THE PERFORMANCE OF LIGHTWEIGHT PLASTIC

FOAMS DEVELOPED FOR FIRE SAFETY

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ABSTRACT

Research on the chemistry of ablation for protection of spacecraft during atmospheric entry has led to the development of a new class of fire-retardant materials; namely, lightweight plastic foams. The foams have been developed principally to protect aircraft structures and externally mounted fuel tanks from onboard fires in flight.

Fire-retardant foams have been made from urethane, isocyanurate, and polybenzimidazole. The density of the foams ranges from 2 to 30 lb/ft^3. Addition of randomly placed quartz fibers to the urethane and isocyanurate foams increases their density and improves the stability of the char formed on heating. For example, by adding fibers in a 10 percent concentration, the density of the urethane foam is tripled and its fire-protection capability is increased five-fold. The fire-protective capability of the isocyanurate foam system is twice that of the urethane foam and four times that of commercial isocyanurate fire-retardant foam.

This paper describes the various fire-retardant materials and illustrates their performance when exposed to a fuel fire. Performance is compared wherever possible with presently available commercial developments. Although the materials were developed primarily for aircraft use, a discussion is given of other possible areas of application.

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INTRODUCTION

The work at Ames Research Center on fire protection and fire suppression was started in September 1967, and was motivated by the realization that the principles utilized in the protection of entry vehicles from aerodynamic heating could be used to give some measure of protection from both spacecraft and aircraft fires. The use of a low-density, polyurethane-based, foam material to suppress a fire and to provide protection for the structure of an aircraft or spacecraft will be discussed and described (ref. 1).

In this program we had laid down certain ground rules that hopefully would avoid the normal long lead times between the generation of an idea and the production of a final useful product. First, we gathered a team of specialists from a number of organizational segments at Ames Research Center so that special skills could be concentrated on the problem in all disciplines needed. Second, we stipulated that only commercially available materials were to be used in the first phase of the program to avoid the time delays in inventing and producing new material systems. This decision produced a product that could be improved with additional work, but very rapid progress was made with this approach.

THEORY

The protection of any structure, entry vehicle or aircraft, against damage by heat can be accomplished by the same basic protective mechanisms. The source of heat is not important; heat generated by fire or by a hot gas cap surrounding an entry vehicle is much the same. In order to damage a

structure, heat must be carried to the structure by either free or forced convection or by radiation. Therefore, in principle, any or all of the heat-protective mechanisms can be utilized to afford protection. (See fig. 1 and ref. 1.)

The simplest form of heat protection is one that provides a high resistance to heat flow between the heat source and the structure. Low density foam with a low thermal conductivity provides this feature. Another important mechanism, often overlooked in fire protection systems but widely utilized in spacecraft thermal-protection systems, is the release of gases from the thermal-protective material when subjected to heat load. These gases serve to protect the system in two important ways. First, gases near the surface flow against the incoming heat, thus impeding the flow of heat to the surface. For example, in a spacecraft being protected against reentry heating, gases can block nearly all the convective heat flow. Second, in protecting against a fuel fire, gases can be made rich in halogens that can chemically scavenge the chain carriers by which fuel flames are propagated and thus serve as fire-extinguishing agents. This principle has been utilized in the polyurethane systems.

Another mechanism that affords protection against fires is the production of char resulting from the action of heat on the materials. If char with low thermal conductivity and high oxidation resistance can be formed, it will not only afford protection by virtue of its low thermal conductivity, but its surface will reach a high temperature and thus will be capable of reradiating a large fraction of the incident heat load. This mechanism is utilized in the systems that we are developing. In the polyurethane foam material, polyvinylchloride has been added, which, when

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heated, causes the polyurethane to form a stable, tough char of low thermal conductivity. This idea came directly from work on thermal protection systems for reentry vehicles.

This emphasizes an important point about the systems to be discussed: these systems react to an applied heat load to provide a number of protective mechanisms not present in a system that does not respond to a fire. Thus, these are not passive systems; rather, they are dynamic systems that provide protection when exposed to a fire (ref. 1).

MATERIALS

The properties desired in a foam system for fuel-fire protection are given in figure 2. Several foam systems have been developed to provide a selection of materials with specific properties for various applications.

Urethane Foam (Ames Type 5I)

Urethane systems were examined and modified to yield the 5I composite foam, a base of α methyl glucoside and propylene oxide. A halogenated polymer, polyvinylchloride, which increases char yield and pyrolizes to release HCl gas that acts as a free-radical flame scavenger, was added to this basic polymer system. An inorganic salt, potassium fluoroborate, also was added to the foam system. The function of the inorganic salt is twofold: the salt produces fire-quenching or suppressing species, and the decomposition products of the salt potentially can react with the degradation products of the urethane foam.

