"NEW FIRE RETARDANT FOAMS AND INTUMESCENTS"

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In 1968 Dr. Parker was awarded the NASA Exceptional Scientific Achievement medal for his pioneering research in reentry technology and on the ablation of heat shield materials. The results of this work have been used to provide protection from fire with a wide range of commercial application.

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PROTECTION OF AIRCRAFT IN GROUND CRASH FUEL FIRES

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INTRODUCTION

Passengers caught in an aircraft ground accident that has resulted in fire have only a very short time to escape. Those failing to exit quickly probably will die from exposure to heat and fumes.

As part of a program of development of fire-retardant materials at Ames Research Center, a concept for passenger survival has been studied which differs from those that have been considered in the past. Previous studies generally have stressed quick-evacuation techniques; some have dealt with possible ways to prevent or control the fire. In contrast, the study at Ames was directed toward the approach of surrounding the passenger compartment with a fire-retardant shell that would protect the occupants long enough for the fire to burn out or for fire-fighting equipment to reach the airplane and extinguish the fire.

This approach has been made possible by the recent development of two new fire-retardant materials: a lightweight foam plastic, called polyisocyanurate foam, and an intumescent paint. The intumescent paint is a material that expands to many times its original thickness when exposed to heat; thus, it insulates the surface on which it is applied. The thermal-protection mechanisms of these materials operate on the same ablative principles as those used to protect the astronauts during reentry. To demonstrate their use in a full-scale application, an airplane fuselage was fitted with the materials and tested in a jet-fuel fire.

This paper describes the fire-protection system and the fire test and presents an analysis of some of the results. It should be emphasized that this constitutes a progess report and that a number of problems remain to be solved before such a system can be used for passenger protection.

PREPARATION OF TEST FUSELAGE

Considerations for Passenger Protection. In the design of a test to demonstrate how these materials could be used to protect passengers, two factors influencing survival in a crash fire must be considered. First, the penetration of heat must be minimized. At the same time, a way must be devised to prevent the intrusion of smoke and toxic gases, which can be lethal even though the temperature is controlled.

A factor that influences both of these threats in the case of a survivable crash is the structural damage that results in rupture of the fuselage. Crash damage was not considered in the present test nor was the presence of windows, which also could be a point of heat and gas penetration. These factors have been purposely omitted because it was believed that the basic concept of passenger protection should be explored first. The effect of crash damage and the protection of windows will be included in future studies.

Installation of Fire-Protection System. Avco Systems Division of Lowell, Massachusetts, under contract to NASA, installed the fire-protection system and conducted the test. For the test Avco procured a surplus McDonnell Douglas C-47 airplane and removed a 7.9 m (26 ft) long section from the fuselage (Figure 7).[1] They divided the section and capped either end by steel bulkheads, making two equal sections typical of traditional airplane construction. One half was left essentially unchanged; the other half was fitted with the thermal-protective materials to form a shell around the passenger compartment. Thus, the test would validate feasibility of a retrofit system for existing aircraft.

The details of the installation of the fire-protection system are shown in Figure 8. The circular frames were first painted with intumescent paint 0.13 cm (0.05 in.) thick. Next, a layer of loosely woven fiber-glass matting was bonded to the skin. The polyisocyanurate foam was sprayed over the matting and was built up to the full 6.4-cm (2.5 in.) depth of the frames and 5 to 8 cm (2 to 3 in.) over the floor structure. Excess foam was trimmed off. To finish the installation, a liner of fiber-glass-epoxy laminate 0.08 cm (1/32 in.) thick was cemented to the foam and then riveted to the frames. This laminate is similar to airliner decorative interior paneling. The floor foam was also covered with the laminate, and all joints were sealed to exclude smoke and gases. The properties of the foam used in the test are given in table 1.

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[1]The tables and figures referenced are not included in this report.

In the unprotected section, the space between the aluminum skin and the interior paneling was filled with 5 cm (2 in.) of fiber-glass batting, a material typical of conventional aircraft insulation.

The steel bulkheads that divided the protected and unprotected sections and capped the two ends were insulated with a 2.5-cm-thick (1 in.) commercial firewall insulation covered with 8 cm (3 in.) of fiber-glass batting.

Instrumentation and Test Arrangement. The fuselage was instrumented to measure both the exterior and interior thermal environments. Thermocouples were used to measure temperatures both inside and outside the cabin. The exterior heat flux was measured by slug-type calorimeters.

The fire test arrangement is illustrated in Figure 9. The test was conducted at Otis Air Force Base, Massachusetts. The fuselage was placed directly on the ground and was flanked by two shallow pits about 9 by 15 m (30 by 50 ft). Water was placed in the bottom of the pits, and 9.5 m³ (2500 gallons) of JP-4 fuel was floated on top of the water in each pit, forming two large fuel ponds. Water-cooled probes containing motion-picture cameras and gas-sampling equipment were positioned at either end of the test fuselage so that they could observe the interior of each section. The probes were arranged so that they could be withdrawn when temperatures became excessive. Several cameras were placed around the vehicle to record the test.

The exterior of the fuselage before the test is shown in Figure 10. The interior of the protected section before the test is shown in Figure 11. Simulated exit signs and an optical target were installed to permit evaluation of possible smoke effects. The interior of the unprotected section appeared much the same as the protected section, except that no exit signs or optical target was installed.

Test Plan. The plan was to ignite both ponds of fuel simultaneously at several points to obtain a uniform buildup of flames over the surface of each pond. The quantity of fuel and configuration of the ponds were calculated to envelop the fuselage completely with flames and to expose the vehicle to maximum heat flux for 10 minutes. It was believed that the unprotected section would be destroyed within 1 to 2 minutes. The protected section hopefully would survive the fire, but fire trucks were stationed nearby in the event that certain monitored thermocouples indicated flame intrusion.

FIRE TEST

The test was made on August 13, 1970. Within ½ minute after ignition, the fire was fully developed. By this time, smoke had already started to penetrate the unprotected section. Occupants of this part of the cabin would have had to have evacuated the vehicle by this time to have survived. ~~Two views of the fire during the test are shown in Figure 12.~~

Throughout most of the test, the entire test section was completely engulfed in flames. Because of the volume of flames and smoke, visual observation of the test section was difficult. About 5 minutes after ignition, a light wind arose from the southeast and directed the flames so that occasionally the end of the protected section was visible. Accompanying this flame shift was a tremendous vortex action of flames around the entire fuselage. This swirling action continued for about 30 m (100 ft) upward. Peaks of the flames reached a height of approximately 60 m (200 ft).

Motion pictures of the interior of the unprotected section, although obscured by dense smoke, show flame penetration within 1 minute after ignition. After 2 minutes, the unprotected section apparently collapsed and was completely destroyed.

Meanwhile, in the protected section, the motion pictures showed no smoke, the gas-sampling probe showed no toxic gas, and the thermocouples showed no temperature change. A power failure prevented further motion pictures of the interior and necessitated removal of the probe containing the motion-picture cameras and the gas-sampling equipment after 5.5 minutes. The last gas sample was taken 5 minutes after ignition and still showed no toxic gases.

The fire lasted for 12 minutes, at which time the fire in the ponds burned out, and only residual flames remained around the edges where fuel had soaked into the dirt mounds surrounding the ponds.

Following the test, the visual comparison between the protected and unprotected sections was dramatic. ~~Figure 13~~ shows virtually no trace of the unprotected section, whereas the foam-protected fuselage is intact. The interior appears habitable, ~~as shown by Figure 14.~~ Some time during tailoff of the fire, flames reached a relatively unprotected floor seam along the top of the dirt mound supporting the test section. Heat penetrated at this point, and eventually resulted in a

slight burn-through, which caused considerable blackening of the walls. This occurred after the main fire burned out and is attributed to the design of the test and not to a failure of the thermal-protective system.

Soon after the fire died down, fire hoses were played on the test section, to preserve it for study, and on the remaining flames around the edges of the ponds.

RESULTS AND DISCUSSION

Cabin Air Temperatures. The cabin air temperature histories were used to analyze the results. These histories are plotted in Figure 15. In the unprotected section, the air temperature rose to 300° C (600° F) in less than 2 minutes after the start of the fire and was climbing rapidly. By this time, the unprotected section was destroyed. In contrast, the temperature in the protected section changed very little for the first 6 minutes; then, as the heat finally penetrated, the temperature rose faster, reaching 150° C (300° F) as the fire burned out in 12 minutes.

To give an idea of the chance that passengers might have had of surviving inside the cabin, a curve labeled "Human tolerance limit" has been plotted. This curve is a composite of two studies of exposure of humans to extreme heat · and represents more severe conditions than existed in our test. Also shown for comparison is the exposure envelope for the sauna-bath ritual, which calls for repeated exposures of 10 to 15 minutes at temperatures from 80° to 100° C (175° to 210° F). This is done for the health. The fact that the temperature in the protected section just reached the human tolerance limit (for more severe conditions) in 12 minutes, as the fire burned out, indicates that, if temperature were the only consideration, passengers could have survived for this time.

Generation of toxic gases is as important a consideration as temperature. Up to 5 minutes into the test, no toxic gases were generated. At this point, the gas-sampling probe was withdrawn; therefore, no measurements were made late in the test. During the last few minutes before burnout of the fire, segments of the fiber-glass-epoxy liner reached temperatures at which partial decomposition of the resin might have occurred. Gases might have been generated that could have been somewhat toxic. Although such gas generation was a possibility, the amount of toxic fumes was not believed to have been sufficiently high to have influenced survivability, even at 12 minutes.

If this test represented an actual airliner crash fire at an airport, fire-fighting equipment generally could have reached the airplane and extinguished the fire in less than 8 minutes. At this

point in the test, conditions were much more favorable for survival than at 12 minutes, and there would be no question of either heat or toxic gases endangering life in the cabin. Thus, the concept of passenger protection was adequately demonstrated by this test.

Consider again briefly the analysis of the cabin air temperature. After the fire burned out in the ponds, small flames remained along the sides of the test section from residual fuel that had soaked into the dirt mounds surrounding the ponds. At 12.5 minutes after the start of the fire, the air temperature suddenly increased, indicating flame intrusion into the cabin. The cracks at the floor-wall intersection are believed to have occurred at this time. The cause of the cracks, which resulted from melting structure, is discussed later. The flame intrusion was probably rather small, being limited to the low flames remaining at the edges of the ponds. At 14 minutes, water hoses were played on the protected section and on the remaining flames, causing the cabin air temperature to drop rapidly.

Sources of Cabin Heating. Although the system of foam, paint, and fiber-glass liner gave satisfactory protection, ways were explored to improve the system, with the objective of indicating how the weight might be reduced. The most useful information from this standpoint is the thermal data. Accordingly, these data were analyzed to identify and evaluate the sources of heating. To aid in the analysis, temperature histories at various locations in the cabin for the last 5 minutes of the test were plotted. A typical history for three locations in the cabin is given in Figure 16. Shown in this figure is the temperature of the air measured in the middle of the cabin, on the fiber-glass liner at a location alongside the air thermocouple, and in the foam 0.6 cm (1/4 in.) away from the fiber glass. Note that the temperature of the air was higher than that of the fiber-glass liner, and the liner temperature was higher than that of the foam. This means that the air was heating the sidewall of the cabin. This reversal in heat-flow direction was unexpected, and it indicates that most of the cabin heating came from heat leaks rather than through the main area of the side walls.

