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THE USE OF A SALT OF p-NITROANILINE AS A COMPONENT FOR INTUMESCENT COATINGS

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ABSTRACT

Airframe structures and avionic devices can be protected against the action of JP-4 fuel fires by the application of salts derived from certain nitro substituted aromatic amines and sulfuric acid, which intumesce when heated to temperatures in the range of 350° to 500° F. Durable coatings for various application methods can be formulated from these salts and acid-resistant polymeric binders. These coatings can provide short-term ablative protection in addition to a fuel-fire quenching action. For example, it has been found that the continuous action of a convectively driven JP-4 fuel fire impinging on the surface of a 1/16-inch thickness of cold-rolled steel plate produces a backface temperature rise to 400° F in 20-30 seconds. Application of 50 mils of an intumescent coating derived from the acid sulfate salt of

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p-nitroaniline in a nitrocellulose binder can effect thermal protection by increasing the time required for the steel backface to reach 400° F to as much as five minutes.

The synthesis and thermochemistry of these intumescent intermediates are described. Chemical evidence is presented which suggests that the acid sulfate salts of certain nitro substituted aromatic amines polymerize thermally to yield thermally and oxidatively resistant heterocyclic polymers with quinoxaline-like structures. Intumescence of coatings formulated from the acid sulfate salt of p-nitroaniline produces between a forty- and two-hundred-fold expansion with the evolution of water and sulfur dioxide as flame quenching species. The black essentially closed cell polymeric foam formed by this process has a density in the range of between 0.1 to 0.3 lb/ft^3. These properties result in a very low thermal conductivity.

Methods for formulating, applying and evaluating practical fire-resistant coatings derived from the amine salt are discussed. The coating properties such as abrasion resistance, adhesion and durability are described.

Test results obtained by immersing test panels protected with this coating in JP-4 fuel fires are compared with those obtained by laboratory simulation of heating environment with radiant energy sources. The efficiency of this coating derived from p-nitroaniline in terms of coating thickness is defined.

INTRODUCTION

To effect short-time protection of thermally sensitive substrates from the action of heat or impinging flames, coatings can be applied which will swell to form an insulating layer. This process of swelling with heat is commonly termed intumescence (ref. 2).

Previously, various approaches to the formulation of intumescent coatings have been developed from basically gas- and char-forming organic substances. For example, the dehydration and expansion of polysaccharides is well known (ref. 1, 2, 5); but any char-forming polymer which passes through a melt phase, with evolution of a gas, expanding to form a low-density char matrix, such as partially reacted epoxy, urethane, phenolic, or urea resins, is potentially a candidate for the preparation of an intumescent coating.

With the advent of the new high-temperature and oxidation-resistant aromatic heterocyclic polymers, such as polybenzimidazoles, polythiazoles, and polyquinoxalines (ref. 3, 4), an alternative to the earlier char-forming materials may be considered to secure improved intumescent coating systems with improved thermal performance.

The general and idealized sequence of reactions required to obtain stable heterocyclic polymers in a low-density foamed form by intumescence is shown in figure 1.

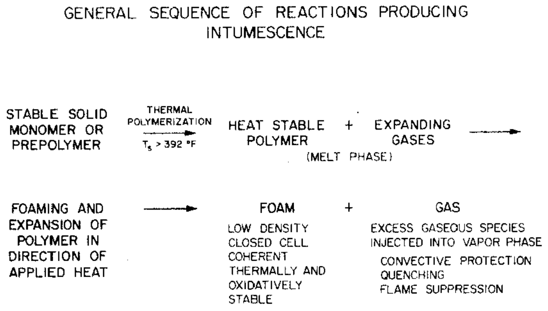


Figure 1.

A monomer or prepolymer which is stable to at least 300°-350° F in solid form should be selected which thermally polymerizes at temperatures greater than 390° F to give a thermally and oxidatively stable aromatic heterocyclic polymer. During the process, the evolution and retention of a fraction of the gases which are by-products of the condensation polymerization should form a low density foam in situ. As indicated in the figure, the reaction must proceed through a molten phase to secure the desired degree of 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 coherent foam structure which will not collapse.

To secure low thermal conductivity, the resultant foam should be predominantly closed cell and of low density. The thermally and oxidatively stable heterocyclic polymer matrix offers an advantage over a carbonaceous matrix obtained from the usual intumescent systems, because of the inherently low conductivity of the polymer matrix. It should be possible to select monomers or prepolymers which polymerize to give off gases as by-products, that in addition to affecting the foaming of the polymer, can diffuse into the flame boundary to effect blocking of convective heat transfer (ref. 2) and interact with the free-radical chain carriers characteristic of hydrocarbon fuel flame processes to quench or suppress the flame propagation processes.