The specific action of these alkali metal salts of fluoroboric acid is shown in figure 3. Degradation forms boron trifluoride, which can serve as

a fire-quenching species and also react with the carbonaceous char to form carborane or boron carbide-like structures. Figure 4 shows a cross section of 5I foam undergoing thermal degradation and frozen in time. We see the outgassing of suppressant and scavenging species that cool the integral char structure as they are injected into the boundary layer. The highly emissive surface reradiates much of the incident flux, resulting in better sustained thermal protection (ref. 2).

The third additive that can be incorporated in foams to provide fire-quenching or suppressing species is micro-encapsulated volatile halogen-bearing molecules. With thermal degradation of the microcapsules, the halogen-bearing molecules are released, resulting in dilution of ejected gases and also providing species that can act as free-radical quenchers on the fuel-fire propagation species of the flame. Figure 5 shows a micro-capsule, or balloon, and fire-retardant filler.

Urethane Systems (Fiber Loaded)

In areas where higher shear loads, both mechanical and thermal, are encountered, fiber-loaded 5I foam may be used. Of many fibers tested, short glass or quartz fibers (about 1/4-in. long) in a 10 percent by weight concentration, performed very efficiently. This will usually increase the density of foam about threefold. However, the improvement in other thermal physical properties may outweigh the weight penalty. In its density range (i.e., 5-6 lb/ft^3), this foam, designated 5I10AQ, performs very well under low heating rates.

Isocyanurate Rigid Foam

To obtain higher char yields than could be obtained with the urethane system, further research was needed. A new system, polyisocyanurate polymers, seemed to be one of the most promising (ref. 3).

An isocyanurate ring structure is formed by the cyclization of three isocyanate groups. The use of a poly-functional isocyanate, such as diphenyl methane diisocyanate (MDI) or a polymeric isocyanate (PAPI), gives rise to a polymeric isocyanurate polymer. Polyisocyanurate polymers exhibit improved temperature stability when compared to a polyurethane polymer. The cyclization reaction is illustrated in figure 6.

The practical problem with the polyisocyanurate polymers for use in low density foam materials is that of brittleness or friability of the foam structures. The brittleness is attributed to the cyclic structure that restricts motion in the polymer chain. The brittleness associated with the polyisocyanurate polymers has limited the use of this polymer system in low density foam applications.

Investigations into methods to reduce the brittleness of the polyisocyanurate polymers were undertaken. The technique demonstrated to have the most utility is that of introduction of urethane linkages into the polyisocyanurate polymer. The disadvantage of this approach is the introduction of less stable urethane linkages in the system, which can lead to flammable gaseous species evolved during thermal degradation; so the choice of polyol to be used and the amount are extremely important. First, the polyol fragment must result in a char independent of the urethane linkage. Second, the reaction to form a high-temperature stable structure should occur prior to the initial urethane linkage degradation to minimize volatile fragment formation. Third, the polyol should have a low hydroxyl number so as to

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convert as few as possible of the isocyanate groups to urethane linkages in the polymer system. Fourth, the polyol should have a high molecular weight and low functionality so as to impart mechanical flexibility to the polyisocyanurate-polyurethane polymer structure.

Acrylonitrile was selected as the grafting monomer because nitrile linkages cyclize to form high-temperature stable heterocyclic ring structures when exposed to a thermal environment. Potassium fluoroborate, which improves char strength in polyurethane foams exposed to thermal environments (ref. 2), and zinc oxide, which aids in the curing of the acrylonitrile fraction, were added to the basic polymer system.

When a closed-cell foam is heated, the gas pressure in the cells increases. Around 250°F the foam is softened to a degree that the increased gas pressure causes the foam to swell. Continued heating in air causes the foam to begin degrading to a carbonaceous char structure while outgassing various compounds and shrinking in size. These changes in size are plotted versus temperature in figure 7. We see that the isocyanurate foam (X-ISO) maintains better dimensional stability than the urethane foam (Ames 5I). If we look at the thermal gravimetric analyses (i.e., weight loss with increasing temperature) of these two foam systems (fig. 8), we can see that the major reduction in weight occurs at a higher temperature with the X-ISO versus the 5I foam. At the higher temperatures we can also note the increased weight of the X-ISO foam, with the realization that this almost 50 percent increase at 1000°F represents the "char yield" we had hoped to increase.

