a result of these incidents and a request from the aircraft industry, the International Aircraft Materials Fire Test Working Group, chaired and administered by the FAA William J. Hughes Technical Center's Fire Safety Section, formed an ad hoc task group for the purpose of conducting and evaluating flammability tests performed on insulation blankets. Members of the group included Boeing, Douglas, Facile, Jehier, Airbus, Orcon, Govmark, and the FAA. Vertical flammability testing of all insulation blanket components (film cover, core material, and complete assembly) is mandated in the Federal Aviation Regulations (FAR) 25.853. In tests performed by the task group members on insulation blankets, it was found that vertical testing does not produce

consistent test results and therefore may not be a suitable indicator of the flammability of thermal acoustical insulation assemblies.

Previously, a test employing a flaming cotton swab at two locations on a folded blanket, developed by a commercial aircraft manufacturer, promised to be effective in consistently identifying thermal acoustical insulation films that propagate flame (see figure below). As part of the test program, the task group evaluated the cotton swab test in a series of round-robin testing performed on the most widely used film covers and assemblies. The test method was slightly modified in terms of sample size and swab placement. The round-robin test results
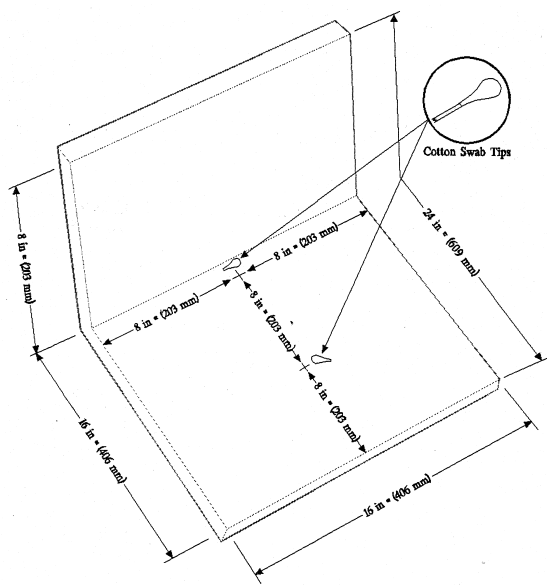
showed that the cotton swab test was a more reproducible test and slightly more severe than the vertical flammability test. This was especially apparent for a particular metallized film/fiberglass assembly. The front face of this particular sample was consumed when subjected to the cotton swab test, although the same sample passed the vertical tests of most laboratories. Because of these findings, the metallized film/fiberglass blanket is no longer being installed in aircraft.

A final technical report entitled "Evaluation of Fire Test Methods for Thermal Acoustical Insulation," DOT/FAA/AR-97/58, was published and distributed. The report contains the round-robin test findings and the version of the standardized cotton swab test developed by the test group. Additionally, the standardized test method will be included in the Materials Fire Test Handbook that is scheduled for release in late 1998. Although not mandated, the cotton swab test is now performed by the world's largest commercial aircraft manufacturers as part of their own internal specifications.

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Oxygen Cylinder Overpack Testing

A fatal in-flight fire occurred onboard a ValuJet DC-9 on May 11, 1996. During this accident, an extremely intense fire fueled by solid oxygen generators erupted in the class D compartment, burned out of control into the passenger cabin, and eventually caused the aircraft to crash, resulting in 110 fatalities. In the wake of this accident, the shipment of oxidizers was banned in all commercial aircraft cargo compartments. In February 1998, industry, pilot, and user groups requested an exemption to allow for the shipment of bottled oxygen in class C cargo compartments, which have fire detection and suppression systems that should detect and suppress a fire. In the event that the fire is not fully extinguished, which would be the case if the origin were a deep-seated fire, the temperatures in the compartment could reach 400°F. The major concern with the shipment of oxygen cylinders under this scenario is that the elevated temperatures would cause the cylinder pressure to increase, causing the pressure relief mechanism to open. If this occurs, the oxygen could cause significant intensification of the fire.