Two sources of heat leaks are identified by the temperature histories shown in Figure 17. The temperatures were measured over a frame and on the fiber-glass liner opposite a region of the foam that had fissured. At both of these points, the temperatures were well above the air temperature. These temperature histories typify the two primary sources of heat leaks. The frames formed highly conductive heat-flow paths through the foam. Calculations indicate that about one-third of the total heat input to the cabin for the last 5 minutes of the test came through the frames. Fissuring of the foam was the second source of heat leaks. The sudden increase in fiber-glass-liner temperature

indicates the appearance of a fissure in the foam. These fissures apparently were the primary source of heat leaks into the cabin, and, according to calculation, contributed over half the heating of the cabin. ~~A photograph of these fissures after the test is shown as Figure 18.~~ The deep cracks, some of which penetrated clear to the fiber-glass liner, were obvious heat-flow paths to the liner.

To minimize heating from the frames, the obvious solution would be to insulate the fiber-glass liner from the frame flanges. Because of its low thermal conductivity, isocyanurate foam would be a good material for this application. Calculations indicate that, if 1.3 cm (½ in.) of foam were placed between the frame flanges and the fiber-glass liner, the heat input from the frames could be decreased to one-fifth of the value with no insulation.

The problem of fissuring of the foam is one that needs further study. Tests have shown that isocyanurate foam in the lower-density range (30 to 40 kg/m³ (2 to 2.5 lb/ft³)) does not fissure. Laboratory studies made since the fire test show that the lower-density foam, because of its greater integrity, provides thermal protection equivalent to that of the higher-density foam (65 kg/m³ (4 lb/ft³)) used in the fire test. This means, of course, that the lower-density foam should give as good protection in a fire as was provided in the test by the higher-density foam. Use of the lower-density foam would have the advantage of providing a much lighter installation.

There are several possible explanations for the fissuring. The most obvious one is that the higher density creates greater stresses upon heating of the foam than the lower density. Spraying the foam, which undergoes an exothermic reaction upon curing, against cold aluminum structure might create built-in stresses that are relieved when the foam is heated. Other processing problems could also have led to the conditions that caused fissuring. These various possibilities must be studied to eliminate fissuring.

Floor-Line Failure. Another area for improvement is the design of the floor-line protection. In order to understand how to improve the design, the cause of failure during the fire test should be examined. ~~Figure 19 illustrates how the failure developed.~~ Dirt had been banked part way up the fuselage wall to create a mound that formed one side of the fuel pond. The mound stopped just below the floor line. This protected the bottom part of the fuselage from the fire, but left exposed a portion of the structure just below the floor line. Heat from the fire finally melted the exposed frames to which the floor beams were fastened. Thus, the support for the floor was removed and this caused the floor to sag just as the fire was burning out. This opened the floor-line cracks and allowed the flames to enter the cabin.

In the foam installation, the floor foam was placed on top of the floor structure, where it did not protect the primary structure. This installation proved satisfactory for the test of the protective concept, but an improvement in design of the protective system would be required for an operational installation. To protect the floor structure properly, the foam should be placed under the structure, as shown in Figure 20. The foam should surround the primary structure to protect it from melting.

Weight Penalty. Because of its ablative character, the fire-retardant foam generally provides increased fire protection with increase in density. Accordingly, the foam in the test fuselage was made heavier than usual, with the intent of providing protection equal to the protection that would have been obtained from a thicker application of lower-density foam in a larger airplane. Analysis of the data from the fire test indicates that the foam installation was heavier than needed for adequate fire protection.

Now consider the various factors that would permit a reduction in weight. First of all, as was mentioned previously, by minimizing the heat leaks, one could expect improved thermal performance, which would permit a reduction in weight. In fact, the indication was that the foam density could be reduced from 65 kg/m^3 (4 lb/ft^3) to about 40 kg/m^3 (2.5 lb/ft^3) with no reduction in performance. Also, by designing for a shorter protection time, such as 8 minutes instead of 12 minutes, the required protection and the corresponding weight could be further reduced.

Based on these considerations, an estimate was made of the weight penalty for installation of a fire-protective system in a typical modern-day airplane — an airliner with a gross weight of 180,000 kg (400,000 lb). The increase in weight is estimated to be 1.5 kg/m^2 (0.3 lb/ft^2) of protected surface area. This would increase the gross weight 770 kg (1700 lb). The corresponding increase in structural-weight fraction would be from 30.0 to 30.4 percent.

It should be pointed out that the protective system discussed in this paper would be essentially a retrofit installation for airplanes currently in service or in production. The foam would be added for the single purpose of fire protection. No advantage would be taken of its other useful characteristics, such as high compressive strength and compressive modulus or acoustical damping properties. To utilize the foam most effectively, the foam and structure should be integrated at the beginning of the structural design phase for a new airplane. With this approach, it is conceivable that the structural gain would permit the addition of foam with no weight penalty.

CONCLUDING REMARKS

A test that constitutes a first step in developing a system to protect passengers in a crash fire has been described. Many problems, such as protecting against fuselage rupture and providing protection for windows, must be solved before such a system can be used. Nevertheless, results of the test give promise of providing protection for passengers caught in a crash fire.

THE PERFORMANCE OF LIGHTWEIGHT PLASTIC

FOAMS DEVELOPED FOR FIRESAFETY

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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 the fire-protection capability is increased fivefold. 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.

The various fire-retardant materials are described in this paper, and the performance of these materials when exposed to a fuel fire is illustrated. Wherever possible, performance is compared with presently available commercial developments. Although the materials were developed primarily for aircraft use, a discussion is given of other possible areas of application.

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.

In this program, certain ground rules were established that hopefully would avoid the normal long leadtimes between the generation of an idea and the production of a final useful product. First, a team of specialists from a number of organizational segments at Ames Research Center was gathered so that special skills could be concentrated on the problem in all disciplines needed. Second, it was 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. These actions provided rapid progress and produced a useful product that could be improved further with additional work.

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. 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 (fig. 11-1).

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 a 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 low thermal conductivity, but the 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 are being developed. In the polyurethane foam material, polyvinylchloride has been added, which, when 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.

An important point about the systems to be discussed is that 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.

MATERIALS

The properties desired in a foam system for fuel-fire protection are as follows.

1. Impact ignition

    a. Low density-void-filling capacity to eliminate atomization of combustible liquids

    b. Closed-cell foam structure with self-sealing skin to prevent outpouring of combustible liquids

    c. Pyrolysis at low temperature and at high rate to give hydrogen bromide, hydrogen chloride, or hydrogen fluoride and free radicals to inhibit ignition

2. Sustained fire protection

    a. Decomposes at moderate rate to give low molecular weight species to suppress flames

    b. Excellent low-heating-rate ablation efficiency to minimize heat transfer to aircraft structures

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 11-2. 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. A cross section of 5I foam undergoing thermal degradation and frozen in time is shown in figure 11-3. The outgassing of suppressant and scavenging species that cool the integral char structure can be seen 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. 11-1).

The third additive that can be incorporated in foams to provide fire-quenching or suppressing species is microencapsulated 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. A microcapsule, or balloon, and fire-retardant filler are shown in figure 11-4.

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. The addition of these fibers usually will increase the density of foam approximately threefold. However, the improvement in other thermal physical properties may out-weigh the weight penalty. In its density range (i.e., 5 to 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 ure-thane system, further research was needed. A new system, polyiso-cyanurate polymers, seemed to be one of the most promising (ref. 11-2).

An isocyanurate ring structure is formed by the cyclization of three isocyanate groups. The use of a polyfunctional isocyanate, such as diphenyl methane diisocyanate (MDI) or a polymeric isocyanate (PAPI), gives rise to a polymeric isocyanurate polymer. Polyisocyanurate poly-mers exhibit improved temperature stability when compared to a poly-urethane polymer. The cyclization reaction is illustrated in figure 11-5.

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 sytem in low-density foam applications.

Investigations into methods to reduce the brittleness of the poly-isocyanurate polymers were undertaken. The technique demonstrated to have the most utility is that of introducing urethane linkages into the polyisocyanurate polymer. The disadvantage of this approach is the in-troduction 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 impor-tant. 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 before the initial urethane linkage degra-dation to minimize volatile fragment formation. Third, the polyol should have a low hydroxyl number so as to 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 stru-tures when exposed to a thermal environment. Potassium fluoroborate, which improves char strength in polyurethane foams exposed to thermal environments (ref. 11-1), 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. At approximately 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 as a function of temperature in figure 11-6. It may be seen that the isocyanurate foam (X-ISO) maintains better dimensional stability than the urethane foam (Ames 5I). If the thermal gravimetric analyses (i.e., weight loss with increasing temperature) of these two foam systems are examined (fig. 11-7), it can be seen that the major reduction in weight occurs at a higher temperature with the X-ISO versus the 5I foam. At the higher temperatures, the increased weight of the X-ISO foam also can be seen, with the realization that this almost 50-percent increase at 1000° F represents the "char yield" that it was hoped to increase.

Increasing the char yield is shown to be a linear function of the molecular structure of the polymer (fig. 11-8 and ref. 11-3). It now can be seen that the consequence of the cyclization of three isocyanate groups to form the isocyanurate ring structure led to a higher number of multiple bonded aromatic linkages per gram. Therefore, the higher percentage of char yield could be foreseen.

Higher Density Rigid Foams

Polybenzimidazole (PBI) (fig. 11-8) currently is being investigated 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 is being investigated for high-temperature applications is polyphenylene. Although not directly used for firesafety, polyphenylene material with a 90- to 95-percent char yield currently is 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 was required by which the fire-protective effectiveness of the newer class of foam composites could be evaluated.

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. 11-2). 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. Data are acquired for backside temperature as a function of time, and observations are made of the physical behavior of the sample in the environment.

A schematic drawing of the Ames T-3 thermal test facility is shown in figure 11-9. 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 in figure 11-9. 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 distributed equally 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 to 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 mimimum throughout the test.

The foam samples used for the test are 12- by 12- by 2-inch specimens. The sample assembly is shown in figure 11-10. The samples are backed with 1/16-inch-thick 2024-T4 aluminum alloy bonded to the surface of the foam with an epoxy resin. The backplate has a 2.5-inch-diameter hole in the center, to which is bonded a 2-inch-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 application in which the foam will be used; and second, it acts as a supporting 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 (1 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 by 12 inches, with a 7-inch-diameter hole in the 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 11-11 are time-temperature histories for a bare control plate, the Ames-modified urethane system 5I (ref. 11-1), 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 backplate 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 disk area. Apparently, better performance results from samples in which fissuring progresses to the backplate adjacent to the center disk but not directly over the disk. Because the disk is shielded from the backplate, 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, it may be seen by the plot for backface temperature as a function of time that the Ames material is better than the conventional polyisocyanurate foam because of the 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. 11-11 for the Ames isocyanurate foam.)

The physical properties of the modified polyisocyanurate foam are tabulated in table 11-I. 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 front-face 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 postcuring the foam to 275° to 300° F to increase char yield; the resulting char yield was 38 percent at 1000° F. These foams were tested ballistically in assemblies such as the one in use at Wright Patterson Air Force Base (fig. 11-12). 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

A utility thermal blanket using the neoprene-isocyanate flexible foam was developed; that is, a 1/2-inch-thick sheet of the flexible foam was placed between two sheets of asbestos, thus forming a sandwich of foam in asbestos. This blanket could be placed over stockpiled materials and afford protection in the event of a fire. To demonstrate the usefulness of the foam, an ammunition can was wrapped with the blanket (fig. 11-13) and immersed in a JP-4 fuel fire. The temperature of the 50-caliber ammunition inside the box was monitored, and the results are plotted in fig. 11-14. The temperature-time history for an unwrapped box also is shown on the same plot. Longer protection times could be expected from a blanket draped loosely over boxes of ammunition than for a single box wrapped tightly as it was for this test.

CONCLUSIONS

It has been shown that the use of low-density plastic foams can be modified for use in effective thermal protection systems. Further work in the areas of reduction of flame spread, smoke generation and classification, and toxic byproducts is continuing.

However, it must be emphasized 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 gaseous products range from mildly to severely toxic.