Increasing the char yield is shown to be a linear function of the molecular structure of the polymer. (See fig. 9 and ref. 4.) We see now

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that the consequence of the cyclization of three isocyanate groups to form the isocyanurate ring structure led to a higher number of multiply bonded aromatic linkages per gram. This then would predict the higher percentage of char yield.

Higher Density Rigid Foams

We are currently investigating polybenzimidazole (PBI) (see fig. 9) for possible use as a refurbishable spacecraft heat shield. In this application, a foam matrix of PBI would be impregnated with a suitable, fire-extinguishing, ablating material. When it is exposed to a heat source, the impregnated material would ablate away leaving the PBI foam. The PBI would then be reimpregnated and reused.

Another high-density material that we are investigating for high-temperature applications is polyphenylene. Although not directly used for fire safety, polyphenylene material with 90 to 95 percent char yield is currently being made at Ames and tested for possible brake lining application.

TESTING RIGID FOAMS

Sustained thermal protection presents a need for more sophisticated tests than have been or are in use as screening tests at many laboratories. The usual small-scale tests provide only limited data that are useful primarily for classification of a new material. On the other hand, full-scale simulation tests are too expensive, unwieldy, and time-consuming for daily screening of candidate materials. Thus, a new test capable of evaluating the fire-protective effectiveness of the newer class of foam composites was required.

A free-burning JP-4 fuel fire gives a total heat flux of approximately 30,000 Btu/ft^{2}hr, of which the radiative component is approximately 90 percent (ref. 3). To achieve a test that would approximate this environment, a specialized thermal test fixture was developed. This thermal test (T-3) allows for limited control of environment and rapid screening of materials. Backside temperature versus time data are acquired, as well as observation of the physical behavior of the sample in the environment.

Figure 10 is a schematic drawing of the Ames T-3 thermal test facility. An oil burner is used to burn JP-4 jet aviation fuel at the rate of approximately 1-1/2 gal/hr in the firebrick-lined chamber, and the combustion products are exhausted out the top rear of the unit. The test facility has the following test areas: (1) directly over the combustion chamber, (2) in the flue to the rear of the combustion chamber, and (3) inside the combustion chamber under direct fire impingement. The flux levels available in each testing area are indicated on figure 10. For test area 1, the major portion of the heat flux (90 percent) is radiative. Area 2 is a reducing environment where the mode of heat transfer is equally distributed between radiation and convection. In area 3, the main mode of heat transfer is mainly convective with direct impingement on the surface of the material.

The T-3 thermal facility is used for foam-screening tests. For most foam screening, area 1 is used, and the flow rate to the burner is adjusted to maintain 10 to 10.5 Btu/ft^{2}sec (36,000-37,800 Btu/ft^{2}hr) total heat flux. The area 1 temperature at the hot face of the sample is maintained at 1700°F minimum throughout the test.

The foam samples used for the test are 12 x 12 x 2-in. specimens. The sample assembly is shown in figure 11. The samples are backed with

1/16-in.-thick, 2024-T4 aluminum alloy, bonded to the surface of the foam
with an epoxy resin. The back plate has a 2.5-in.-diameter hole in the
center, to which is bonded a 2-in.-diameter aluminum calorimeter of the
same class and thickness. The aluminum back or supporting plate has a
dual function. First, it represents a more practical approach to the ap-
plication in which the foam will be used; and second, it acts as a support-
ing plate for the foam in the T-3 test and prevents any warping of the foam
sample during test.

After a period of conditioning at standard laboratory conditions (one
week at 74°F and 50 percent relative humidity), the samples are tested in
the T-3 thermal facility. A mask of asbestos millboard, 12 X 12 in. with a
7-in.-diameter hole in its center, is placed against the face of the foam
and then placed over area 1. The aluminum backface temperature is recorded
continuously for the test duration.

Plotted in figure 12 are time-temperature histories for a bare control
plate, the Ames-modified urethane system 5I (ref. 2), the Ames-modified
polyisocyanurate system, and a conventional polyisocyanurate foam. The plot
shows that the Ames-modified polyisocyanurate foam is far superior to the
conventional polyisocyanurate foam presently available. Even the Ames-modified
polyurethane foam gives backface temperature-time histories equivalent or
better than the conventional polyisocyanurate foam. The major reason for the
poor showing for the conventional polyisocyanurate foam is that deep fissures
develop during thermal test. Application of the back or support plate to the
conventional polyisocyanurate foam results in catastrophic thermal-stress
failure, which is characterized by the loud sounds heard during tests. The
rapid temperature rise for conventional isocyanurate foam results when fissures

progress directly to the temperature-sensing disc area. Apparently, better performance results from samples in which fissuring progresses to the back plate adjacent to the center disc but not directly over the disc. Since the disc is shielded from the back plate, the temperature is not a true representation of the substrate temperature and is not shown on the figure. Even though Ames urethane foam has a char yield less than the conventional polyisocyanurate foam, the backface temperature vs time plot is better than the conventional polyisocyanurate foam because of superior char integrity of the Ames polyurethane. Therefore, it is significant that a high char yield must be obtained, and that char integrity is necessary for sustained thermal protection. (See fig. 12 for the Ames isocyanurate foam.)