In order to determine the level of hazard associated with gaseous oxygen release during a Halon 1301-suppressed cargo compartment fire, four full-scale tests were conducted inside a 169-cubic-foot LD-3 cargo container (see photograph at top of page). Previously, tests were conducted inside a large industrial convection oven to determine the temperature and time required to cause pressure relief activation of three different-sized oxygen cylinders commonly used in commercial transport aircraft. The cylinders were placed inside the oven and an externally mounted pressure gauge was connected to the cylinder valve head to monitor the pressure rise. As the test began, the oven temperature was ramped to 400°F,

which represented the temperature level typically reached during a Halon 1301-suppressed cargo compartment fire. Pressure relief activation typically occurred after the surface temperature of the cylinder had reached only 300°F, within 15 minutes from the start of the test. This information was then used to set up the full-scale tests in which gaseous oxygen was bled into the actual deep-seated fire.

During the full-scale tests, the cargo fires were allowed to burn for a short duration before Halon 1301 was discharged into the container. After the suppressant concentration stabilized to about 3%, the minimum design concentration for inerting, a quantity of oxygen from a remotely located cylinder was discharged to simulate the relief of oxygen from an overpressurized cylinder. When the surface temperature of an empty "dummy" cylinder inside the LD-3 test container reached 300°F, the flow of oxygen was initiated. Although the amounts of oxygen were very modest in comparison to the amount typically stored in one crew breathing cylinder, which range from 76 ft^{3} to 115 ft^{3}, the tests demonstrated that a halon system could not always contain an oxygen-enriched fire (see photograph on next page).

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Additional oven tests were conducted using a 76.5 ft^3 oxygen cylinder placed inside several types of cylinder cases, commonly referred to as overpacks. The overpacks were available in a variety of constructions, all for the purpose of protecting the cylinder from impact damage that may occur during shipment (see photograph below). The tests were run to determine the level of thermal protection, if any, that might result when the cylinders are subjected to elevated

temperatures. Two custom-made overpacks were tested containing insulating materials aimed specifically at providing thermal

protection. Tests showed that some common overpacks have the ability to protect the cylinder from pressure relief activation for nearly 60 minutes in a 400°F environment, while other types designed specifically for thermal protection can prevent rupture disc activation for extended periods of time.

The FAA is considering a thermal-protection performance standard recently developed by the FAA William J. Hughes Technical Center's Fire Safety Section for oxygen cylinder overpacks based on these tests. The standard will consist of two tests, an open-flame burnthrough test and an oven test, which address thermal protection requirements before fire detection (and agent discharge) and during fire suppression, respectively. During the oven test, a nitrogen-charged cylinder placed in the test overpack will be exposed to a 400°F environment. The overpack must prevent the cylinder rupture disc from activating for 90 minutes. During the burnthrough test, a 16- by 24-inch sample representing the overpack construction will be exposed to an intense, 1800°F open flame for 5 minutes. The test sample must prevent flame penetration, and the backface temperature must not exceed 400°F at any time during the test. By meeting this combined standard, the cylinder overpacks will effectively prevent the release of oxygen during a typical deep-seated cargo compartment fire.

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Initial Development of an Exploding Aerosol Can Simulator

The Montreal Protocol Treaty, signed by nearly all industrialized nations around the world, banned the manufacture of ozone depleting halons. Halons are effective gaseous extinguishing agents that are used in four major applications in commercial aircraft: cargo compartments, engine nacelles, hand-held extinguishers, and lavatory trash receptacles. Because of the diminishing availability of halons, the FAA has been developing minimum performance standards (MPS) for replacement agents and systems in each of these areas. In commercial transport aircraft, the largest quantity of halon is used in the extinguishers in the cargo compartment. The MPS being developed for cargo compartments encompasses four fire test burning scenarios: surface, simulated bulk loaded luggage, simulated containerized luggage, and exploding aerosol cans.