REFERENCES

11-1. Parker, J. A., Riccitiello, S. R.; Gilwee, W. J.; and Fish, R. H.: Development of Polyurethane for Controlling Fuel Fires in Aircraft Structures. SAMPE J., April/May 1969.

11-2. Riccitiello, S. R.; Fish, R. H.; Parker, J. A.; and Gustafson, E. J.: Development and Evaluation of Modified Polyisocyanurate Foams for Low Heating Rate Thermal Protection — Preliminary Data. Paper presented at Symposium on Flammability of Plastics, Society of Plastics Engineers, New York, May 1970.

11-3. Parker, John A.; and Winkler, Ernest L.; The Effects of Molecular Structure on the Thermochemical Properties of Phenolics and Related Polymers. NASA TR-R-276, Nov. 1967.

TABLE 11-I.- PHYSICAL PROPERTIES OF AMES URETHANE AND ISOCYANURATE FOAMS

[TEST CONDITIONS — 75° ± 2° F, 50 ± 2 percent RH]

Physical properties of Ames urethane and isocyanurate foams	ASTM method	Ames urethane	Ames ICU
Nominal density, lb/ft^3	(D 1622)	2.5	2.5 to 2.7
Thermal conductivity:			
Btu-in/ft^2-hr-°F	(C 177)	0.175	0.150
W/cm-°C		0.00025	0.00022
Flame resistance	(D 1692)	Self-extinguishing	Self-extinguishing
Compressive strength:			
Parallel, psi	(D 1621)	25	27
Perpendicular, psi	(D 1621)	15	19
Compressive modulus:			
Parallel, psi	(D 1621)	600	1000
Perpendicular, psi . . .	(D 1621)	360	500
Tensile strength, parallel, psi	(D 1623)	21	30
Shear strength, perpendicular, psi	(C 273)	15	14

TABLE 11-I.- PHYSICAL PROPERTIES OF AMES URETHANE AND ISOCYANURATE FOAMS - Concluded

[TEST CONDITIONS — 75° ± 2° F, 50 ± 2 percent RH]

Physical properties of Ames urethane and isocyanurate foams	ASTM method	Ames urethane	Ames ICU
Water absorption, volume, percent	(D 2127)	5	3.5
Backface temperature			
Time to 200° F, sec	Ames T3	210	366
Time to 400° F, sec	Ames T3	390	786

INCIDENT
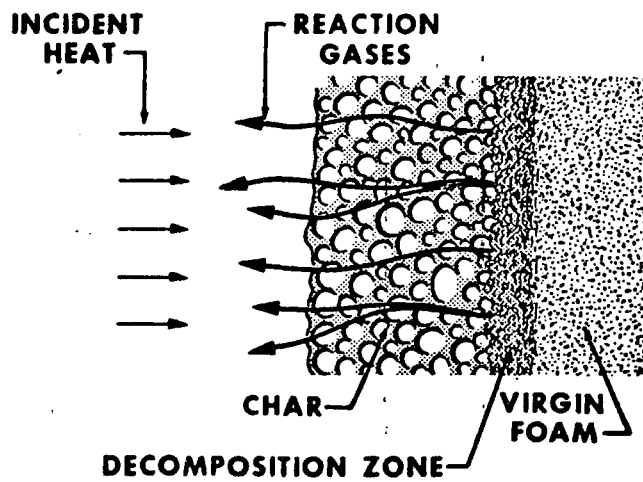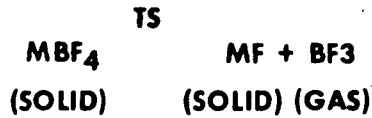HEAT ⌐

⌐ REACTION
  GASES

CHAR ⌐

VIRGIN
FOAM ⌐

DECOMPOSITION ZONE ⌐

Figure 11-1.- Pyrolysis mechanism of
  char-forming ablators under uni-
  directional heating.

PRIMARY CHEMICAL DISSOCIATION

TS

MBF_4 $\longrightarrow$ $MF + BF3$

(SOLID) (SOLID) (GAS)

(ENDOTHERMIC PROCESS
H950°F 29 KCAL/MOLE)

SECONDARY REACTIONS OF VAPOR SPECIES

BF_3 {

TRANSPIRATION ◊ CONVECTIVE BLOCKING OF ACTIVE FLAME SPECIES

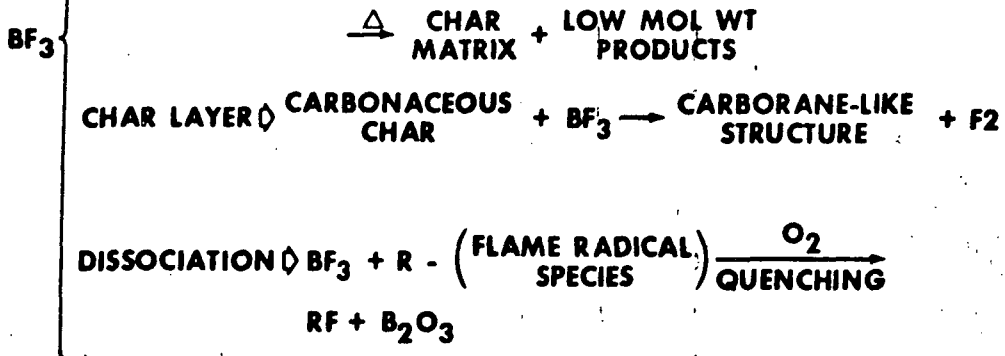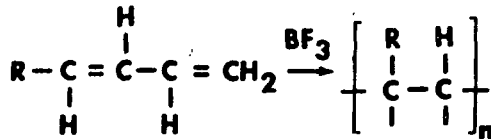PYROLYSIS ZONE ◊ POLYMERIZATION CATALYST FOR
COMBUSTIBLE FRAGMENTS

$$R-C=C-C=CH_2 \xrightarrow{BF_3} \left[\begin{array}{cc} R & H \\ | & | \\ C-C \\ | & | \end{array} \right]_n$$

$\xrightarrow{\Delta}$ CHAR MATRIX + LOW MOL WT PRODUCTS

CHAR LAYER ◊ CARBONACEOUS CHAR + BF_3 $\longrightarrow$ CARBORANE-LIKE STRUCTURE + F2

DISSOCIATION ◊ BF_3 + R - $\left(\begin{array}{c} \text{FLAME RADICAL} \\ \text{SPECIES} \end{array} \right) \xrightarrow[\text{QUENCHING}]{O_2}$

RF + B_2O_3

Figure 11-2.- Thermochemical action of alkali fluoroborules.

CO$_2$ HCl BF$_3$ H$_2$O

800-1000 °F

600-800 °F
400-600 °F

70 °F

SUBSTRATE

DIFFUSION AND THERMAL CONTROL SKIN

CHAR ZONE + INORGANIC SALT

PYROLYSIS ZONE OF POLYURETHANE FOAM

PYROLYSIS ZONE OF HALOGENATED POLYMER
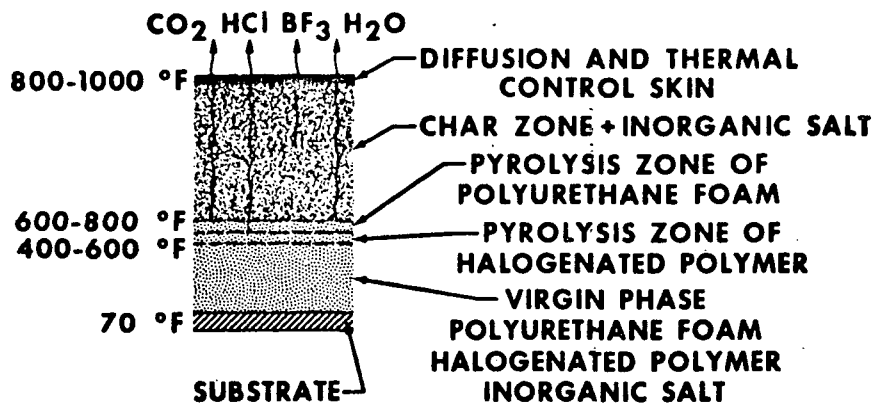
VIRGIN PHASE
POLYURETHANE FOAM
HALOGENATED POLYMER
INORGANIC SALT

Figure 11-3.- Response of Inorganic salt + halogenated polymeracetate-modified polyurethane foam to the heating input of a fuel fire.

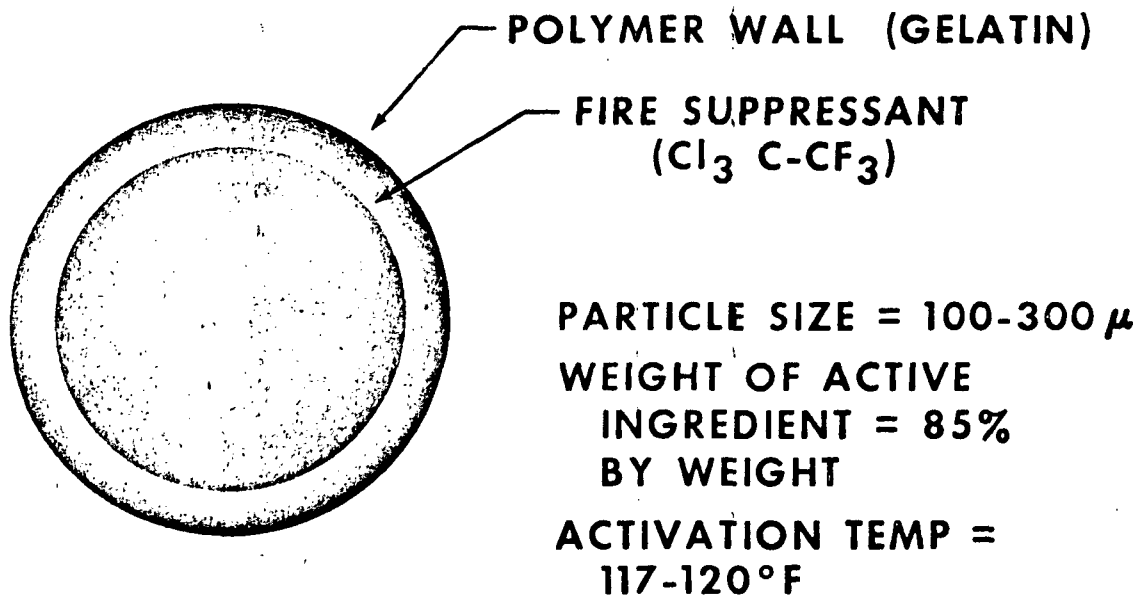POLYMER WALL (GELATIN)

FIRE SUPPRESSANT
(Cl$_3$ C-CF$_3$)

PARTICLE SIZE = 100-300 μ

WEIGHT OF ACTIVE
INGREDIENT = 85%
BY WEIGHT

ACTIVATION TEMP =
117-120°F

Figure 11-4.- Encapsulated fire-suppressant particle (microballoon).

83

Figure 11-5.- Isocyanurate structure.

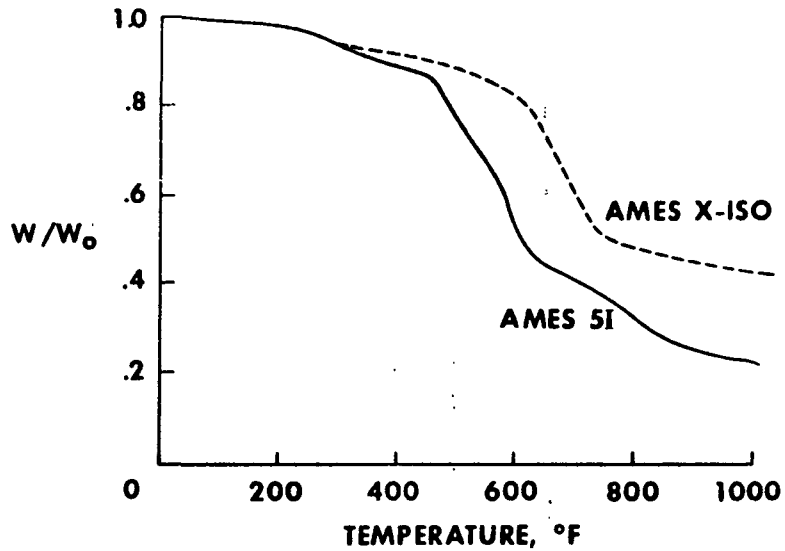Figure 11-6.- Dimensional stability in air of
Ames foams.

