COMBUSTION TOXICOLOGY OF EPOXY/CARBON FIBER COMPOSITES

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INTRODUCTION

The Chemical Research Projects Office has a continuing effort in researching and developing materials for aerospace applications. Many of these materials are polymeric systems for high temperature and/or long-term use. An outgrowth of this effort has been the development of polymers with improved fire safety. In the recent study of risks (or nonrisks) using epoxy/carbon fibers in commercial transport operations, fire effects on the release of fibers was important; therefore, the fire effects on the epoxy composite were studied. Experimental programs were established in the Navy because some advanced aircraft contain epoxy composites. The Navy was also interested in developing a safety protocol, especially with regard to exposure of experimentalists and ship's crew to the pyrolysis products of the epoxy composite. These results could also help establish a data base for subsequent industrial or military fires.

EXPERIMENTAL SYSTEM

In our laboratory a combustion toxicology test is being developed to screen new materials. This system is called the radiant panel test facility. Presented here are a description of the facility and some preliminary results from tests on a Navy 3501-6AS composite, a typical composite for fighter aircraft.

The test facility was designed

1. To expose a material to a simulated fire condition.
2. To determine the pyrolysis products generated.
3. To study the effects of the pyrolysis products on test animals.

Figure 1 shows an overall view of the test system. At the top of the chamber is the sample exposure area; at the bottom are the atmospheric and animal test areas. Figure 2 shows the sample exposure area. Suspended in a vertical configuration from a load cell, the sample can be exposed to a radiant flux and/or a small JP-5 pool fire or small hydrogen ignition flame. The radiant source is an electrically powered panel which can provide up to

5 W/cm^2 flux at the sample surface. The JP-5 pool fire is achieved by burning JP-5 in a small pan beneath the sample. Ventilation of the chamber can be varied.

In the atmospheric analysis area, there are 3 kinds of atmospheric probes, shown in figure 3. A hypodermic syringe was used to obtain samples of volatile components such as CO, O_2, and CO_2. These were analyzed by chromatography and infrared. Aerosol samples were trapped on a 1 µm filter. In some cases aerosol samples were also obtained from scrapings of deposits on the chamber walls. Samples were analyzed using chromatography and mass spectrometry. Where possible, photomicrographs of the aerosols were also taken to examine size. A scrubber was used to absorb acidic or basic gases, such as HCN, H_2S, and NH_3. Scrubbing solutions were analyzed using specific ion electrodes.

Two types of test animals were studied, rats and mice. Rats were restrained so they only inhaled the atmospheres. Their respiratory and cardiac responses were recorded during exposure. The rat module is shown in figure 4. Blood enzymes in the rats were also analyzed. The concentration of these was indicative of tissue necrosis in the lungs and the neural, cardiovascular, liver, and kidney systems. The rats were also autopsied a few days after exposure.

Mice in the tests were conditioned to jump on a pole to avoid an electric shock in a grid on the cage floor. The test module is shown in figure 5. The mice learned to jump given a light or sound signal warning that the grid was to be electrified. Delays in reaction time due to exposure are a measure of the animals' ability to escape. The time delay given the light or sound is a measure of the loss of avoidance response; the delay given the shock is a measure of the loss of escape response. This test is a modification of one developed at the Stanford Research Institute.

In all tests both types of animals were observed for overt symptoms during exposure. In some cases tests for mutagenicity were also run.

In the original panel chamber design, the ratio of the sample weight to chamber volume was scaled similar to the ratio of panel weight to passenger cabin volume in a wide-bodied jet. At the beginning of the Navy tests, this ratio was not available for military applications, so the wide-bodied jet weight-to-volume ratio was used. Future tests will include a lower ratio indicative of composite usage on advanced aircraft in aircraft carrier hangar decks. In one of the present tests, the smallest sample, this ratio also was similar to that proposed for a fuel saving application of epoxy/carbon fiber composites as face sheets for wall panels in advanced commercial aircraft. Tables 1 and 2 summarize these typical weight-to-volume ratios.

RESULTS AND DISCUSSION

The epoxy resin tested has a molecular structure similar to that shown in figure 6. Thermogravimetric analyses (TGAS) of the resin in nitrogen and in air are shown in figure 7.

The resin in both cases begins to pyrolyze at about 300° C. In nitrogen it gives a char yield of about 35% at 650° C. In air, at 650° C, it is about 2% or almost totally consumed.