Previous research and testing has shown that cargo compartment fires involving aerosol cans are particularly dangerous. For more than a decade the chlorofluorocarbon propellant used in aerosol cans has been replaced with hydrocarbon blends that include fractions of propane, butane, and isobutane. These flammable gases would normally be prohibited on passenger carrying airplanes, but there is an exception for up to 75 ounces per person for medicinal and toilet articles when carried in checked baggage only. During a fire, heated aerosol cans will overpressurize and rupture, releasing the flammable hydrocarbon-based propellant with explosive force. The resultant overpressure in the compartment is of particular concern. The compartment lining system may become dislodged allowing the protective fire suppression agent to escape, and the fire and smoke may spread to other parts of the airplane. Halon 1301 has proven to be extremely effective at mitigating an explosion caused by heated aerosol cans and therefore the halon replacement agents and systems must also perform at an equivalent level.

Because aerosol can explosions are extremely variable and unpredictable, a simulator was constructed which can replicate an exploding aerosol can. The initial simulator design used a steel pipe pressure vessel mated to a high-rate discharge (HRD), electrically actuated solenoid valve. The vessel contained ports and valves to allow for the transfer of the base product (initially isopropyl alcohol) and hydrocarbon propellant (typically propane). The contents were heated by blowing a hot-air gun against the surface of the steel vessel, effectively raising the pressure. When the pressure was sufficient to burst a standard can, approximately 210 psig, the contents were released over a set of direct current (DC) spark igniters (see drawing below).
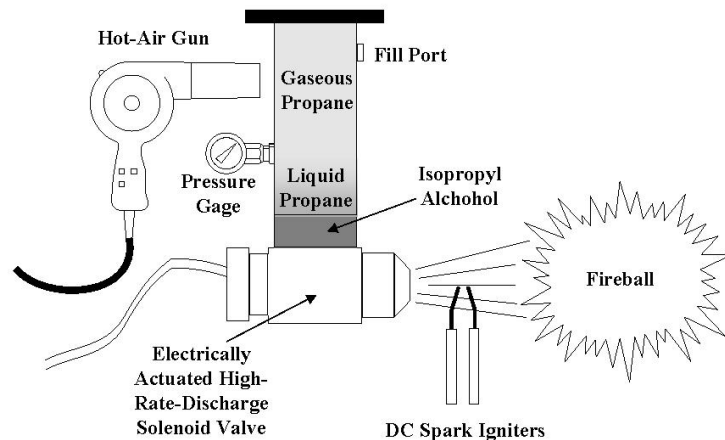
Initial tests were performed using the simulator in an open area to observe the flame propagation pattern and to test the general operation of the device. The mix of constituents used were representative of a large hairspray can (16 ounces), consisting of 3.52 ounces (weight) of liquid propane and 2.50 ounces (weight) of isopropyl alcohol. The mix produced a large fireball of about 12 feet in diameter, slightly larger than a typical exploding hairspray can, which produces about an 8-foot-diameter fireball (see photograph below). The simulator tests were then conducted in the confined space of a B727 cargo compartment. The simulator was mounted to the forward bulkhead, and the mix was released into the compartment over the spark igniters, which were situated approximately 3 feet from the nozzle exit. The ensuing explosion caused severe damage to the entire compartment. The forward and aft bulkheads collapsed, and the cabin floor above the compartment ceiling liner was blown out of place. There was also evidence of severe overpressure inside the structure, as several rivet heads on the exterior skin surface failed under tension. In order to measure the effectiveness of Halon 1301 at mitigating this event, a repeat test

was performed with the entire compartment inerted with Halon 1301 at a concentration of 6.5%. Upon release of the heated constituent mix into the inerted compartment, no explosion event took place and no perceived pressure rise inside the compartment was observed.