Figure 11-7.- Char yield in nitrogen of
Ames foams.
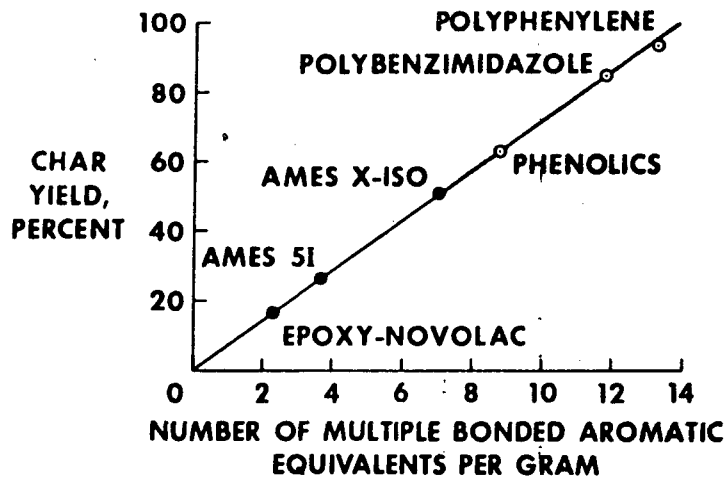
Figure 11-8.- Correlation of primary
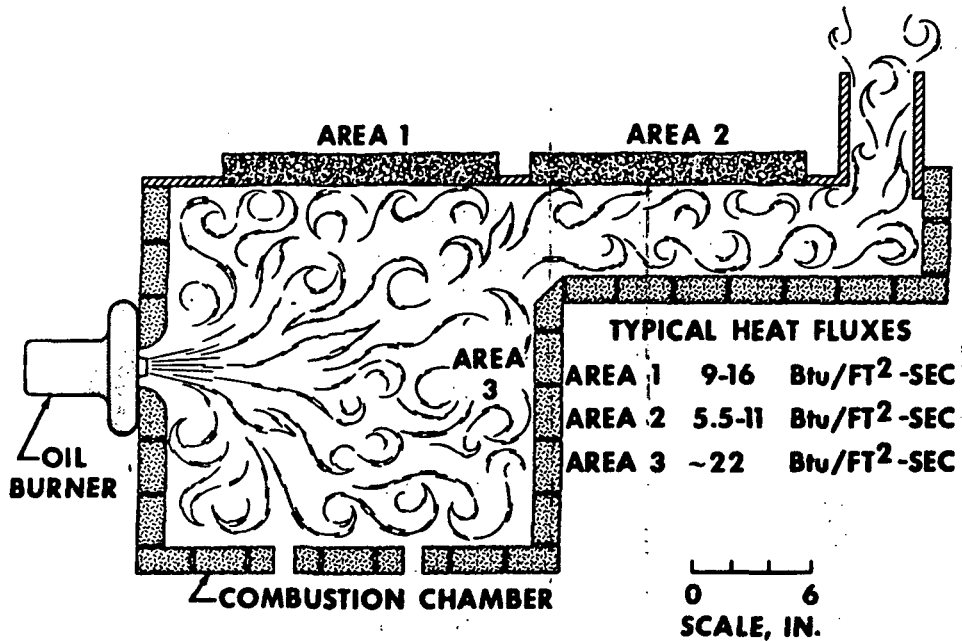thermochemical char yield with
molecular structure.

AREA 1   AREA 2

AREA
3

TYPICAL HEAT FLUXES
AREA 1   9-16   Btu/FT^2-SEC
AREA 2   5.5-11   Btu/FT^2-SEC
AREA 3   ~22   Btu/FT^2-SEC

OIL
BURNER

COMBUSTION CHAMBER

0   6
SCALE, IN.

Figure 11-9.- Ames T3 thermal test facility (JP-4 fuel).

TEMPERATURE
SENSING DISK

0.0625 IN.
ALUMINUM
BACKING PLATE

2 IN. THICK
SAMPLE

0.5 IN.
ASBESTOS
EDGE MASK
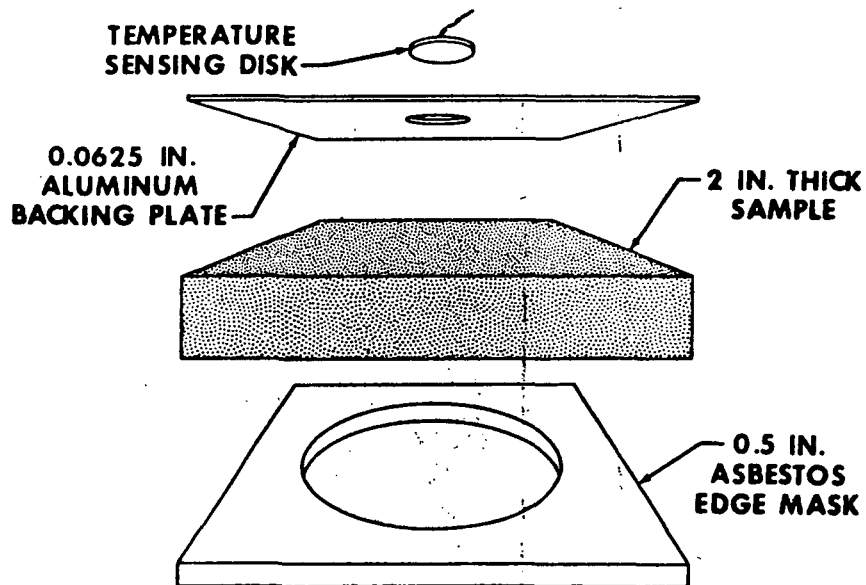
Figure 11-10.- Sample foam assembly.

HEATING RATE = 10 Btu/FT^2 SEC
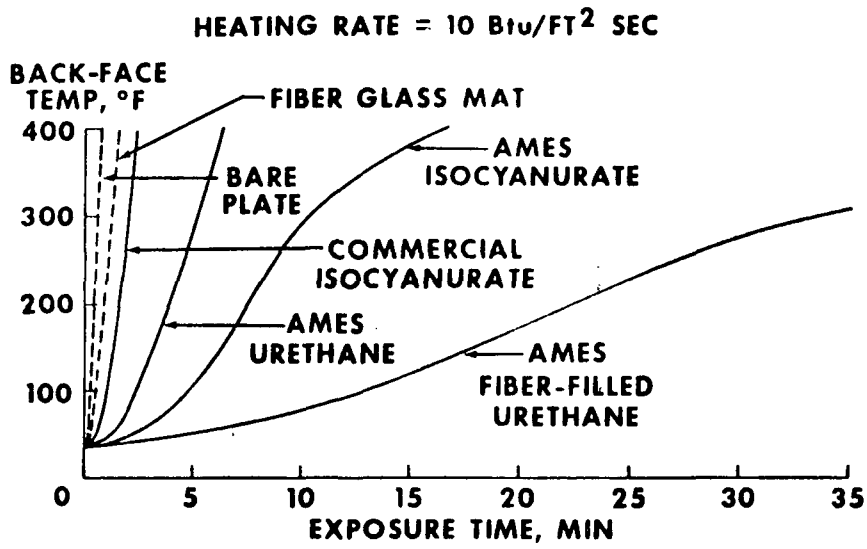
Figure 11-11.- Performance of various fire-retardant
foams in JP-4 fuel fire.

BORELINE TARGET AREA 5.5 IN. × 7 IN.
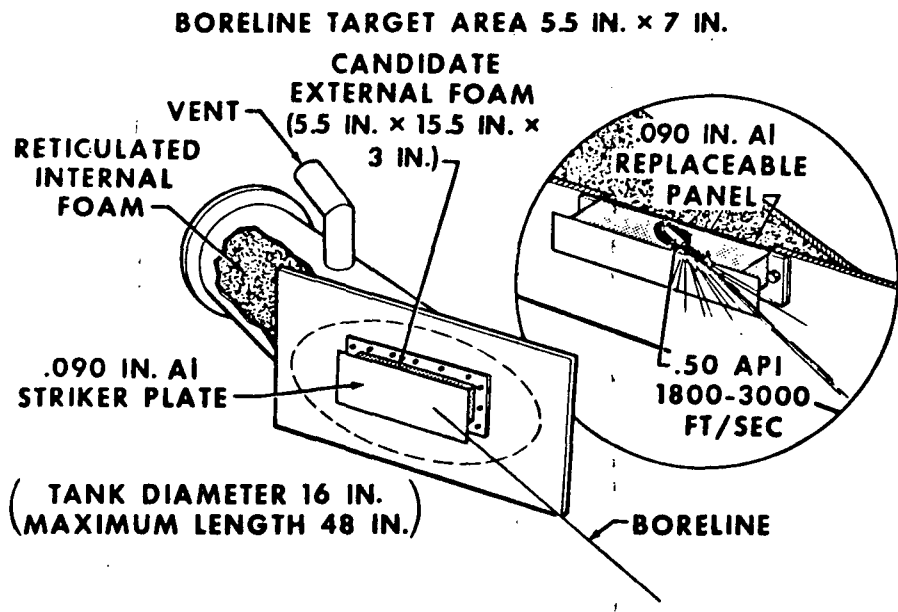
Figure 11-12.- Wright-Patterson Air Force Base test
cell-17-gallon capacity tank. .

ASBESTOS
WRAPPED
LEAD

FUEL
SUPPLY

GRID SUPPORT

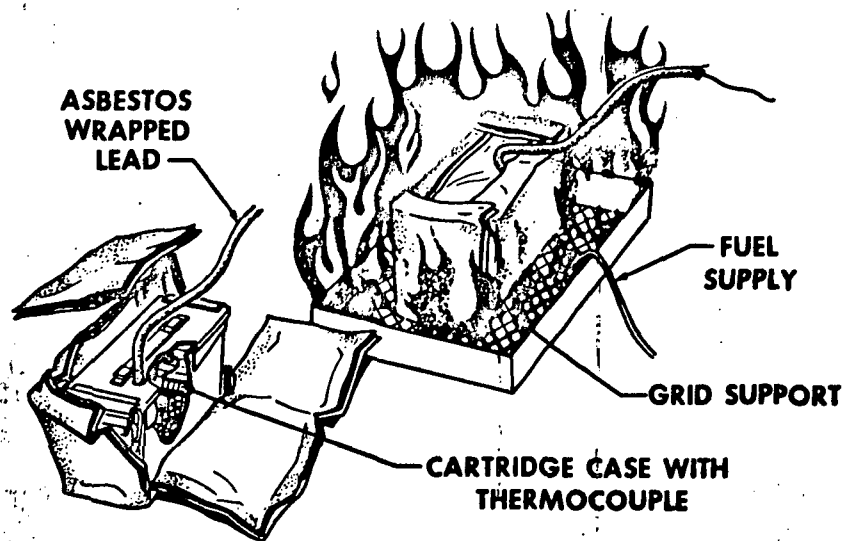CARTRIDGE CASE WITH
THERMOCOUPLE

Figure 11-13.- Test of foam blanket to protect
ammunition box.

