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ABLATIVE CHARACTERISTICS OF POLYETHYLENE AND OTHER THERMOPLASTICS

R. W. FARMER

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FOREWORD

This report was prepared by the Thermally Protective Plastics and Composites Section, Plastics and Composites Branch, and was initiated under Project No. 7340, "Nonmetallic Composites and Materials," Task No. 734001, "Thermally Protective Plastics and Composites." It was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. R. Farmer (MANC) as the Project Engineer. The report was submitted by the author in October 1969.

Many of the items described in this report were commercial items that were not developed or manufactured to meet any Government specification, to withstand the tests to which they were subjected, or to function as applied during this study. Any failure to meet the objectives of this study is no reflection upon any of the commercial items discussed herein or upon any manufacturer.

This technical report has been reviewed and is approved.

J. D. RAY
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ABSTRACT

The ablative characteristics of polyethylene and four substituted hydrocarbons were examined in arc heated air. The order of increasing penetration rates was polytetrafluoroethylene, a tetrafluoroethylene-hexafluoropropylene copolymer, polychlorotrifluoroethylene, polyethylene, and polyoxymethylene. Penetration rate was related tc melting, softening, and viscous flow; molecular structure; sample thickness; secondary reactions; and surface temperature.

A polyaminoborane analogy to polyethylene and a tetramethylammonium hydrotriborate derivative of boron hydride underwent penetration at rapid rates. Boron nitride was an efficient conducting heat sink. There was intense, wide-band radiative emission for all three boron-containing, noncharring materials.

Three nominal heat flux conditions of 100, 300, and 500 Btu/ft^2- sec were employed with effluent air enthalpies of 1090 to 3350 Btu/lb, stagnation pressures of 0.29 to 0.78 psig, and test times to 180 seconds. The macro test used a one-inch diameter sample and water-cooled copper support. The major evaluation variables included effluent penetration time, exposure time, heat flux, sample thickness, sample features and surface temperature.

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NOMENCLATURE

Term	Definition	Typical Units
A	Frequency factor	1/sec
C	Solid specific heat, constant pressure	Btu/lb-^{o}R
e	Base of natural logarithms	dimensionless
E	Activation energy	Btu/lb-mole
ΔH	Total heat of reaction	Btu/lb
k	Thermal conductivity	Btu/sec-ft-^{o}R
q_c	Calorimetric heat flux	Btu/ft^2-sec
q_c^*	Cold-wall effective heat of ablation	Btu/lb
R	Gas constant	Btu/lb-mole/^{o}R
T	Surface temperature, degrees absolute	^{o}R
T_o	Temperature at rear of solid, degrees absolute	^{o}R
v	Surface recession velocity, constant	ft/sec
X	E/RT	dimensionless
β	Property parameter	lb^2/ft^4-sec
γ	$(T - T_o)/T$	dimensionless
ρ	Solid density	lb/ft^3

SECTION I
INTRODUCTION

Thermoplastic ablative materials provide efficient thermal protection in hyperenvironments involving high gas enthalpies and relatively mild mechanical forces. In contrast to charring ablators like phenolic resin reinforced with carbon cloth or silica cloth, they usually undergo ablation with a high rate of gas formation at low surface temperature without the formation of a carbonaceous surface char. With increasing heat flux or surface shear, the erosion resistance typically decreases.

The absence of a surface char, good insulation, low density, low porosity, predictable performance, availability, and other features of thermoplastic ablators lend themselves to specialized ablative applications. The thermoplastics, with or without a reinforcing cloth, fiber, or filler, can be tailored to a variety of environments.

This report summarizes the screening of five thermoplastics in an air arc heater environment. The thermoplastics were polyethylene, polyoxymethylene, and three halohydrocarbons. An inorganic polymer and two other boron-containing materials were also examined. A novel macro test, tailored to evaluate materials of difficult fabricability or limited availability, was used with a 120 KW air arc heater.

SECTION II
EXPERIMENTAL MATERIALS

The thermoplastics were classified as variations of polyethylene

$$(CH_2CH_2)_n$$

with halogen substitution

$$(CFClCF_2)_n \text{ - polychlorotrifluoroethylene (Kel-F 81)}$$

and then complete fluorination

$$(CF_2CF_2)_n \text{ - polytetrafluoroethylene (Teflon TFE)}$$

Other pseudoanalogs involved a pendant fluorocarbon group

$$\left(CF_2CF_2CF_2\underset{\displaystyle CF_3}{\underset{|}{CF}}\right)_n \text{ - tetrafluoroethylene - hexafluoropropylene copolymer (Teflon FEP)}$$

an oxygen in the backbone

$$(CH_2OCH_2O)_n \text{ - polyoxymethylene (Delrin)}$$

or a boron-nitrogen inorganic

$$(BH_2NH_2)_n \text{ - polyaminoborane (PAB-5).}$$

QMB-3 or tetramethylammonium hydrotriborate - $(CH_3)_4NB_3H_8$ - a crystalline derivative of boron hydride, was a second boron-containing material. Both PAB-5 and QMB-3 closely resembled boron nitride in appearance and surface texture but were less than one-half as dense, more friable and soft, and had a low order of thermal stability. Samples of boron nitride were also run to compare with these two materials.