A summary of the actual test conditions for the preliminary experiments is shown in table 3. Besides sample weight or a different sample mounting, the major difference between experiments was a flame or nonflame condition. The kinds of atmospheres generated varied markedly depending on whether the resin burned. The sample burned only when both radiation and an ignition source (the hydrogen flame) were present.

When flames occurred there was an increase in CO_2 and decrease in O_2 compared to a nonflame case. Flames also resulted in large quantities of HCN being generated, while little was generated in the nonflame case. In one case a flash-over condition resulted and HCN was even more evident. Flames also changed the nature of the aerosol; aerosol material found as major components in the nonflame case was not apparent in the flame case. Typical atmospheric analyses exemplifying these characteristics are shown in tables 4-7.

Toxic effects were more severe for the flaming condition in the animal tests. In the nonflame case, although animals survived the test, they exhibited symptoms which could represent a decrease in ability to escape (see table 8). These animals also were exposed to one potential carcinogen, aniline, and therefore might show long-term health effects. (The fertilized egg tests also showed the atmosphere generated had potential mutagenic and other effects.) In the flame case not only was there a decrease in ability to escape, measured by the avoidance and escape response, but also many mice died. Although the rats survived these tests, on autopsy there was extensive pulmonary edema and kidney damage. Some typical results are shown in table 9, and figures 8 and 9.

FUTURE WORK

Additional tests are planned with a 5208 resin at lower weight-to-volume ratios similar to aircraft stored in a hangar deck. These tests will include exposure to a small JP-5 fuel fire. The JP-5 test system is shown in figure 10. A typical test on a small JP-5 fire in the chamber without epoxy or test animals is shown in table 10 and figure 11. The toxic effect of the JP-5 fuel pyrolysis alone will be studied as a baseline for comparison.

In addition, separate studies with test animals are underway to try to determine whether the animal symptomology can be correlated with just the histories of CO, HCN, or HCN/CO mixtures generated in previous panel tests. Tests using just the aniline histories may determine if aniline or its reaction products cause the kidney damage. Because of the presence of potential carcinogens, a new host mediated assay is being developed to test for mutagenicity of aerosols reaching the lungs of test animals.

TABLE 1.- TYPICAL PANEL WEIGHT TO VOLUME RATIOS

	Cabin volume	Panel weight	Ratio
Commercial aircraft Wide-bodied jet			
Case A - Total panel - state-of-the-art (fiberglass facesheet and honeycomb)	840 m^3	136×10^6 g	1.62×10^{-3} g/cm^3
Case B - Advanced aircraft Face sheet alone Epoxy/carbon fiber construction	840 m^3	4.05×10^5 g	4.82×10^{-4} g/cm^3
Case C - Military application Advanced aircraft in hangar deck	3.16×10^4 m^3	3.16×10^6 g	1.36×10^{-4} g/cm^3

TABLE 2.- SAMPLE RATIOS IN RADIANT PANEL SYSTEM

Chamber volume	Sample size (g)	Ratio (g/cm^3)	% Involvement		
			Case A	Case B	Case C
113.3 liters	200.0	1.76×10^{-3}	108	365	1294
	184.0	1.62×10^{-3}	100	--	--
	100.0	8.8×10^{-4}	54	182.5	647
	54.8	4.82×10^{-4}	--	100	--
	50.0	4.4×10^{-4}	27	91.3	323.5
	15.5	1.36×10^{-4}	--	--	100
	10.0	8.8×10^{-5}	5.4	18.3	64.7
	5.0	4.4×10^{-5}	2.7	9.1	32.4

TABLE 3.- EXPERIMENTAL CONDITIONS

[Navy 3501-6AS epoxy/graphite panels; 0.51 cm thick, 40 plys; chamber volume 113.3 liters]

Experiment no.	Sample size	Sample weight, g	Flux, W/cm^2	Exposure time, min	Flame	Mount	Atmospheric probes	Animal tests
3501-6AS-1	15.24 cm × 15.24 cm	198.2	2.25	20	None	Water-cooled block	Aerosol, gas, scrubber	Fertilized eggs
3501-6AS-2	↓	198.3	2.48	↓	None	Load cell	Aerosol, gas	Mice
3501-6AS-3	↓	199.1	↓	↓	H_2 flame	↓	Gas, scrubber	Mice/ rats
3501-6AS-4	↓	198.0	↓	↓	↓	↓	Aerosol, gas, scrubber	None
3501-6AS-5	7.62 cm × 7.62 cm	48.0	↓	↓	↓	↓	Aerosol, gas, scrubber	Mice/ rats