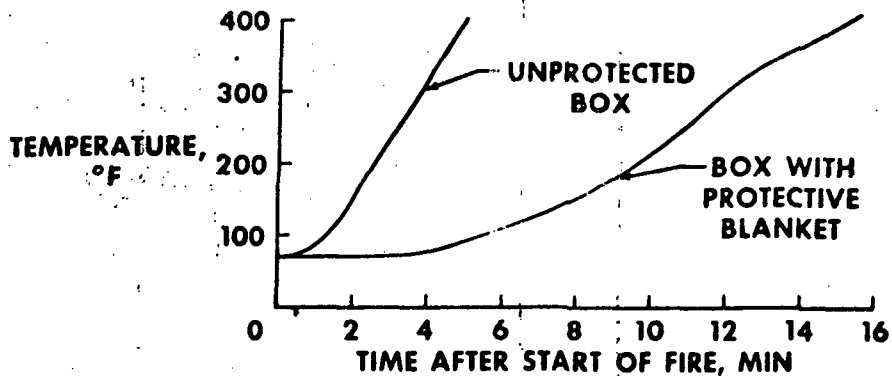
Figure 11-14.- Time-temperature history of 50-caliber
cartridge in ammunition box, JP-fuel fire.

INTUMESCENCE: AN IN SITU APPROACH TO

THERMAL PROTECTION

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NASA Ames Research Center
Presented by Dr. John A. Parker at the WESRAC-Fireproofing and Safety
Symposium, May 27, 1971, Los Angeles, California
ABSTRACT

The phenomenon of intumescence, the swelling of a substance upon
the application of heat, has been used for many years in the form of
surface coatings as a means of protecting fire-sensitive building mate-
rials. With regard to experience gained at the NASA Ames Research
Center in the areas of polymer chemistry and ablation technology for
thermal protection, intumescent systems that may serve to protect a
variety of heat-sensitive components, such as fuels, explosives, struc-
tural materials, and even man, have been reexamined. In this paper,
the evolution of intumescent coatings from the older carbohydrate-
phosphoric acid systems, through the nitroaniline bisulfate salts orig-
inally used by NASA, to the newer nitroaniline-sulfonic acids,
quinonedioxime-acid mixtures, and nitroanilinosulfones, is described.
In the case of the nitroaniline derivatives, the intumescence is modeled
as a thermal self-polymerization of the aromatic compounds passing through
plastic states, being expanded by evolving gaseous products to form
finely textured, low-density foams. These foams have low thermal con-
ductivity, high emissivity, and good resistance to ignition. The gases
that are evolved during the polymerization reaction and that are injected
into the fire zone further serve as flame quenchers. The resulting poly-
meric foams are polyheterocyclic structures similar to polyquinoxalines
or polyphenoxazines. The development of several useful coating systems
to effect fire protection in a variety of applications is discussed.
Potential applications ranging from the prevention of weapons cookoff
to the improvement in the firesafety of building materials are
illustrated in simulation tests.

INTRODUCTION

As a result of the disastrous fires aboard the Apollo spacecraft
and on the aircraft carrier U.S.S. Forrestal in 1967, the attention
of the Thermal Protection Group at the NASA Ames Research Center (ARC),

whose previous task was the development of heat-shield materials and thermal-protection coatings for spacecraft, was directed to the study of protecting heat- and fire-sensitive materials in general.

One immediate goal was the development of a means of thermal protection for stored bombs to prevent detonation when the bombs are subjected to the heat of burning fuels. The bombs must be protected for a time that is sufficient either to deploy firefighting equipment or to jettison the bombs. To accomplish this short-time thermal protection, it was desired to coat the bombs with a material that would swell, upon heating, to form a thermally resistant insulating layer. This process or phenomenon of swelling with heat is called "intumescence" (ref. 12-1).

Many people are familiar with a form of intumescence in the novelty item known as Pharaoh's Serpents. Another example of this phenomenon is the classroom demonstration that is used to introduce the subject of carbohydrate chemistry to college freshmen. In this demonstration, the dehydrating action of concentrated sulfuric acid on sugar produces a voluminous amount of black, low-density, carbonaceous solid.

The use of the intumescent process in the form of coatings to provide thermal protection for flammable substrates is not new. As an example, such coatings have been applied to cellulosic ceiling tiles for nearly 20 years. Early versions of these coatings made use of a reaction similar to the sugar and acid mixture mentioned previously in that the coatings consisted of a mixture of a carbohydrate, such as starch, as a char-forming material and a dehydrating catalyst, such as ammonium bisulfate or ammonium phosphate, compounded with a binder. Upon heating, these materials initially released ammonia gas, and the resulting sulfuric or phosphoric acid subsequently acted on the carbohydrate to yield the low-density, carbonaceous char, formed by the action of the liberated ammonia and steam (ref. 12-2). Continuing efforts by chemical and coating manufacturers to improve the intumescent coatings, both in the use as coatings and as thermal protectors, have led to the use of various other carbonific substances that usually are drawn from the class of polyols, such as pentaerythritol and dipentaerythritol. Other gas-producing materials and catalysts, such as ammonium polyphosphate, melamine phosphate, phosphoramide, and dicyandiamide, also have been used in improved versions (refs. 12-1 to 12-3). The main drawback to the use of these previously developed coatings has been the lack of long-time stability to outdoor weathering. This deficiency has limited the use of those materials to interior or protected environments. What has been needed is a coating that is able to withstand continuous outdoor exposure — conditions of high humidity, rain, wide fluctuation in ambient temperature, and, for bomb application, exposure to salt spray.

With the advent of new high-temperature and oxidation-resistant polymers, such as polybenzimidazoles, polythiazoles, polyphenoxazines,

and polyquinoxalines (refs. 12-4 to 12-7), the possibility was suggested that new kinds of char-forming materials might be developed to secure improved intumescent coating systems with high-temperature resistance that also would be nonburning, nonsmoking, and nontoxic, if a method could indeed be found by which these polymers could be made thermally and in place. A general and idealized sequence of reactions required to obtain stable heterocyclic polymers (in sufficiently low density to be useful) formed by the process of intumescence is shown in figure 12-1. The approach for this research was the selection of monomers or prepolymers that are stable to at least 300° to 350° F and that thermally react at temperatures greater than 390° F to give the thermally and oxidatively stable, aromatic, heterocyclic polymers. During the process, the evolution of some and the partial retention of a fraction of the gases that are byproducts of the condensation polymerization should form a low-density foam in situ. As indicated in figure 12-1, the polymerization reaction must proceed through a molten phase to secure the desired degree of plasticity during the expansion. To obtain efficient thermal protection, the polymerization and expansion reaction should occur preferably in the direction of the applied heating. Another important requirement of this polymerization process is that a sufficiently high degree of polymerization be obtained by the time the expansion is completed to obtain a mechanically coherent foam structure that will not collapse.

To secure a low thermal conductivity, the foam obtained by this process should be predominantly closed cell and of low density. The possibility should exist to select monomers or prepolymers that polymerize to give off gaseous byproducts that, in addition to effecting the foaming of the polymer, can diffuse into the flame boundary to block convective heat transfer (ref. 12-1) and interact with and suppress free-radical chain carriers that are characteristic of the flame-propagation process.

APPLICATION OF THE REACTIONS OF SUBSTITUTED
NITRO-AROMATIC AMINES AS INTUMESCENT MATERIALS

The formation of voluminous, black, spongy foam from the action of heat on a mixture of sulfuric acid and p-nitroacetanilide had been described by Alyea (ref. 12-8). In the study made at ARC, a number of variously substituted nitro-aromatic amines were examined for intumescent properties (fig. 12-2).

As indicated in figure 12-2, the expanded black polymer was formed from both o-nitroanilines and p-nitroanilines, as well as from substituted derivatives. These materials gave excellent expansion of 70 to 240 times the original volume. The process was found to occur within

a temperature range of 390° to 500° F. Acetylation of the amino group
did not seem to affect the intumescent process. It was observed quali-
tatively that the resultant dark polymeric foam was extremely resistive
to the erosive action of an intense hydrocarbon gas flame. Originally,
the belief was held that this intumescent reaction of nitroanilines
could be caused only with concentrated sulfuric acid; however, subse-
quently, it was found that the use of concentrated phosphoric and poly-
phosphoric acids also promoted the reaction.

The observation of the effect of heat and sulfuric acid on
p-nitroaniline led quickly to the development of the associated bisul-
fate salt as a dry compound, which is useful as an intumescent agent.
This compound was prepared easily from inexpensive, readily available
materials. The preparation and properties of this material are shown in
figure 12-3 (refs. 12-9 and 12-10). Upon heating the p-nitroaniline
bisulfate to temperatures greater than 430° F, a yield of black foam of
approximately 50 to 54 percent by weight is obtained that is stable to
temperatures greater than 1020° F.

To investigate in detail the reactions that occur during intumes-
cence, three analytical techniques were used. Thermogravimetric analysis
(TGA) of the weight loss of a sample of p-nitroaniline bisulfate was
made, elemental analysis of the thermally reacted material was obtained,
and, in a separate experiment, the kinds of gases produced were deter-
mined by gas chromatography.

An 8-milligram sample of the p-nitroaniline bisulfate described
previously was heated in dried, deoxidized nitrogen at a rate of 5.4° F
per minute. The weight loss was determined by means of a Cahn recording
electrobalance and plotted as a function of sample temperature
(fig. 12-4). The empirical formula for the initial salt can be written
as shown at the right of figure 12-4. The theoretical weights that cor-
respond to the thermolytic process also are shown. Three distinct and
sequential reactions can be seen to occur in going from room temperature
to 430° F, at which point, a sudden intumescence is initiated. The
weight loss associated with each of these three distinct processes is
equivalent, on a mole basis, to the loss of one molecule of water. This
loss produces a change in the composition of the residue material as
indicated in the empirical formulas at the right of the thermogram. The
water produced during this induction phase (that is, before intumescence)
does not contribute to the foaming process but rather is injected direct-
ly into the adjacent gas boundary. As indicated in the thermogram, intu-
mescence occurs at temperatures greater than 450° F with elimination of
sulfur dioxide, and more water is eliminated at temperatures greater than
600° F.

Chromatographic analysis of the gases eliminated during the intumescence confirmed that sulfur dioxide and water, both good flame quenchers, were produced. Elemental analysis obtained on the black intumesced foam that was formed at 482° F was obtained as shown in figure 12-5. The analysis indicates that nearly all the sulfur is lost and all the nitrogen is retained.

Coatings were prepared using the p-nitroaniline bisulfate compound as the intumescing agent. The coatings performed quite well in the proper environment, as will be described subsequently. However, because of the nature of the material (a salt of a weak base and a strong acid), it was easily affected by the presence of moisture, giving an extremely acidic milieu that both affected the vehicle in which it was combined and corroded metallic substrates upon humid exposure. To circumvent these deficiencies, other intumescing agents were desired that were neither easily hydrolyzed nor acidic.

One of the primary reactions between sulfuric acid and nitroaniline is sulfonation of the ring. By keeping mixtures of these ingredients at temperatures below that of intumescence, fair yields of p-nitroaniline-o-sulfonic acid were prepared, isolated as an almost white powder. This compound was found to intumesce quite easily at 450° F and to give a char yield of 50 percent. The product of intumescence resembles and is similar in analysis to the materials obtained from p-nitroaniline bisulfate. The ring sulfonation in this second compound overcame the problem of hydrolytic stability encountered with p-nitroaniline bisulfate, but the problem of acidity remained. It was found that the ammonium salt of this sulfonic acid also would intumesce, but at a somewhat higher temperature (572° F). This material is prepared easily from the commercially available sodium salt by reaction with ammonium chloride. The TGA of this material is shown in figure 12-6.