The physical properties of the modified polyisocyanurate foam are tabulated in figure 13. The data require little comment other than to note the favorable properties of the polyisocyanurate foams. The tensile and compressive properties of the polyisocyanurate are superior to the Ames polyurethane foam. The most significant feature of the polyisocyanurate foam is the increased times to reach specific backface temperature.

Many factors enter into the improved backface temperature-time histories of the foam composites. These are reradiation from the frontface surface, transpiration cooling, thermal conductivity, endothermic decomposition, and surface recession and thermal conductivity. These factors were improved in the modified polyisocyanurate foam as indicated by the higher char yield and integrity and lower thermal conductivity, resulting in longer time to reach specific backface temperatures.

NEOPRENE-ISOCYANATE FLEXIBLE FOAMS

To achieve a "nonburning" flexible foam system, Ames modified a neoprene-isocyanate foam by adding a halogenated copolymer, "Saran A," and post-curing the foam to 275-300°F to increase its char yield; the resulting char yield was 38 percent at 1000°F. These were ballistically tested in assemblies such as the one in use at Wright Patterson Air Force Base and shown in figure 14. The internal reticulated foam is present to reduce hydraulic "ram effect" and internal ullage explosions. The candidate foam is placed outside the cell between a function plate and the back cell wall. When corrected for off-bore hits, the number of fires per round in the flexible foam is reduced to zero.

FLEXIBLE FOAM FIRE BLANKET

The same flexible foam becomes a utility thermal blanket when placed between asbestos sheets, Silvabestos (JM). An ammunition can wrapped with the blanket (fig. 15) and immersed in a JP-4 fuel fire results in times (fig. 16) for 50 caliber API ammo inside to the box to reach the indicated temperatures.

CONCLUSIONS

We have shown that the use of low density plastic foams can be modified into effective thermal protection systems. Further work in the areas of reduction of flame spread, smoke generation and classification, and toxic by-products is continuing.

It must be emphasized, however, that the effectiveness of many fire suppressant or extinguishing materials lies in the generation of a large quantity of gaseous products. For the most part, these range from mildly to severely toxic.

REFERENCES

1.   "Preliminary Data from Studies of Fire Retardant Materials." Introduction by G. Goodwin, 1968.

2.   J. A. Parker, S. R. Riccitiello, W. J. Gilwee, R. H. Fish, Development of polyurethane for controlling fuel fires in aircraft structures. Sampe J., April/May, 1969.

3.   S. R. Riccitiello, R. H. Fish, J. A. Parker, E. J. Gustafson, "Development and Evaluation of Modified Polyisocyanurate Foams for Low Heating Rate Thermal Protection." Preliminary Data, Symposium on Flammability of Plastics, Society of Plastics Engineers, New York, May 1970.

4.   J. A. Parker and E. Winkler, "The Effects of Molecular Structure on the Thermochemical Properties of Phenolic and Related Polymers." NASA TR-R-276.