TABLE 4.- NO FLAME — AEROSOL ANALYSIS[a]
[Radiant-panel test 3501-6AS-2]

Organic volatile material	Aerosol concentration			
	No. 2[b]	No. 3[c]	No. 2[b]	No. 3[c]
	ppm in gas form		mg liquid/m^3	
Aniline	83.8	68.3	320	260
n,n dimethylaniline	7.4	11.0	37	55
p-toluidine	7.9	10.9	35	48
n-etaniline	2.0	1.8	10	9
Methylquinoline	17.3	8.2	102	48
Quinoline	13.2	7.5	7	40
Indole	5.6	2.2	27	11
Methylindole	9.6	4.4	52	24

[a]Aerosol no. 1 was too diluted for analysis.

[b]Time was 5-10 min; total gas was 0.982 liters; total volume of methanol was 2.7 ml.

[c]Time was 10-20 min; total gas was 1.964 liters; total volume of methanol solution was 2.5 ml.

TABLE 5.- FLAME — SCRUBBER ANALYSIS — CN^- GAS CONCENTRATION IN ANIMAL TEST AREA[a]
[Radiant-panel test]

	Flame	Flame	Flashover
Time, min	3501-6AS-3	3501-6AS-4	3501-6AS-5
	CN^-, ppm[b]	CN^-, ppm[c]	CN^-, ppm[d]
0-7	6.2	Trace	400
7-13	533	460	1052
13-17	446	302	972
17-20	180	304	890

[a]Hydrogen cyanide analysis may have had H_2S interference. Analysis being refined. Hydrogen sulfide, however, is also very toxic.

[b,c]Sample flowrate 80 ml/min.

[d]Sample flowrate 160 ml/min.

TABLE 6.- NO FLAME — GAS ANALYSIS[a]
[Radiant-panel test 3501-6AS-2]

Time, min	CO, ppm	CO_2, %	O_2, %	CH_4, ppm	CH_2CH_2, ppm	CH_3CH_3, ppm	Propane, ppm	Propylene, ppm
5	0	0.68	20.13	---	---	---	---	---
7	200	.83	20.06	10	---	---	---	---
9	510	.83	20.08	26	70	200	40	250
12.5	1000	1.03	19.9	500	70	340	120	340
15	1480	1.04	19.7	618	130	440	310	400
18	2040	1.20	19.5	720	150	500	230	430
20	2200	1.26	19.5	694	140	520	270	380

[a]SO_2 and HCN were not found. Two unknown peaks may be COS and CH_3Cl. Maximum concentration for COS was 300 ppm, and maximum concentration for CH_3Cl was 650 ppm.
Flux level 2.48 watts/cm^2

TABLE 7.- FLAME (FLASHOVER) — GAS ANALYSIS IN ANIMAL CHAMBER
[Radiant-panel test 3501-6AS-3]

Time, min	Gas concentration			
	CO_2, %	CO, ppm	O_2, %	Hydrocarbons
0	1.54	0	17.92	Trace
4	1.65	0	17.44	
8	2.96	1060	16.3	
12	3.17	2200	15.47	
16.4	4.14	2620	15.01	
20.2	3.90	2500	15.12	

Flux level 2.48 watts/cm^2

TABLE 8.- OBSERVATIONS OF MICE DURING THE BURN AND POST EXPOSURE
[Radiant Panel Test 3501-6AS-2]

Time into burn	Observations
0 min	Animals moving, exploring, cleaning movements, active; no sweating apparent. All animals appeared normal.
2 min	Appearance of smoke at feed-through.
3.5 - 4.0 min	Appearance of smoke in chamber. Mice agitated.
5.0 - 7.0 min	Much movement, agitation, jumping behavior, attempts to climb chamber walls. Beginning to exhibit loss of coordination, some staggering.
10 min	Mice jumping, attempting to escape. Some cleaning motions. Chamber very smoky and poor visibility.
15 min	Only 1 mouse observed moving; most not visible. Animals moving on top of box appeared normal, exploring, and active. Appearance of sweat and/or aerosol deposition (yellow) on fur.
20 min	Mice were active. Fur moist with yellow sweat or aerosol.
25 min	Animal movements unsteady. Some mice obviously moribund. Movements slow and disorganized.
30 min	Animals appeared incapacitated and unable to move in a coordinated manner. Movements weak.