The intumescent reaction of the p-nitroaniline-o-sulfonic acid, or the associated ammonium salt, is not discussed in this report. However, the sulfonation of the aromatic ring is probably not a necessary step in the intumescent reaction, and the ring-substituted sulfonic acid actually acts as an in situ source of sulfuric acid when this compound is heated. Thus, the reaction is similar to that of p-nitroaniline and sulfuric acid.

Continuing research into the reactions of nitrogenous aromatic compounds has produced two other intumescent systems of interest. These systems are bis-(4-nitroanilino)-sulfone that intumesces when heated alone, and p-benzoquinone dioxine that intumesces when heated with concentrated sulfuric or phosphoric acid. In all these types of intumescent reactions, the role of the acid apparently is primarily that of dehydration.

Although it has been speculated that the polymer formed during the intumescence of p-nitroaniline bisulfate may be a laddered polyquinoxaline or polyphenoxazine (ref. 12-11), no direct proof has yet been obtained. The materials obtained in the thermal reaction of all these classes of compounds are insoluble in all solvents tried, including concentrated sulfuric acid. Spectroscopic examinations have been inconclusive, and the scissioning reactions tried have, thus far, not yielded fragments that would aid in structure elucidation. The primary investigative means used has been the elemental analysis of the black materials obtained and has led to the speculation that structures of the products of the thermal reactions are combinations of recurring units shown in figure 12-7, all derivable from the starting materials by addition, dehydration, hydrolysis, rearrangement, and ring closure to varying degrees depending on the temperature to which the material is exposed. These structures are similar to those proposed by Szita and Marvel (ref. 12-12) and Stille and Freeburger (ref. 12-13) for polymers derived from more complex starting materials in nonintumescing systems.

COATINGS

Two intumescing agents described in the previous section, p-nitroaniline bisulfate and the ammonium salt of p-nitroaniline-o-sulfonic acid, were formulated into practical, useful, coating systems. The key to the successful formulation of these coatings has been the selection of a binder system that does not interfere with the intumescent process, is compatible with the intumescing agent, and will not contribute significantly to the flammability of the system. The vehicle should be either thermoplastic or easily degraded thermally in the same temperature range in which intumescence takes place.

The use of the p-nitroaniline bisulfate salt also required that the vehicles selected as binders be relatively stable to strong acid. Water-based vehicles that are commonly used in paints were also eliminated from consideration with the bisulfate salt because of their hydrolytic instability. Two vehicles were selected for use with the p-nitroaniline bisulfate: nitrocellulose and a phenolic resin modified acrylonitrile-butadiene polymer. The formulations are given in tables 12-I and 12-II. The formulation using the ammonium salt of p-nitroaniline-o-sulfonic acid is shown as 45B3. This material did not have the rather strict limitations of vehicle selection as with the first salt, because it is neither acidic nor hydrolytically unstable. These coatings were prepared by common paint-making techniques and were suitable for conventional brush or spray applications. The air-dried coatings had good initial properties.

TESTS AND POSSIBLE APPLICATIONS OF COATINGS

Measurements in a typical JP-4 fire with free convection showed that heating rates applied to surfaces immersed in such fires are approximately 30 000 Btu/hr/ft^2, approximately 90 percent in the form of radiation. This fact made it possible to run screening tests on candidate intumescent coatings in the beam of a solar simulator (fig. 12-8) that is capable of the delivery of 30 000 Btu/hr/ft^2 to a 2-inch-diameter specimen at a distance of approximately 4 inches from the focus.

This arrangement was used to screen various thicknesses of the intumescent coatings described previously. The spectral distribution of the solar simulator beam, which has its peak in the visible portion of the spectrum, did not match that of the JP-4 fire, which peaks at approximately 2.5 microns; however, the thermal-protection process appears to be independent of this difference in spectral distribution.

Intumescent coating formulation 341 was applied in thicknesses from approximately 0.007 inch to approximately 0.065 inch on a 0.060-inch-thick cold-rolled steel substrate. The test specimens, which were 1 inch in diameter, were surrounded by thermal insulation to eliminate edge effects, and a thermocouple was mounted on the backface to provide the time-temperature history.

The test of an intumescent coating specimen in the solar simulator beam is more severe than a JP-4 fire for two reasons. Although the average heating rate at the surface is 30 000 Btu/hr/ft^2, the intumescence causes the surface to grow outward toward the focus where the heating rate is higher. Furthermore, there is a radial energy gradient in the beam, and the irradiance is slightly higher on axis than the average value over the area of the test specimen.

A history of the substrate backface temperature during the test in the solar simulator is shown in figure 12-9. The bare metal without the coating reached 400° F in approximately 20 seconds. On a similar metal substrate with the intumescent coating, the intumescence began within approximately 10 seconds and was nearly complete within 20 seconds.

The thermal insulation provided by the intumescence caused a much slower temperature rise of the metal substrate. The increasing slope that occurred later shows the effect of the intumescence growing closer to the focus of the solar simulator, where it experiences a much higher heating rate.

The results of numerous tests in the solar simulator beam and in JP-4 fires are given in figure 12-10. These results show how the time required for the substrate to reach a given temperature varies with intumescent coating thickness. Temperatures of 300° and 400° F were chosen as limits, for presenting these data. The relationship is linear, as might be predicted, because the thickness of the intumescence after heating is directly proportional to the thickness of the coating before heating. As can be seen in figure 12-10, the times to reach 300° and 400° F are shorter for the solar simulator tests than for the fuel fires, demonstrating the greater severity of the solar simulator tests.

The fact that the coating formulation 341, using nitrocellulose as the binder, intumesces to give a thick, stable, closed-cell polymer that is highly resistant to heat leads immediately to the possibility of its application in such places as an airplane where fuel lines or hydraulic lines exist in fairly restricted volumes. A fire in such a location would be extinguished if the intumescence filled the available volume. To test this, a simulated section of fuselage was built, and two 2-inch-diameter tubes (simulating fuel lines) were installed through holes in the section. This test setup (fig. 12-11) was 12 inches wide and 5-1/2 inches deep. The ends and one side of this box were sprayed on the inside with the intumescent coating to a thickness of 0.040 inch. A fuel pan containing 200 cubic centimeters of JP-4 was placed under the box, and the fuel was ignited. The fire caused the intumescent coating on the surface to fill the available volume, thus extinguishing the fire before 30 cubic centimeters of the fuel had been consumed.

Because of the nature of the p-nitroaniline bisulfate salt and its high loading in formulations 341 and 410-1A, these coatings did not retain good properties upon long exposure to humid environments. The acidity of this salt caused corrosion of metallic substrates and deterioration of the vehicles. However, in certain controlled or protected environments, or if suitably protected by a top coating, the coatings have great utility as just described.

The intumescent coating, formulation 45B3, is composed of the ammonium slat of p-nitroaniline-o-sulfonic acid dispersed in a binder composed of equal parts of a polysulfide polymer and an epoxy resin. After application, the coating has a hard, glossy, abrasion-resistant surface. It has good adherence to the substrate.

The coating has been tested for its effectiveness in protecting a structure from fire. The heating of a 1/16-inch-thick steel plate with and without the protection of the coating is shown in figure 12-12. The tests were made in a specially constructed furnace that exposed the samples to a controlled JP-4 fire. With no protection, the temperature of the plate rose to 400° F in less than 1 minute. When the plate was

protected with an 80-mil-thick coating, the heating of the plate to 400° F was delayed for 5 minutes.

The effect of a high-humidity, high-temperature environment on the thermal performance of the coating has been measured. The results of this test also are shown in figure 12-12. The temperature history of a coated steel plate that had been exposed for 30 days to high humidity (90 percent) at a temperature of 100° F is compared with the temperature history of the coated plate that had been conditioned in the laboratory atmosphere (50-percent humidity, 73° F). The comparison shows that exposure to the humid environment had no significant influence on the thermal protection afforded by the coating. The small difference between the curves is within the limits of experimental reproducibility for this test.

Samples of the coating also have been exposed for a 90-day period to the natural weather conditions on the roof of the laboratory. Coating samples on 3- by 6-inch steel plates were placed at a 45° angle above the horizontal, facing south. During the period of exposure, approximately 9.7 inches of rain fell. The coating was darkened by the exposure, but its intumescence was not affected. Figure 12-13 is a photograph comparing an exposed test sample with a control sample, both of which were heated in an oven to complete intumescence following the exposure. No important difference in the intumescent characteristics of the two samples is evident. The coating thus shows good stability under humid environments for at least a 10-day period. Two environmental tests are continuing.

A slightly modified version of the 45B3 formulation was applied to a simulated bomb casing consisting of a section of 5-inch pipe with 1/4-inch wall thickness. The time for the interior wall of the pipe to attain a temperature of 400° C, the critical temperature for the explosive charge, was approximately 8 minutes. The time for an uncoated section of pipe to reach the same temperature was approximately 30 seconds. The intumesced coating appeared to have acceptable char integrity and adhesion, which were better than other coatings tried. A full-scale test using 500-pound bombs is currently in progress.

Many applications of intumescent coatings are possible; for example, on electric motor casings; in fuel and chemical plants and tank farms; and on engine canopies, ventilator grids, and building exteriors. At the present state of development, it is not recommended that these coatings be used in populated or unventilated areas because of the quantities of sulfur dioxide released.

Preliminary specifications for the various coating systems have been established and are available from NASA headquarters.

A research contract has been let to study further intumescent coating systems, especially the relationship of the properties of several classes of polymers as vehicles, in combination with certain selected NASA-developed intumescing agents. The influence of polymer type, cross-link index, glass transition temperatures, and other properties on the intumescent process is expected to result from such a study.

Other ongoing research within NASA will study the chemistry of intumescence and the synthesis of other intumescing agents, with the objectives of developing materials more suitable for use in viable environments and developing a range of activation temperatures. Another possible result is the use of the intumescent materials as an inexpensive, refurbishable, heat-shield material.

ACKNOWLEDGMENT

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TABLE 12-I.- VOID-FILLING THERMAL PROTECTION COATING

[Formulation 341]

Material	Weight
Part A	
Nitrocellulose, ethanol-wet (12% N)	8.0
Methyl ethyl ketone	28.6
Part B	
p-nitroaniline bisulfate	43.7
Toluene	19.7
Butyl acetate	19.7

TABLE 12-II.- THERMAL PROTECTION COATING

(a) Formulation 410-1A

Material	Weight
Phenolic modified acrylonitrile-butadiene rubber solution	29.4
p-nitroaniline bisulfate	44.0
Cyclohexanone	14.5
Methyl ethyl ketone	12.15