APPLICATION OF THE REACTIONS OF NITROSUBSTITUTED AROMATIC AMINES AS INTUMESCENT MATERIALS

Earlier, Alyea (ref. 5) described the formation of a voluminous black, spongy foam from the action of heat on a mixture of sulfuric acid and p-nitroacetanilide. In the present study, a number of variously substituted nitro-aromatic amines were examined for intumescent properties as shown in figure 2.

spongy black polymers to understand the overall chemical reactions taking place in order to control and define the intumescence and to prepare a definite solid monomer to form the basis for the development of a reliable intumescent coating.

THERMOCHEMISTRY OF p-NITROANILINE AND ITS SULFURIC ACID DERIVATIVES

In order to evaluate the role of concentrated sulfuric acid in the thermal polymerization, samples of p-nitroaniline as a slurry in alcohol were mixed with various amounts of concentrated sulfuric acid, dried, and heated in a shallow dish on a hot plate maintained at 480° F until intumescence occurred. The amount of black polymeric foam formed was collected and the yield determined gravimetrically. The results obtained from these experiments are given in figure 3.

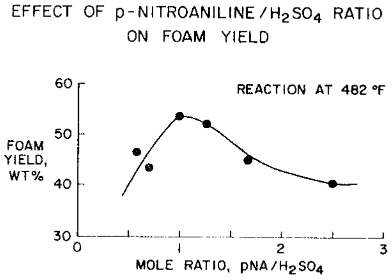
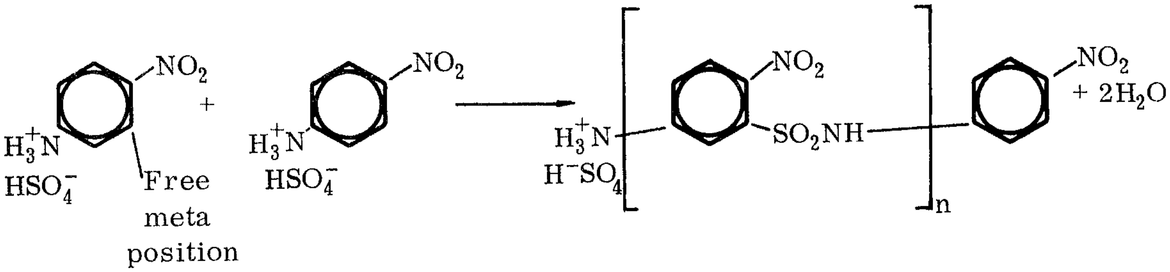


Figure 3.

elimination of three molecules of water to give an expandable thermoplastic heterocyclic prepolymer. Although the aromatic amino group is generally ortho-para-directing in substitution reactions, it is known that in a strongly acidic medium, as for instance concentrated sulfuric acid, the aromatic ammonium group is exclusively meta-directing (ref. 8). The fact that only derivatives with free meta positions have been found to undergo this intumescent process is indicated by the loss of two molecules of water.

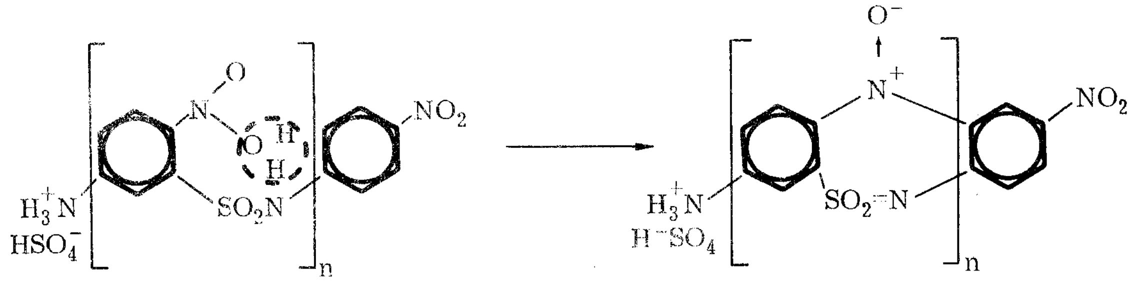


I

II

Reaction 1

The initiation of this pre-polymerization as proposed is believed to occur by an attack of the amine bisulfate (I) on the free meta position with the elimination of two molecules of water over the temperature range from 200°-350° F as shown in figure 5 with the formation of an intermediate sulfonamide (II). A third molecule of water is eliminated above 350° F to give the N-oxide (III), as follows:

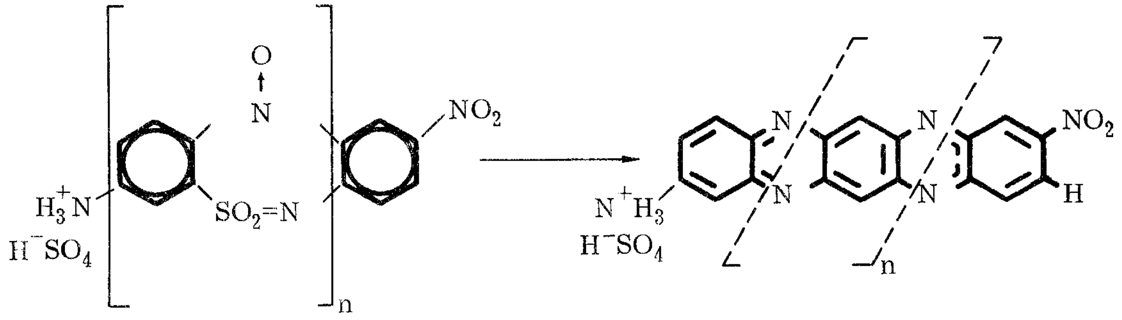


II

III

Reaction 2

As indicated in the thermogram intumescence occurs above 450° F with elimination of sulfur dioxide and water to give the poly-quinoxaline polymer (IV) which comprises the black foam.



III

IV

Reaction 3

At temperatures greater than 600° F there is the elimination of one additional molecule of water, presumably due to completion of reactions two and three accompanied by cross linking of the laddered polyquinoxaline. As shown in the thermogram, at temperatures greater than 600° F, the nitrogen is eliminated with the formation of a stable char network. The overall qualitative process is outlined in figure 6.

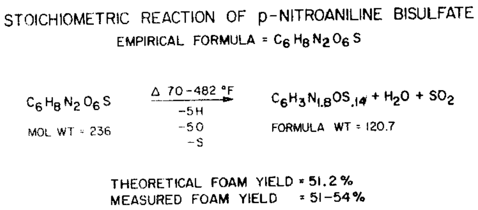


Figure 6.

In order to examine directly the kinds of gases produced by this thermal polymerization process, a gas chromatographic analysis was performed on gases formed during the intumescence of p-nitroaniline bisulfate at 592° F. The results are shown in figure 7.

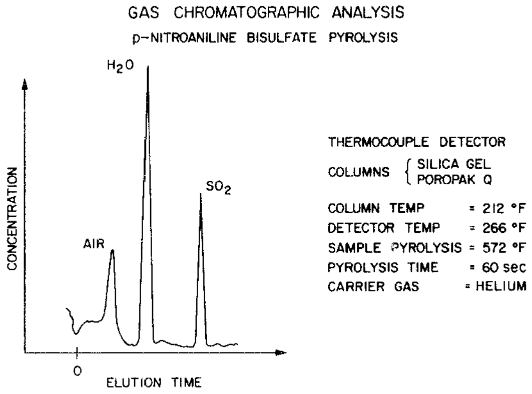


Figure 7.

In this figure the relative concentration is plotted as a function of the elution time on both silica gel and Poropak Q columns. It can be seen that the two principal gases produced are water and sulfur dioxide. This result is consistent with the reaction mechanism outlined above.

EMPIRICAL ELEMENTAL ANALYSIS OF BLACK INTUMESCENT POLYMERIC FOAM FORMED AT 482° F

CALCULATED FOR: $C_6 H_3 N_{1.8} OS_{.14}$

	C	H	N	S	O
CALCULATED:	59.66	2.48	20.88	3.71	13.27
FOUND:	59.65	2.51	20.77	3.64	13.43

Figure 8.

With this identification of the gases evolved during intumescence, and the elementary analysis (figure 8) of the black polymer foam formed in 51-54 percent yield at 482° F, an overall stoichiometric reaction for the polyquinoxaline can be written as shown in figure 9.