TABLE 8.- CONCLUDED

Time post-exposure	Observations
15 min	Brownish deposit on fur and skin of all mice. Rinsing in H_2O did not remove this. Movements slow and labored; ataxic. Breathing difficult and rapid in all mice. Appeared to be able to see, but some mice squinting and/or eyes partially closed. Perhaps some sensory irritation. Two mice appeared extremely ill.
95 min	All mice active, cleaning themselves (this would be an additional source of toxicants). Feeding, active, some scratching (irritation?). #10 possible eye damage; eye closed. Darting movement and shaking of extremities as if to get rid of irritant.
24 hr	Animals huddled together sleeping. Some eye squinting and scratching. After weighing, the animals were active and eyes appeared normal. Much cleaning and grooming.
48 hr	In general all animals appeared normal, healthy, and active, with slightly rapid breathing. Little deposition is left on their coats; somewhat more on tails and ears. Occasional squinting was observed. Animals appeared slightly jittery and exhibited very quick responses to sound (almost overly so). When removed for weighing they began exploring actively. When left undisturbed they tended to huddle in the corners, sleeping.
120 hr	All animals clean. Eyes and behavior appeared normal.

TABLE 9.- FLAME — SUMMARY OF BEHAVIORAL CHANGES IN MOUSE RESPONSE EXPERIMENTS

Test no.	Time of behavioral changes, sec		
	Loss of avoidance response	Loss of escape response	Estimated time of death
3501-6AS-3	352	704	985
3501-6AS-5	218	478	*a*

[a]Not possible to estimate.

TABLE 10.- JP-5 PYROLYSIS GAS ANALYSIS

Run No.	Time (min)	O_2 (%)	CO_2 (%)	CO (ppm)	Hydrocarbons (ppm)	Comments
3-2	0	21.2	0.05	0	0	Circular pan ~4 in.^{2} 5.5 g fuel, 1.41 g lost, analyses near animal test area, no HCN or H_2S detected
	2	19.1	1.5	200	--	
	5	17.4	2.76	400	--	
	10	17.37	2.76	500	50	
3-3	0	20.8	0.04	0	0	Circular pan ~4 in.^{2} 3.54 g fuel, 1.22 g lost, analyses near animal test area, no HCN or H_2S detected
	2	18.9	1.98	160	0	
	5	18.0	2.76	450	0	
	10	17.7	2.82	340	--	
	20	18.3	2.0	220	--	
3-7	0	21.2	0.04	0	0	Circular pan ~4 in.^{2} 3.53 g fuel, 1.37 g lost, analyses near flame, no HCN or H_2S detected
	1	11.9	8.24	1,300	280	
	2	14.4	6.23	820	110	
	3	16.4	4.28	500	40	
	5	17.54	2.84	330	0	
	11	17.46	2.78	350	0	

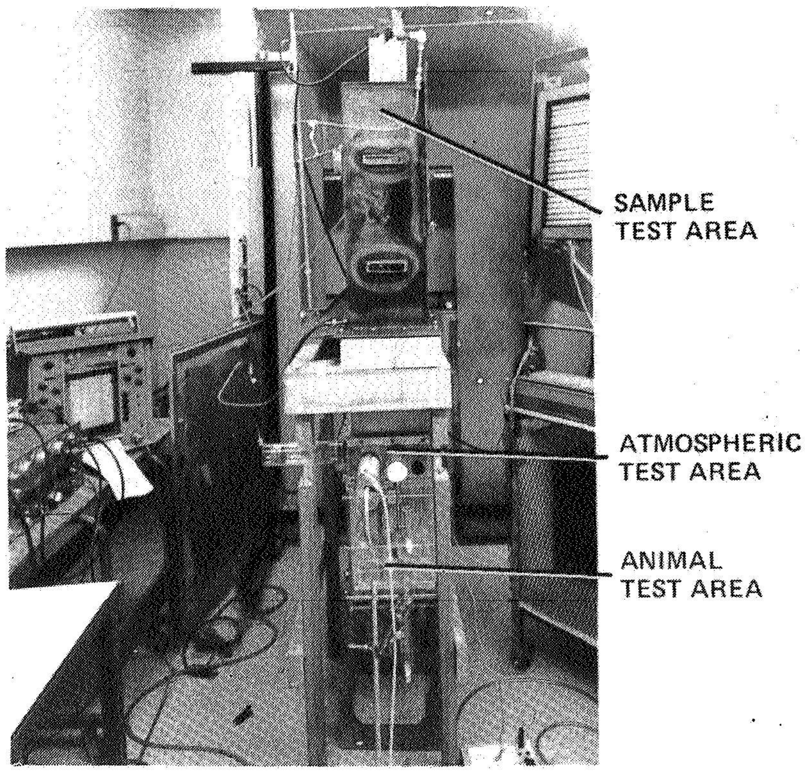


Figure 1.- Radiant panel facility.