Several additional proof-of-concept tests employing the aerosol simulator were conducted using LD-3 Unit Loading Device (ULD) containers as the confining space. The hydrocarbon propellant mix exploded with violent force, blowing the bifold door off its hinges. The container sustained heavy damage in the form of long cracks due to overpressure. During the simulator event, a pressure rise of 8 psig was measured in the container. This test result was more severe than an actual aerosol can explosion, which typically generates enough force to disengage and partially swing open the bifold door. Several additional tests corroborated these results. As with the B727 tests, the effectiveness of Halon 1301 at mitigating these types of events was also investigated. Several additional tests were conducted in the LD-3 container which was inerted to various concentrations prior to simulator activation. During the tests, there was no explosion in the LD-3 container even when the concentration of Halon 1301 was as low as 1%. These results illustrated the effectiveness of halon against this type of threat, even at substantially reduced concentrations. Although the tests exhibited the ability of Halon 1301 to prevent explosions at 1% concentration, the results differ from published literature, which indicates higher concentrations (e.g., 6.7% for propane) are required to suppress this type of explosion. Further testing will be

conducted to examine this discrepancy. The results of this work are published in Technical Note DOT/FAA/AR-TN97/103, "Initial Development of an Exploding Aerosol Can Simulator."

Although the simulator used a mix of constituents representative of a large hairspray can, the explosion event is much more severe. A major reason for the consistent potency of the simulator lies in its ability to form a large, combustible vapor cloud, promoting complete combustion.

Further refinement of the simulator is currently underway. At present, large aerosol cans are being overpressurized under a variety of conditions in an attempt to cause the most violent explosion. These tests are being conducted in a large pressure vessel outfitted with high-speed pressure transducers to measure the pressure rise. This data will be used to adjust the output of the simulator so that a severe but realistic MPS test condition can be achieved. Halon replacement agents, most notably water spray, will be tested to determine their effectiveness against the standard exploding aerosol can fire threat.

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Effect of Acid Spills on Aircraft Structure

The FAA conducted tests to evaluate the effects of a spill of a strong corrosive acid such as hydrochloric acid (HCl) on aircraft interior skin and to determine the time required for a spill of Department of Transportation (DOT) allowable volumes and concentrations to cause catastrophic failures.

This work was conducted in response to a request by the agency that regulates transport of hazardous materials, the Research and Special Programs Administration, Department of Transportation (RSPA DOT).

Four spill tests were conducted with concentrated HCl onto various sized sections of a Boeing 747 aircraft skin. Epoxy paint was used to coat all the cut or scraped surfaces that were not being evaluated by the test.

Test specimens for the first three tests ranged in size from a 6" x 6" section to a 3' x 3' section. Each specimen included a section of the ribs and the rivets connecting the skin to the ribs. One liter of concentrated HCl, the maximum allowable DOT volume for passenger aircraft, was poured onto the interior surface of the 3' x 3' skin or placed into a Pyrex glass pan containing the smaller samples.

The last test used a 2" by 7" strip of a B-747 skin with two scratches placed scratched surface up in a Pyrex container holding 1 liter of concentrated HCl.

Test data indicated that the epoxy coated interior aluminum skin is resistant to acid attack. The acid reacted vigorously with scratched skin surfaces, creating a wide hole in the skin along the scratch line. Test data also indicated that a spill of concentrated HCl can eat completely through the rivets and ribs and may result in a significant loss of structural rib strength.

A detailed report describing this study, "Effects of Concentrated Hydrochloric Acid Spills on Aircraft Aluminum Skin," DOT/FAA/AR-TN97/108, was published in July 1998.
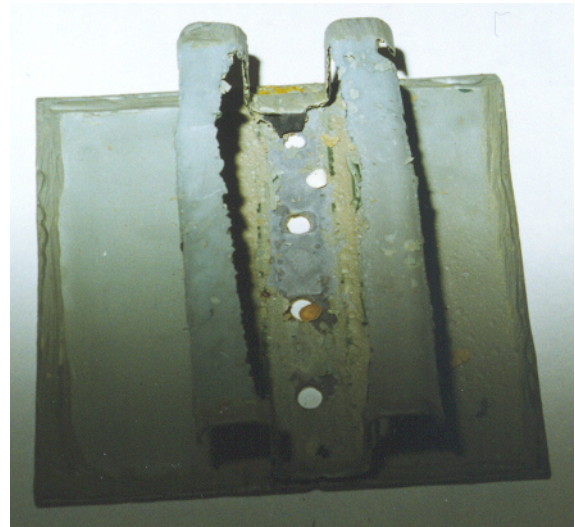
A 6" x 6" Section of B-747 Skin After an 85-Minute Exposure to 1 Liter of Concentrated HCl Solution
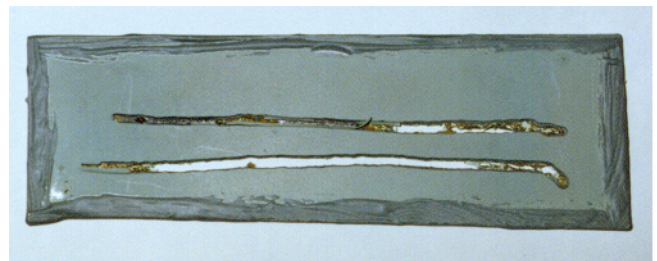
Scratched 2" x 7" Strip of B-747 Skin After a 90-Minute Immersion in 1 Liter of Concentrated HCl Solution