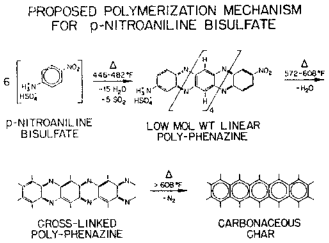


Figure 9.

This empirical formula agrees quite closely with that proposed for the polyquinoxaline polymer.

Analogous equations can also be written starting with o-nitroaniline leading to a similar polyquinoxaline polymer structure. The in-situ formation of the stable, laddered polyquinoxaline polymers is not limited to ortho- and para-nitroaniline derivatives, but the reactions may be general for a variety of nitro-substituted aromatic amines with available meta positions.

Polyquinoxaline polymers are not novel, having been studied by several groups of investigators (ref. 4), but the synthetic process was more involved than the direct one involved here.

It should be pointed out that the mechanism and structures of the intermediates taking place in this process are speculative. Additional research is planned by the authors to resolve the mechanism of these processes. But whether the proposed mechanism is correct or not, it can be concluded from the foregoing thermal analysis of the bisulfate derivative of p-nitroaniline, that the thermal polymerization of this derivative meets the requirements established for the desired general process of intumescence.

DEVELOPMENT OF A PRACTICAL COATING SYSTEM FROM p-NITROANILINE BISULFATE

The key to the application of the foregoing thermal polymerization process as a stable and useful coating system to effect thermal protection has been the selection of a coating and binder which does not interfere with the intumescence process. The coating vehicle must be relatively stable to strong acids and yet be thermally vitiated in about the same temperature range in which the intumescence takes place. This action can be accomplished by the use of either thermoplastic polymers or those which are easily degraded thermally. Of several vehicles investigated nitrocellulose has been found to be suited for this application.

Coatings suitable for conventional brush or spray application have been prepared by compounding the formulation given in table I.

Table I

COMPOSITION OF INTUMESCENT COATING
BASED ON p-NITROANILINE

Ingredients	Weight Percent
Methyl Ethyl Ketone	32.8
Nitrocellulose	6.9
p-Nitroaniline	27.5
Ethyl Alcohol	13.1
Sulfuric Acid	19.7

In this formulation, the p-nitroaniline bisulfate can be formed directly in the nitrocellulose solution, or alternately, the preformed p-nitroaniline bisulfate salt can be added to the other ingredients. The resultant formulation is ball milled to give an easily processed intumescent, air-drying paint with the properties as shown in table II.

Table II

TYPICAL PAINT PROPERTIES

Non-volatiles, Wt. %	54
Density, g/cc	1.09
Viscosity, Brookfield, 25° C, cps	1300
Fineness of Grind, Hegeman Scale	4+
Pigment/Binder Ratio, Wt.	6.9
P-NA/Acid Ratio, Wt.	1.4

The air-dried coating obtained from this paint has a density of 1.36 gm/cc (85 lb/ft^3). It is a hard, tough integral coating. The degree of intumescence produced by exposing a 20-40 mil coating to the continuous action of a JP-4 fuel fire is characterized by a 54 percent weight loss, a linear expansion of about 70 times the original thickness and a resultant density of 0.3 lb/ft^3.

The effect of a limited number of environmental conditions, on intumescence, adhesion and appearance have been evaluated as shown in table III.

Table III

EFFECT OF SOME ENVIRONMENTS ON THE INTUMESCENT COATING ON CR-STEEL, WITH A ZINC CHROMATE PRIMER AND NITROCELLULOSE TOP COAT

Test (24 hr.)	Intumescence	Adhesion	Appearance
Water Immersion	None	None	None
Sea Water Immersion	None	None	None
JP-4 Fuel Immersion	None	None	None
Humidity, 93% RH, 97° F	Slight Retardation	Partial Lifting	Slight Darkening
Oven aging, 120° F	None	None	None

The test coatings have been applied directly over the zinc chromate since this primer is commonly employed in aircraft applications for corrosion protection. Under certain circumstances, it may be necessary to use a sealer coat before application of the intumescent coating system.

TEST EVALUATION OF INTUMESCENT COATING SYSTEM BASED ON PNA-NITROCELLULOSE

Measurements in a typical JP-4 fuel fire with free convection showed that heating rates applied to surfaces immersed in such fires are about 30,000 Btu/hr/ft^2. It was also concluded that of the applied heating rate, about 90% was in the form of radiation. This environment is considered to be typical of that in which the intumescent coatings described in this paper may be applied to provide short-time thermal protection.