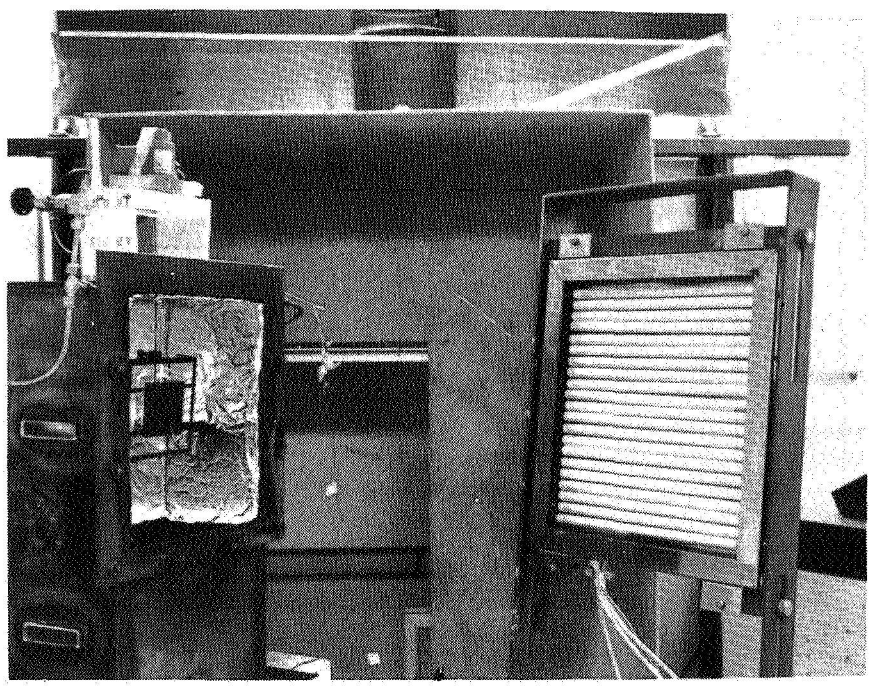


Figure 2.- Sample test area.

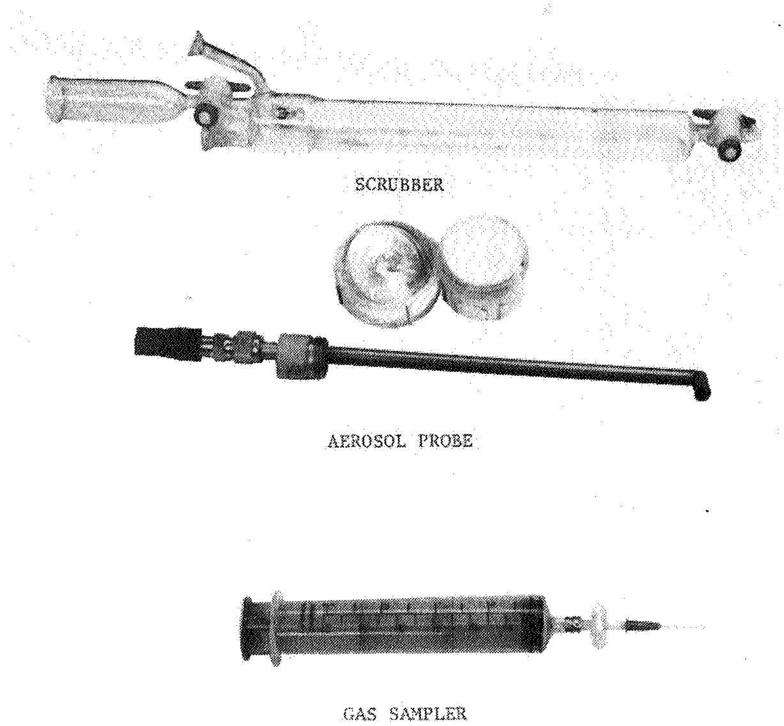


Figure 3.- Atmospheric test probes.