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A Computer Program for Predicting the Probability of a Fuel Tank Explosion

A software model was developed to assess the hazard of a fuel tank explosion at discrete points in time. The model employs experimental data of ignition energy (E_{ign}) required to cause fuel tank vapors to ignite as a function of fuel flash point temperature, fuel temperature, and altitude (pressure). In order to assess the probability of a fuel tank explosion during an entire flight and evaluate the effect of changes to the fuel temperature and/or fuel flash point, it is necessary to sum the total of $E_{ign} < E_{spark}$ from time equal to zero till the time corresponding to the end of flight, where E_{spark} is the energy of the ignition source. Dividing by the total flight time in minutes would determine the norm of $E_{ign} < E_{spark}$.

A probability input screen provides the user the ability to specify flash point(s) of the fuel (T_{FP}) in °F and assign a distribution to T_{FP} (if desired). The spark probability (F_{spark}) distribution can be selected using a curve that is resident in the program or inputted by the user.

The flight scenario screen allows the user to develop the flight profile. Here, an altitude (Z) versus time profile is entered. Altitude is entered in thousands of feet and time in minutes.

Also entered in the flight scenario screen is the temperature of the fuel (T_{fuel}) versus time profile. Fuel temperature is input as °F and time is entered in minutes. It should be noted that the temperature being entered (T_{fuel}) should be the hottest measured or calculated fuel temperature in the tank at that time with the following exception. When the fuel temperature starts to decrease in flight and the hottest measured or

calculated ullage temperature at a specific time is hotter than the fuel temperature at that same time, one should use the maximum fuel temperature recorded up to that time or the ullage temperature at that specific time, whichever is less.

From the above input, the model will extrapolate T_{fuel} and altitude (Z) and calculate the probability of an explosion, given that a spark occurs, for each minute of the flight profile (P). These probabilities will then be weighted (based on the flash point distribution), totaled, and divided by the total flight time of the flight profile. This yields the average probability of an explosion over the entire flight, given a spark occurs (P_f).

The primary output of the model (as shown in the graphic on the following page) is as follows:

- Graphical representation of the flight profile

- Altitude (1,000 feet) versus time (minutes)

- Fuel temperature (°F) versus time (minutes)

- Color-coded potential hazard range based on the altitude and flash point that show when T_{fuel} versus time crosses into the range of a potential hazard.

- Average probability of an explosion over the entire flight, given a spark occurs (P_f).

- Maximum probability of an explosion over the entire flight, at time (t) into flight, given that a spark occurs (P_{max}).
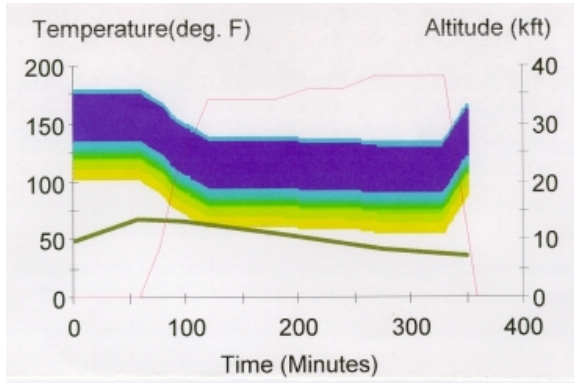
Flight Scenario
Exponential Distribution