The fact that almost all of the heat transfer is in the form of radiation made it possible to run screening tests of candidate intumescent coatings in the beam of a convenient, repeatable radiation source. A solar simulator, shown in figure 10, having a 2.5 kW xenon arc lamp was used to irradiate the test coatings. The lens system used in the tests gave a divergent beam capable of delivering 30,000 Btu/hr/ft^2 to a 2-inch diameter specimen at a distance of about 4 inches from the focus.

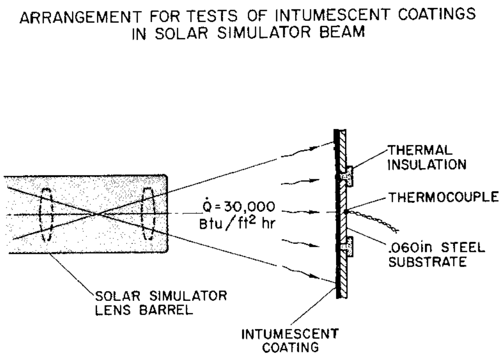


Figure 10.

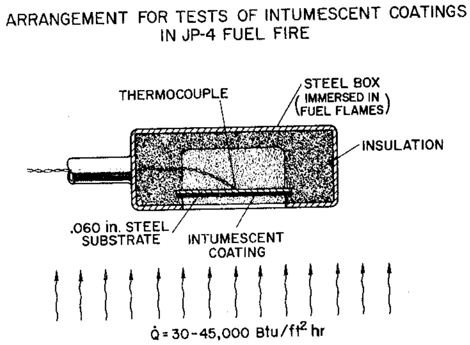
This arrangement was used to screen various thicknesses of the intumescent coating described above. The spectral distribution of the solar simulator beam which has its peak energy in the visible portion of the spectrum did not match that of the JP-4 fire which peaks at about 2.5 microns. As will be seen,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

The intumescent coating was applied in a range of thickness from about 0.007 inch to about 0.065 inch on a cold rolled steel substrate 0.060 inch in thickness. The test specimens were one inch in diameter. They 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 fuel fire for two reasons. Although the average heating rate at the surface is 30,000 Btu/ft^2/hr, 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.

Some intumescent coating samples were also tested on the surface of a steel box, figure 11, which was thermally insulated with asbestos and a 1 inch thickness of 2.5 lb/ft^3 polyurethane foam behind the sample so that the back of the sample would not be heated except by conduction through the coatings.

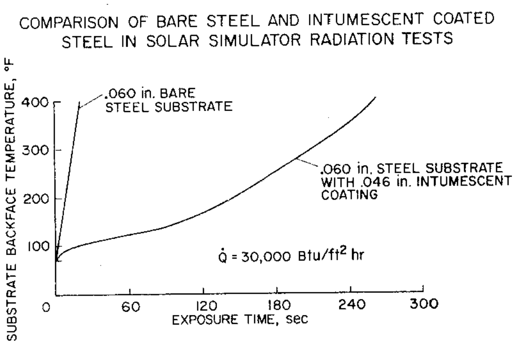
The test sample of intumescent coating with the thermocouple in the back of the 0.060 inch steel substrate was placed face down and the box was completely enveloped by the fuel fire.



ARRANGEMENT FOR TESTS OF INTUMESCENT COATINGS IN JP-4 FUEL FIRE

Figure 11.

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



COMPARISON OF BARE STEEL AND INTUMESCENT COATED STEEL IN SOLAR SIMULATOR RADIATION TESTS

Figure 12.

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

The results of numerous tests in the solar simulator beam and in JP-4 fuel fires are given in figure 13. These results show how the time required for the substrate to reach a given temperature varies with intumescent coating thickness. Temperatures of 300° F and 400° F were chosen as limits for presenting these data. The relationship is linear as might be predicted, since the thickness of the intumescence after heating is directly proportional to the thickness of the coating before heating. As can be seen in the figure, the times to reach 300° F and 400° F are shorter for the solar simulator tests than for the fuel fires, demonstrating the greater severity of the solar-simulator tests.

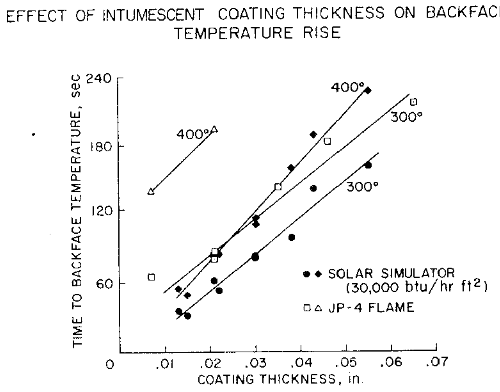

EFFECT OF INTUMESCENT COATING THICKNESS ON BACKFACE TEMPERATURE RISE

Figure 13.