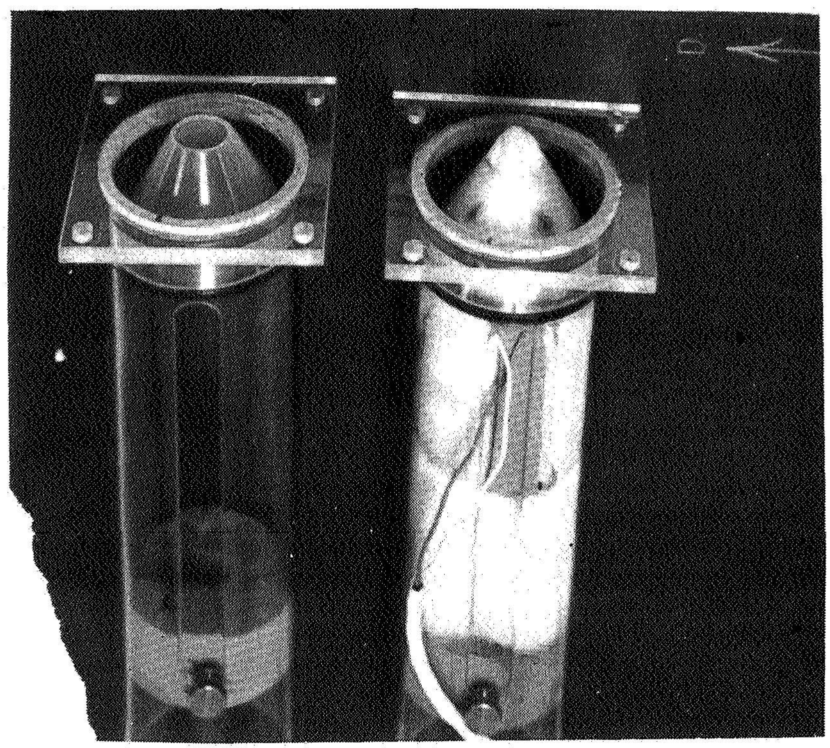


Figure 4.- Animal test area - rat module.

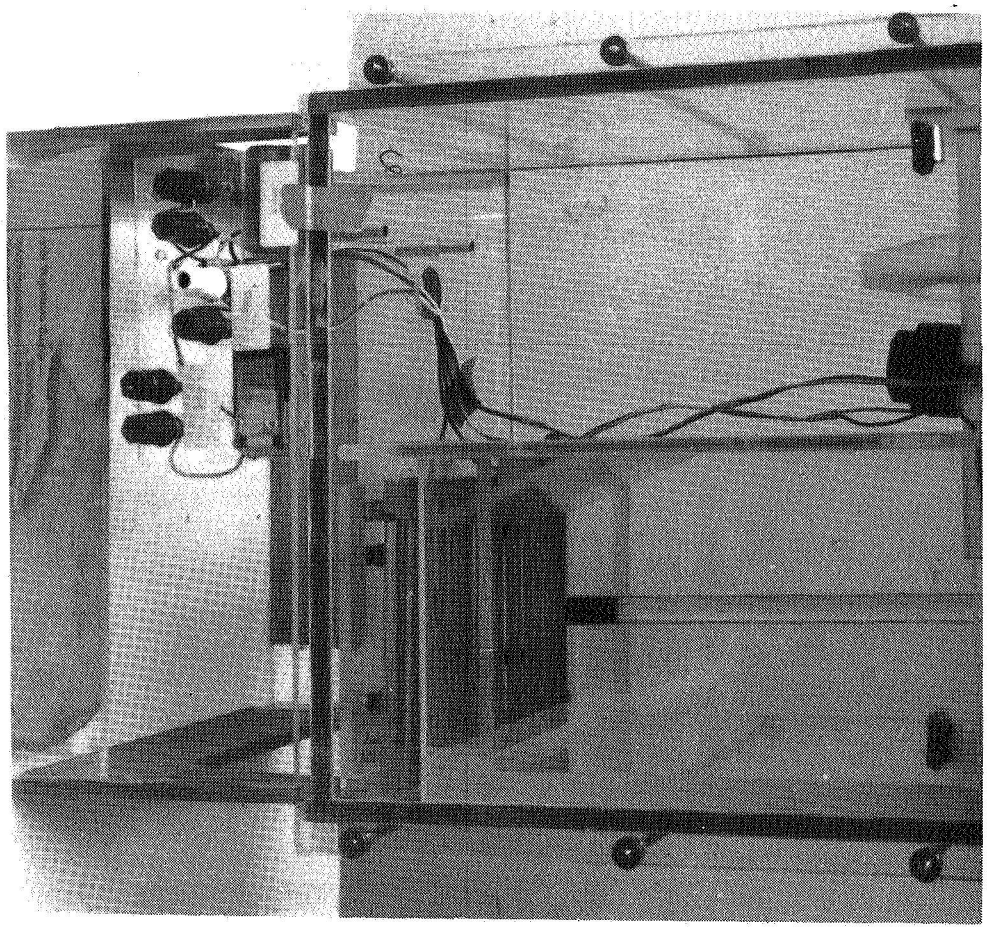


Figure 5.- Animal test area - mouse chamber.