(b) Formulation 45B3

Material	Weight
Part A	
Polysulfide polymer	14.1
Ammonium p-nitroaniline-o-sulfonate	57.0
Methyl ethyl ketone	28.9
Part B	
Epoxy resin, liquid	14.1
Toluene	14.7
Part C	
Tri(dimethylaminomethyl)phenol	2.8
Toluene	2.8

```
                    THERMAL
                    POLYMER-
    STABLE SOLID    IZATION      HEAT STABLE  +   EXPANDING  →
    MONOMER OR      ─────────→   POLYMER          GASES
    PREPOLYMER      > 392° F              (MELT PHASE)

    FOAMING AND
    EXPANSION OF
    POLYMER IN      ─────────→   FOAM      +      GAS
    DIRECTION OF
    APPLIED HEAT         ⎡LOW DENSITY  ⎤  ⎡EXCESS GAS-   ⎤
                        ⎢CLOSED CELL  ⎥  ⎢  EOUS SPECIES⎥
                        ⎢COHERENT     ⎥  ⎢  INJECTED INTO⎥
                        ⎢THERMALLY    ⎥  ⎢  VAPOR PHASE ⎥
                        ⎢  AND OXIDA- ⎥  ⎢CONVECTIVE    ⎥
                        ⎢  TIVELY STABLE⎥ ⎢  PROTECTION  ⎥
                                         ⎢QUENCHING     ⎥
                                         ⎢FLAME SUP-    ⎥
                                         ⎣  PRESSION    ⎦
```
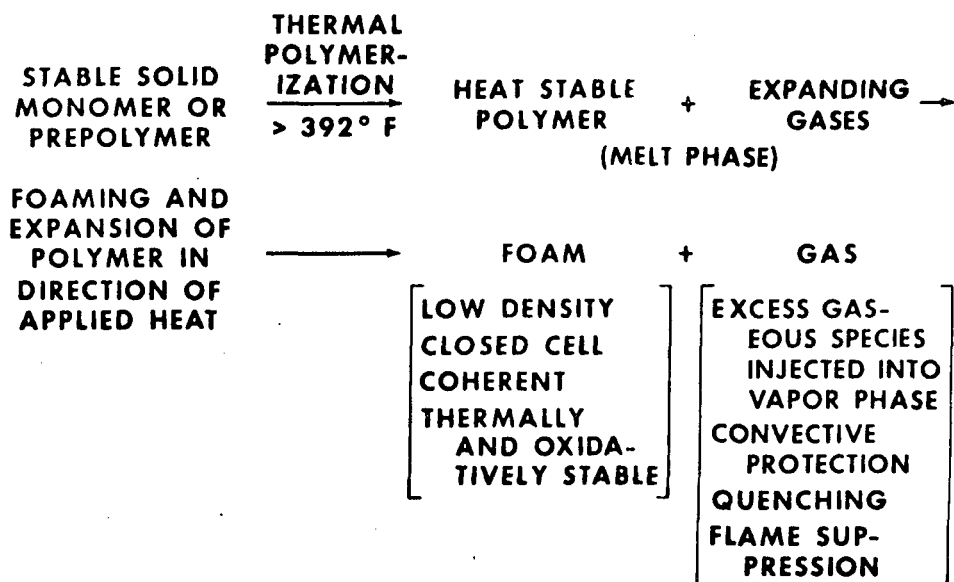
Figure 12-1.- General sequence of reactions
producing intumescence.

```
    THERMAL
    POLYMERIZATION
    PROCESS
    OCCURS WITH:                Δ
    o -NITROANILINE          > 392° F
    p-NITROANILINE          ───────────────→   SPONGY BLACK
                            CONCENTRATED       POLYMERIC FOAM
    p-NITROACETANILIDE      SULFURIC OR
    5-NITROISATOIC          POLYPHOSPHORIC         +
      ANHYDRIDE ETC             ACID              GAS
```
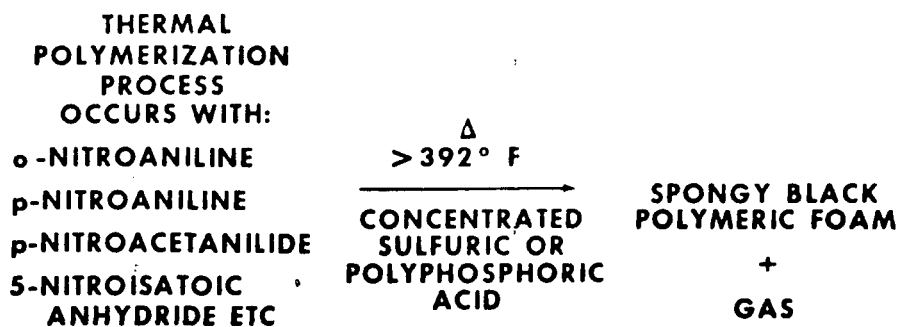
Figure 12-2.- Intumescent reactions of substituted
nitro-aromatic amines.

$$NH_2$$
$$1.0 \ \bigodot + 1.0 \ H_2SO_4 \longrightarrow$$
$$(CONC)$$
$$NO_2$$

$$\overset{+}{NH_3} \ (HSO_4)^-$$
$$\bigodot$$
$$NO_2$$

p-NITROANILINE   p-NITROANILINE BISULFATE

293° F_____MELT POINT_____392° F (DECOMP)
138_____MOL WT_____236 (CALCULATED)
                               236 (MEASURED)
YELLOW SOLID__ APPEARANCE_____LT YELLOW SOLID

$$\left(\begin{array}{c} \text{SOLUBLE IN ALCOHOLS,} \\ \text{KETONES INSOLUBLE IN} \\ \text{BENZENE, TOLUENE, ETHER} \end{array} \right)$$
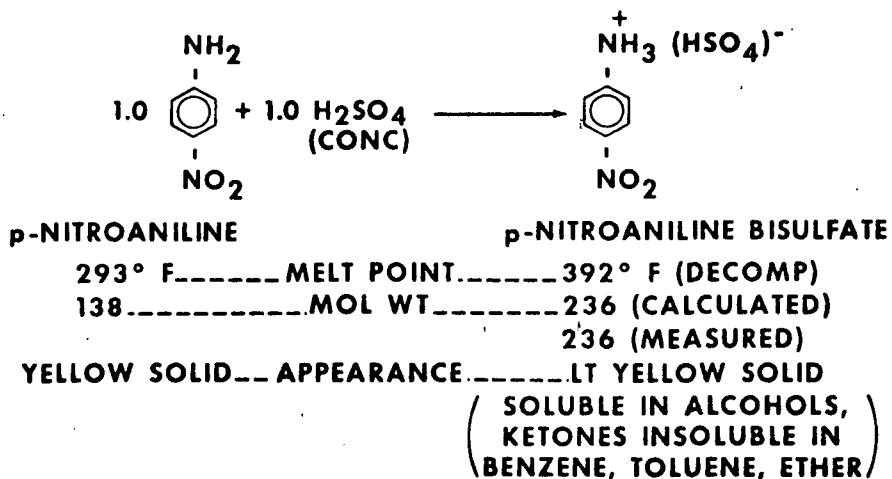
Figure 12-3.- Synthesis and characterization of intumescent intermediate p-nitroaniline bisulfate.

WEIGHT FRACTION REMAINING	THEORETICAL WEIGHT	EMPIRICAL FORMULA	LOSS
1.0	1.00	$C_6(H_2O)_4(SO_2)N_2$	H_2O
	.92	$C_6(H_2O)_3(SO_2)N_2$	H_2O
	.85	$C_6(H_2O)_2(SO_2)N_2$	H_2O
	.78	$C_6(H_2O)(SO_2)N_2$	
.5	.50	$C_6(H_2O)N_2$	SO_2
	.424	C_6N_2	H_2O

REGION OF INTUMESCENCE

0   400   800   1200
TEMPERATURE, °F

$(C_6H_3N_{1.8}OS_{.14})$
EMPIRICAL ELEMENTAL ANALYSIS OF FOAM AT 52% CONVERSION
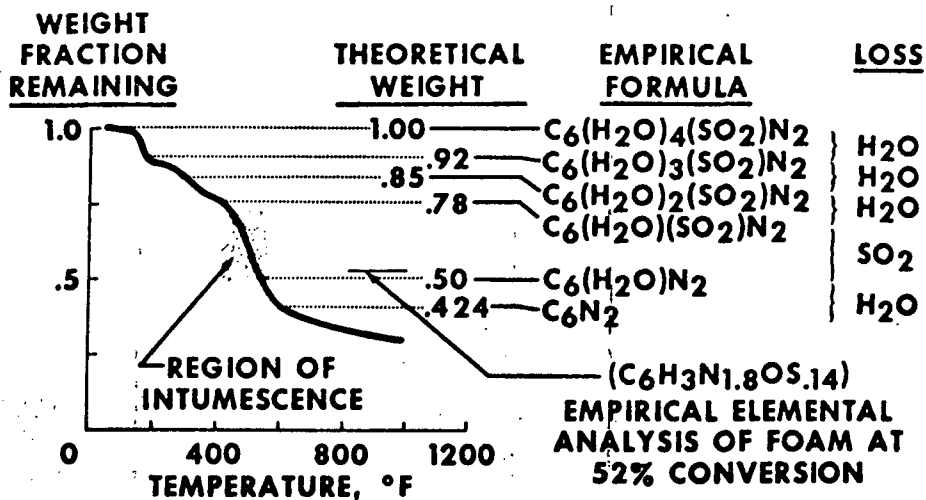
Figure 12-4.- Typical TGA of p-nitroaniline bisulfate (5.4° F/min in N_2).

C	H	N	S	O
59.65	2.51	20.77	3.64	13.43%

WHICH CALCULATES TO GIVE AN EMPIRICAL FORMULA:

$$C_6 H_3 N_{1.8} O_{1.0} S_{.14}$$

Figure 12-5.- Elemental analysis of black intumesced polymeric foam formed from p-nitroaniline bisulfate at 482° F.
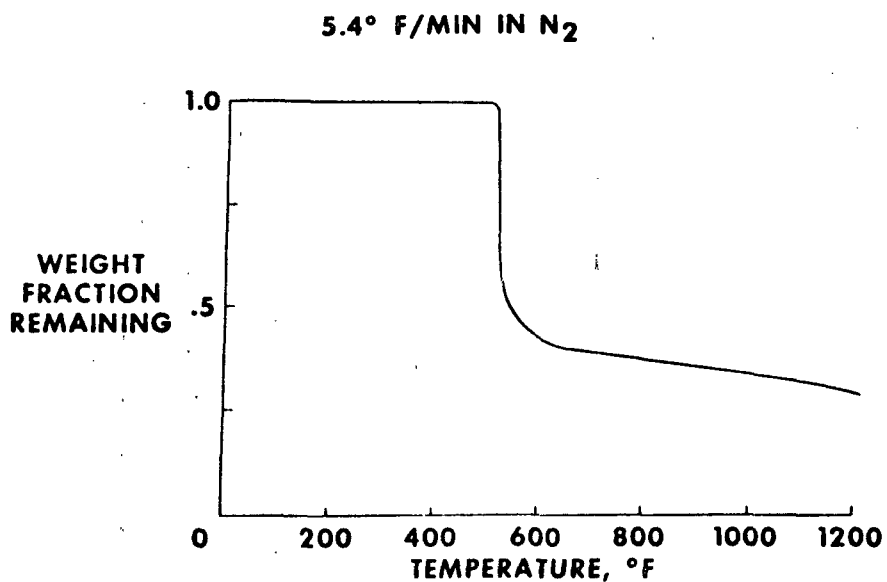
5.4° F/MIN IN N$_2$

Figure 12-6.- The TGA of p-nitroaniline-o-sulfonic acid, ammonium salt (5.4° F/min in N$_2$).
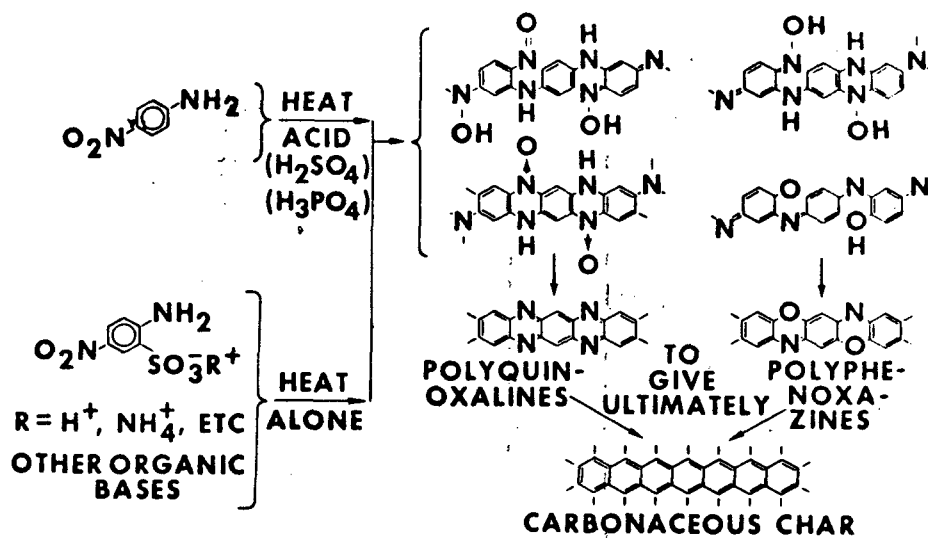
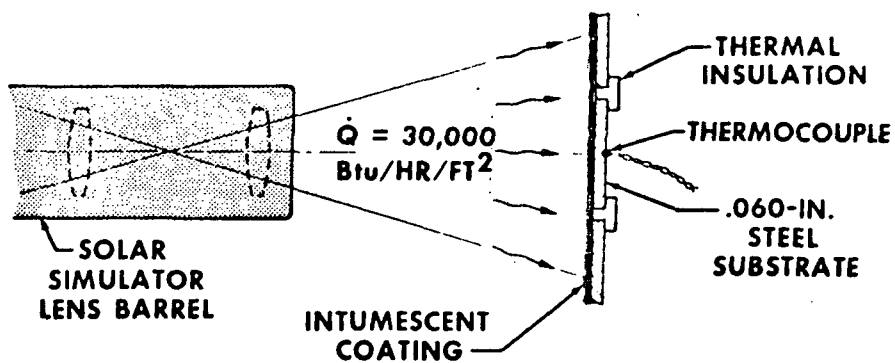Figure 12-7.- Proposed generalized mechanism for polymerization.