The fact that the coating intumesces to give a thick, stable, closed-cell polymer which is greatly resistant to heat leads immediately to the possibility of its application to places in 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. In order to test this use, 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 shown in figure 14 was 12 inches high, 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 .040 inch. A fuel pan containing 200 cc of JP-4 aircraft fuel was placed under the box and the fuel was ignited. The fire caused the intumescent coating on the surface to fill the available volume, as seen in figure 15, thus extinguishing the fire before 30 cc of the fuel had been consumed.

Another use of the coating is as applied to fiberglass cloth which can be suspended as a blanket in areas of aircraft structures where need for ready accessibility for servicing precludes coating the structural surfaces. This would include such areas as those containing electrical or electronic gear, or fuel pumps. Intumescence of the coating on the blanket would fill the volume and extinguish the fire as in the use described above. In addition to these uses, many other applications of the intumescent coating, e.g., aircraft, passenger compartment ventilating ducts are currently being investigated.

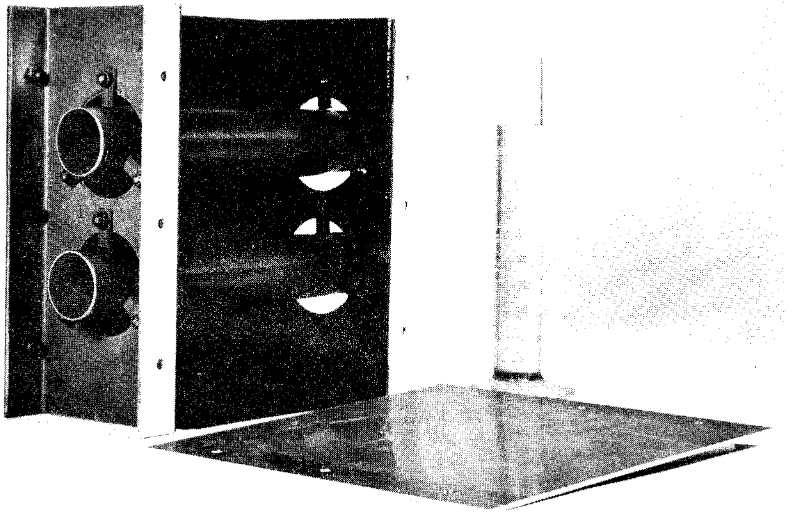


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Figure 14. The simulated fuselage section with intumescent coating and 200 ml of JP-4 aircraft fuel.

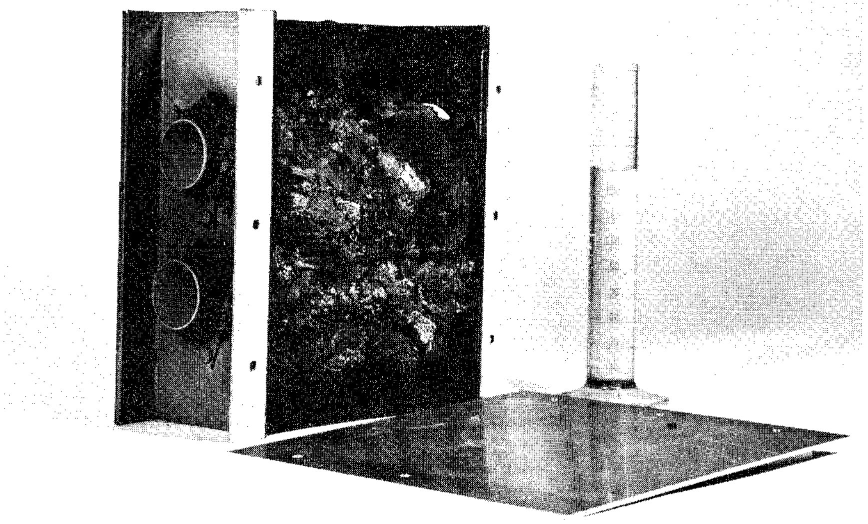

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Figure 15. The simulated fuselage section after it had extinguished the fire. Approximately 170 ml of fuel remained.

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