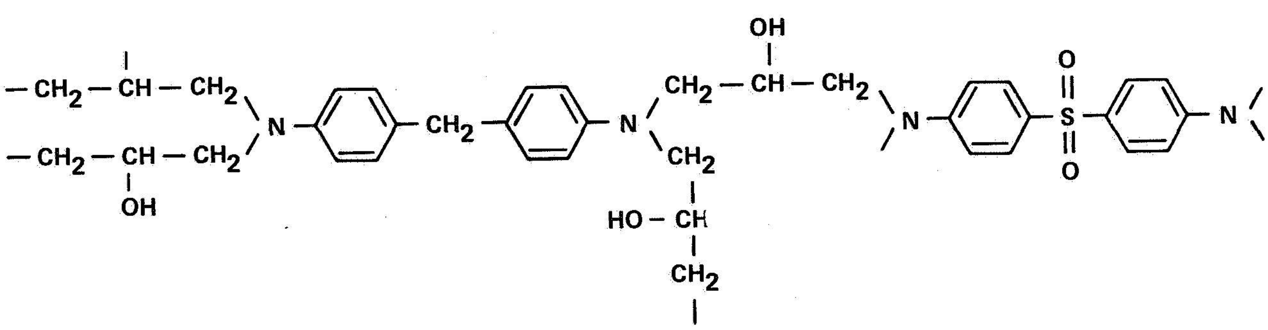
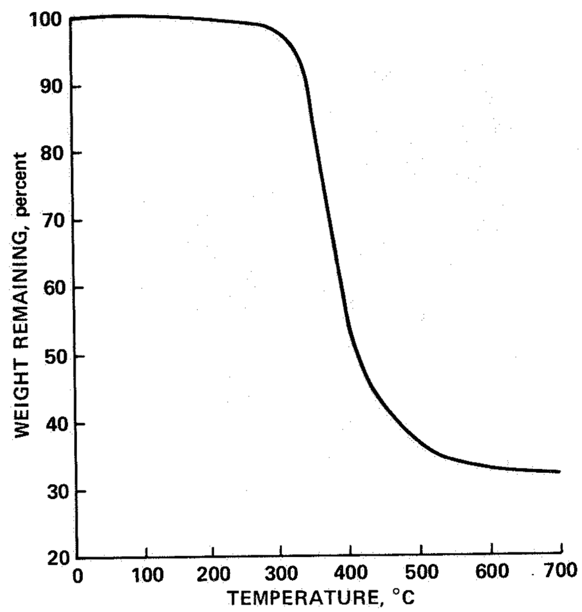
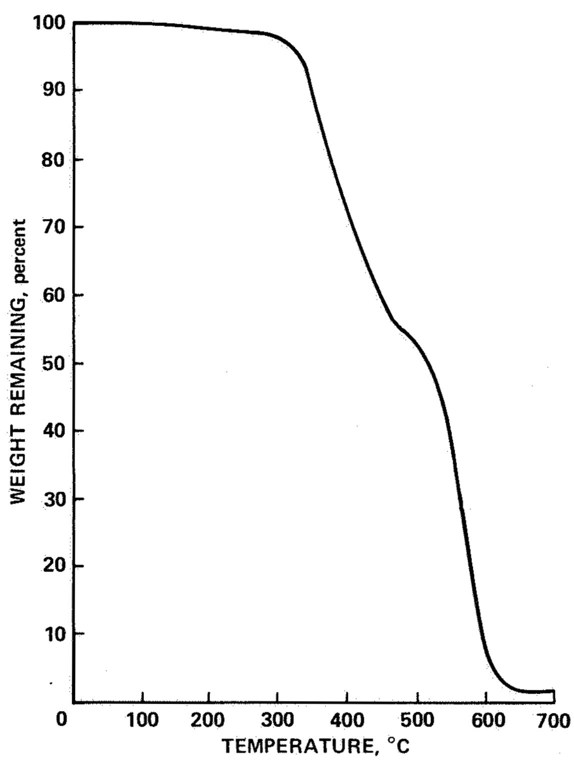


Figure 6.- Resin molecular structure.



(a) N_2.



(b) Air.

Figure 7.- Thermogravimetric analysis of resin.