Figure 12-8.- Arrangement for tests of intumescent coatings in solar simulator beam.

FORMULATION NUMBER 341
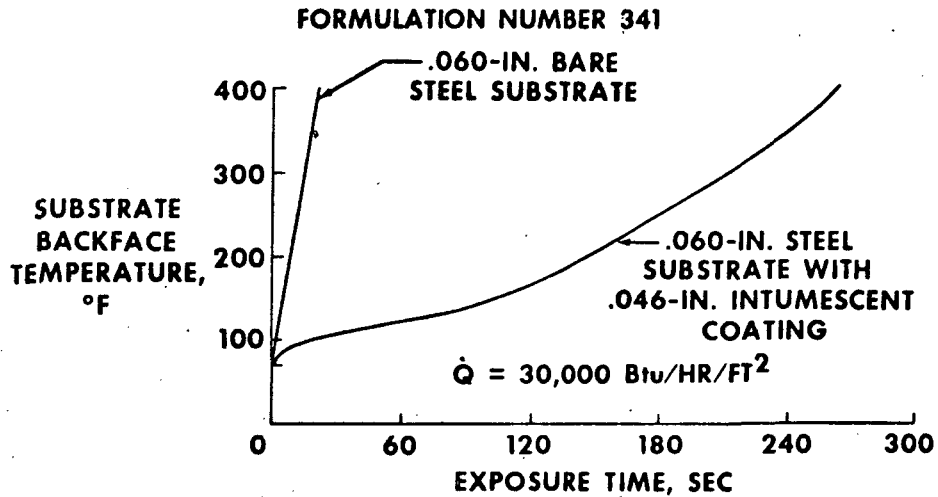
Figure 12-9.- Comparison of bare steel and intumescent coated steel in solar simulator radiation tests (formulation 341).
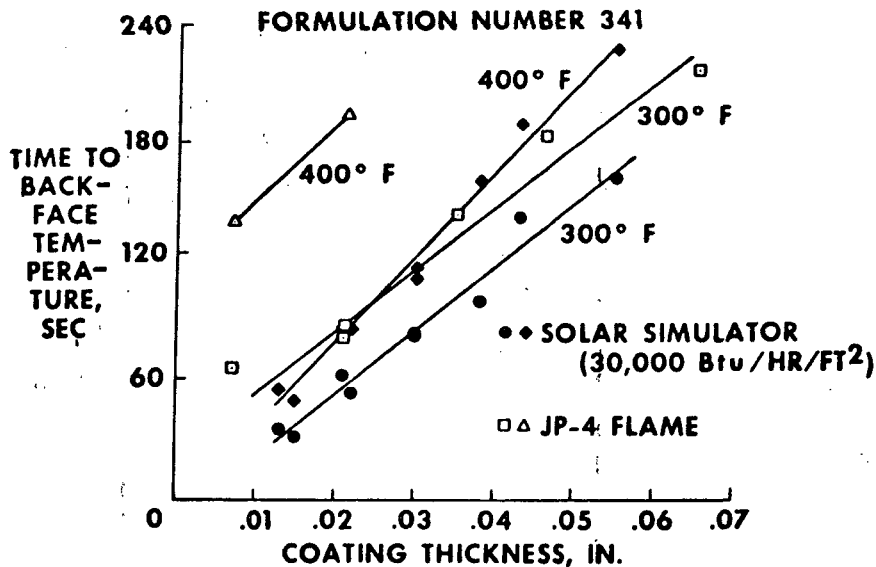

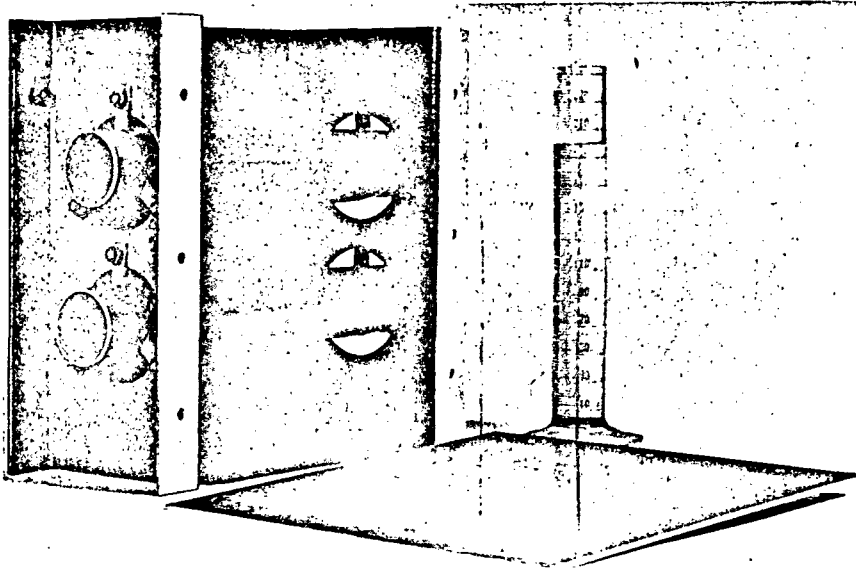Figure 12-10.- Effect of intumescent coating thickness on backface temperature rise (formulation 341).

Figure 12-11.- Test setup of simulated fuselage
section coated with void-filling thermal
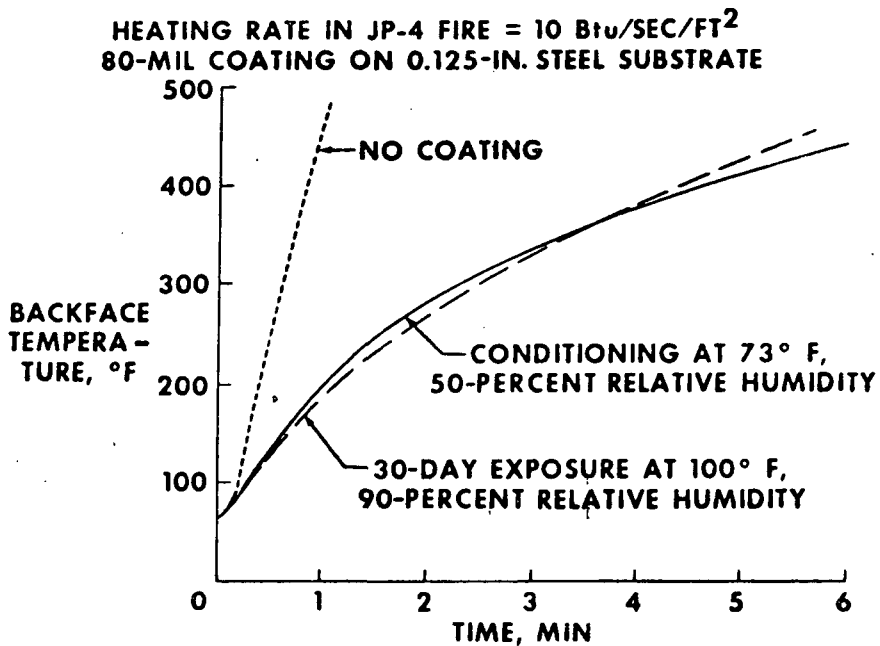protection coating (formulation 341).

HEATING RATE IN JP-4 FIRE = 10 Btu/SEC/FT^2
80-MIL COATING ON 0.125-IN. STEEL SUBSTRATE

NO COATING

CONDITIONING AT 73° F,
50-PERCENT RELATIVE HUMIDITY

30-DAY EXPOSURE AT 100° F,
90-PERCENT RELATIVE HUMIDITY

BACKFACE TEMPERATURE, °F

TIME, MIN

Figure 12-12.- Fire-protective effectiveness of 45B3
intumescent coating.

STANDARD
LABORATORY
ATMOSPHERE

SOUTHERN
EXPOSURE
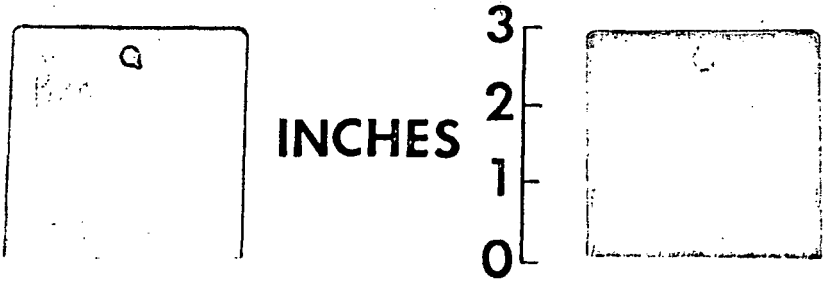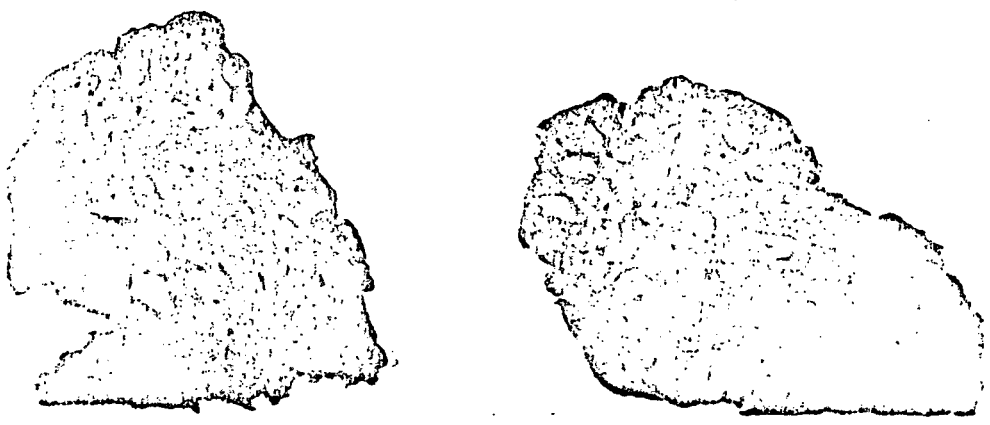(~10 IN. RAINFALL)

INCHES

3
2
1
0

Figure 12-13.- Intumescence of 45B3 coating after 90-day
exposure to outdoor environment (coating thickness
40 miles.)