The results are estimates based on a limited amount of available data. Although it was felt that for most cases to be analyzed that both off gassing of O_2 from the fuel and misting or sprays of fuel can be ignored, that may not always be the case. For large quantities of fuel and small ullage spaces, the off gassing of O_2 from the fuel may raise the O_2 level in the ullage significantly (3% to 5%) thus reducing the spark energy needed for ignition. Should fuel be sprayed into a tank during flight, the lower flammability limit would be greatly decreased, making the above calculation invalid.

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## Flammability Hazard of Jet A Fuel Vapor in Civil Transport Fuel Tanks

A study was undertaken by a Fuel Flammability Task Group composed of recognized fuel and combustion specialists to investigate the flammability and explosiveness of fuel within an aircraft fuel tank. The task group reviewed all available reports on the subject and discussed the data with technical experts from Boeing Commercial Airplane Company, California Institute of Technology, and the National Transportation Safety Board. The scope of the review included jet fuel definitions and specifications, jet fuel flammability data, influences of various factors on fuel flammability, and predictive analyses and models for flammability. The group reported their findings in DOT/FAA/AR-98/26, "A Review of the Flammability Hazard of Jet A Fuel Vapor in Civil Transport Aircraft Fuel Tanks." The report discusses the impact of this knowledge on the needs for in-flight fuel fire prevention. The report did not offer a single, definitive answer to the question of when fuel tanks contain a flammable vapor, but it does identify the research necessary for a better understanding of fuel flammability in aircraft fuel tanks. It also presents a methodology that, within limits, can be used to compare the probability of a flammable mixture in a tank when the fuel temperature, flash point, and/or aircraft altitude are varied. While adequate for a fuel tank safety analysis to be carried out in the near term, it should be recognized that the correlation formulas are based on several assumptions and, therefore, have serious limitations. The formulas represent only an interim solution to a complex problem. Accordingly, it is strongly recommended that it be replaced with an improved approach when new data are developed. A comparison between the formula and experimental data is shown below. The implications of analytical approximation in terms of ignition energy contours in the temperature-altitude plane are shown in the graph at the bottom of the page.
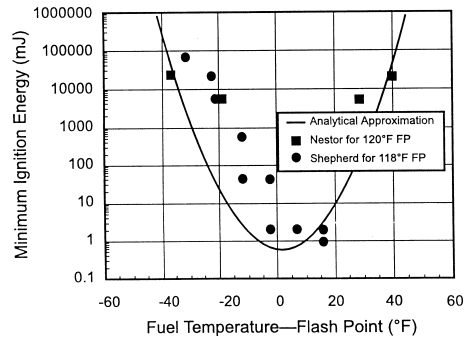
Comparison of Correlation With Minimum Ignition Energy (MIE) Data for Jet A Fuel at 14,000-ft Altitude

The task group found present methods for predicting in-flight fuel temperatures to be inadequate. The development of reliable heat transfer models and the ability to calculate the flammability of the ullage space in an aircraft fuel tank are in the early stages. Therefore, the ability to reliably evaluate different strategies to reduce the flammability of fuel in aircraft fuel tanks has not been proven.
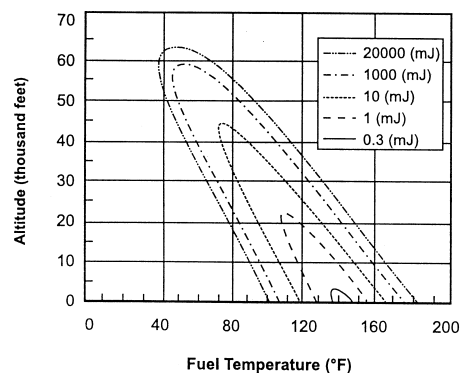
Predicted Constant Ignition Energy Contours for a Fuel with a Flash Point of 120°F (49°C)

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