Figure 8.- Pulmonary edema.

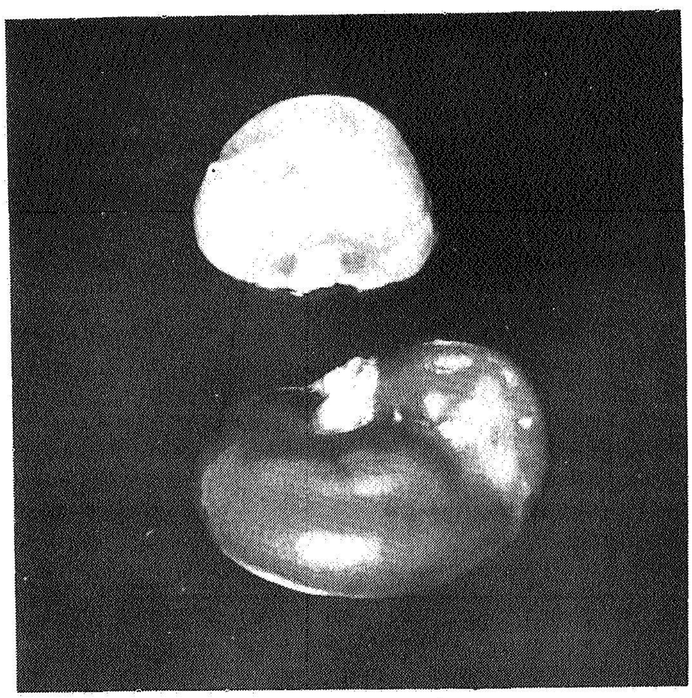


Figure 9.- Tissue necrosis. Radiant panel test 3501-6AS-5.

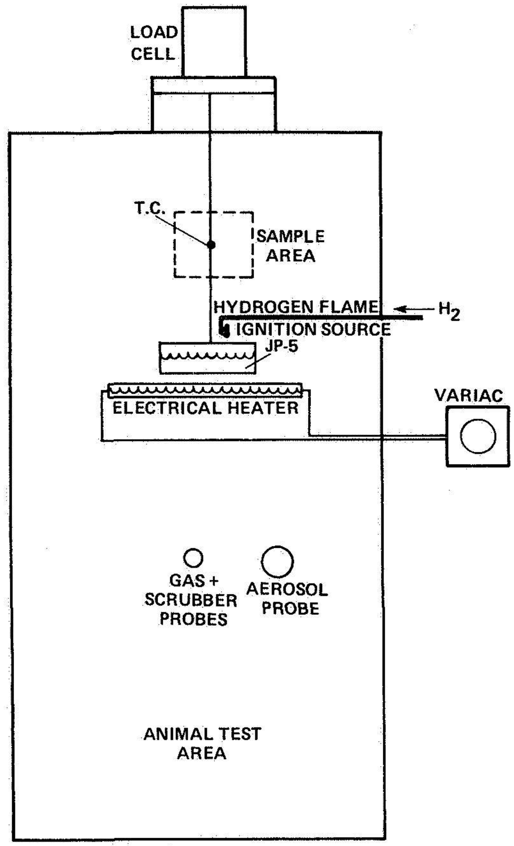


Figure 10.- Modified radiant panel facility for JP-5 tests.

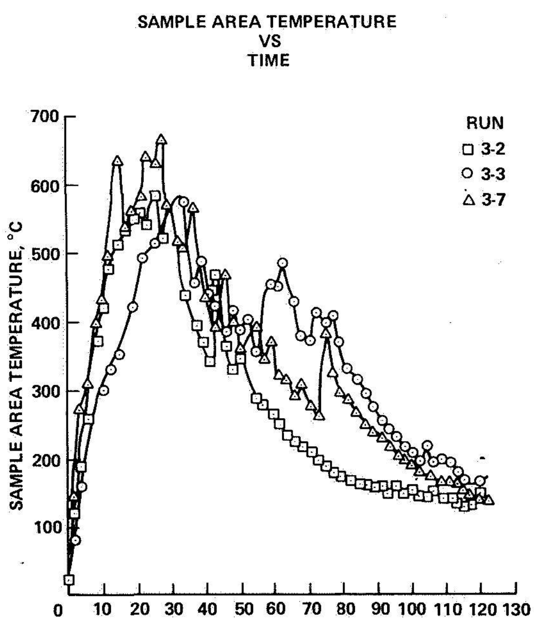


Figure 11.- Sample temperature vs time for JP-5 fire test.