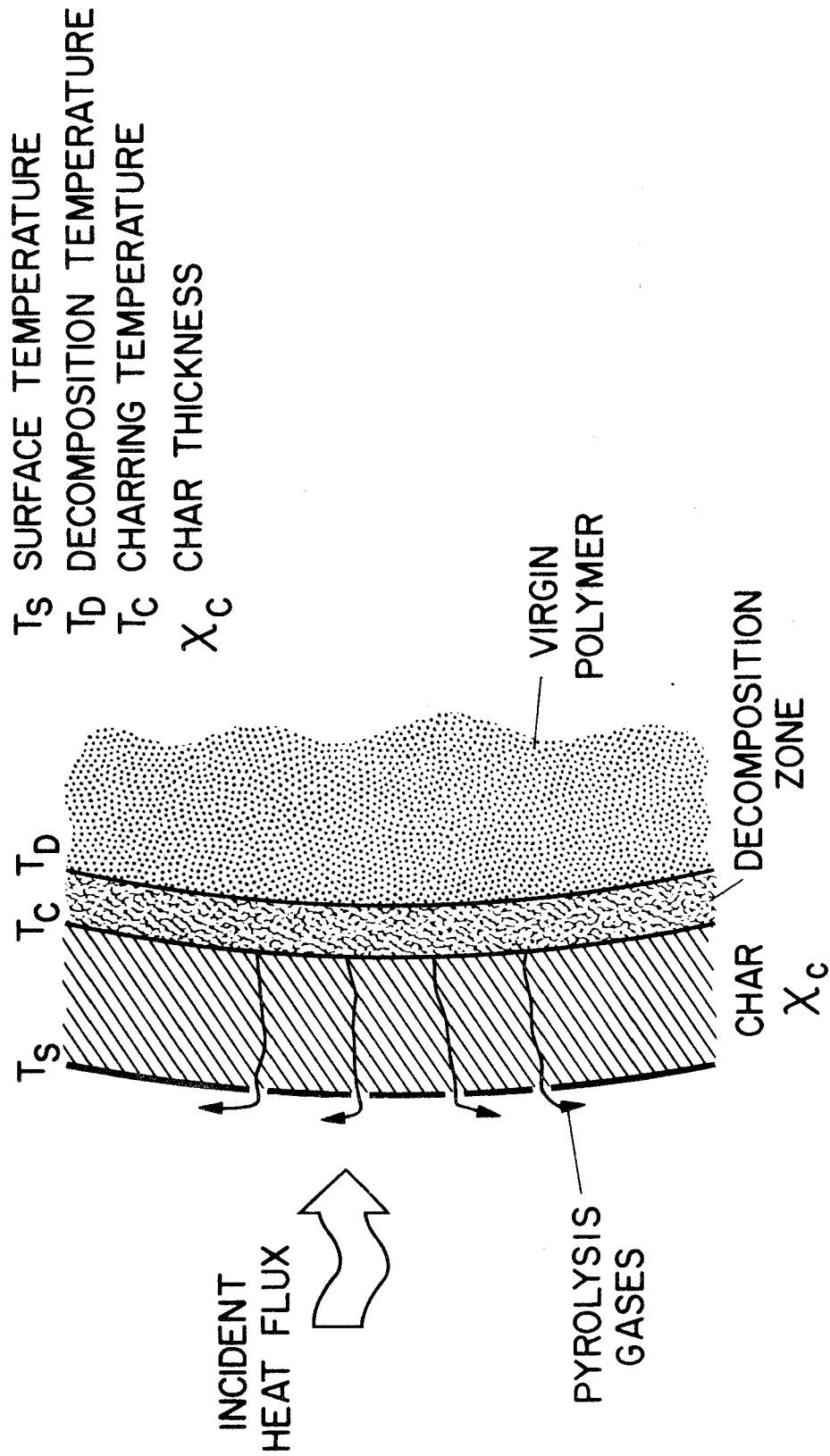# PYROLYSIS MECHANISM OF CHAR FORMING ABLATORS UNDER UNIDIRECTIONAL HEATING

T_S SURFACE TEMPERATURE
T_D DECOMPOSITION TEMPERATURE
T_C CHARRING TEMPERATURE
X_C CHAR THICKNESS

VIRGIN POLYMER

DECOMPOSITION ZONE

T_C T_D

T_S

CHAR
X_C

INCIDENT HEAT FLUX

PYROLYSIS GASES

Fig. 1

FOAM PROPERTIES DESIRED FOR FUEL-FIRE SUSPENSION

IMPACT IGNITION

- LOW DENSITY-VOID-FILLING CAPACITY TO ELIMINATE ATOMIZATION OF COMBUSTIBLE LIQUIDS

- CLOSED CELL FOAM STRUCTURE WITH SELF SEALING SKIN TO PREVENT OUT-POURING OF COMBUSTIBLE LIQUIDS

- PYROLYSIS AT LOW TEMPERATURE, AT HIGH RATE TO GIVE HYDROGEN BROMIDE, HYDROGEN CHLORIDE OR HYDROGEN FLUORIDE AND FREE RADICALS TO INHIBIT IGNITION

SUSTAINED FIRE PROTECTION

- DECOMPOSES AT MODERATE RATE TO GIVE LOW MOLECULAR WEIGHT SPECIES TO SUPPRESS FLAMES

- EXCELLENT LOW HEATING RATE ABLATION EFFICIENCY TO MINIMIZE HEAT TRANSFER TO AIRCRAFT STRUCTURES

Fig. 2