The ablative macro method used a one-inch diameter sample. Discs of the five thermoplastics and boron nitride were machined from commercial rod stock to 1/16, 1/8, or 1/4 inch thickness. PAB-5 and QMB-3 samples were prepared by cold-pressing powder under vacuum (see Appendix). The nominal thickness was 1/8 inch.

SECTION III
EXPERIMENTAL PROCEDURES

A modified Giannini-Plasmadyne Corporation Model L-40 air arc heater was used for hyperthermal screening (Reference 1). The three conditions were referenced by a nominal heat flux of 100, 300, or 500 Btu/ft^2-sec (Table I). The corresponding ranges of other major parameters included 1090 to 3350 Btu/lb for enthalpy, 0.29 to 0.78 psig for stagnation pressure, and run time to 180 seconds.

The screening macro test was relatively simple. The one-inch diameter disc was first measured and weighed. The support was a water-cooled annular ring of copper construction. The disc was spring loaded against a small shoulder near the face of the holder.

TABLE I

HYPERTHERMAL PARAMETERS*

Heat Flux, Btu/ft^2-sec	100	300	500
Gas Enthalpy, Btu/lb	1085±15	2260±40	3350±260
Stagnation Pressure, psig	0.288±0.004	0.614±0.014	0.782±0.042
Gas Velocity, ft/sec	445±5	945±20	1205±65

*Deviation limits for at least 56 samples at each heat flux level.

After arc ignition and adjustment, the sample holder was rapidly inserted into the effluent by a sliding mechanism. This simultaneously actuated a timer. The timer was tripped by a photocell detector facing the rear of the disc at the instant of effluent penetration. Only ultraviolet arc radiation was "seen" by the detector. To do this, a dichroic mirror was placed in front of the detector. The mirror rejected sample infrared radiation and avoided premature tripping.

The sample data included exposure and penetration time as well as density, thickness and weight. A visual description of behavior during exposure was recorded along with the front surface temperatures registered by an infrared, optical, and total radiation pyrometer. The five thermoplastics and boron nitride were run in triplicate for three thicknesses at the three heat flux levels. In most cases, PAB-5 and QMB-3 were run in duplicate at the three conditions using a nominal 1/8 inch thickness disc.

The heat flux was measured by a guarded, water-cooled copper calorimeter. The diameters of the measuring and guard areas were 0.5 and 3.5 inches, respectively. Additional arc heater measurements or estimates included effluent bulk enthalpy and bulk temperature at the nozzle exit; effluent stagnation pressure and velocity at the sample location; coolant heat loss; input nitrogen/oxygen flow rates; and input power. The arc was operated well within subsonic flow using a shaped nozzle with a one-half inch exit diameter.

SECTION IV
DISCUSSION OF RESULTS

1. THERMOPLASTICS

Penetration rate was the primary ablative performance criterion. The penetration rate was the ratio of initial sample thickness to the exposure time as registered by the photocell detector.

The increasing penetration rate ranking of the materials was Teflon TFE and Teflon FEP > Kel-F > Delrin and polyethylene (Table II, Figures 1 through 5). The penetration rates varied by a factor of about 3.6 ranging from 0.0071 in./sec (7.1 mil/sec) for 1/16 inch thick Teflon TFE at 100 Btu/ft^2-sec to 25 mil/sec for 1/4 inch thick Delrin at 500 Btu/ft^2-sec.

The penetration rate increased with increasing heat flux. The difference between maximum and minimum values for the three heat fluxes ranged from 10.3 mil/sec for 1/8 inch thick Kel-F to 12.4 mil/sec for 1/4 inch thick Delrin. The average spread was 11 mil/sec.

The penetration rate decreased with increasing thickness at constant heat flux. The difference between maximum and minimum values for the three thicknesses ranged from 0.3 mil/sec for Delrin at 500 Btu/ft^2-sec to 2.5 mil/sec for Teflon TFE at 500 Btu/ft^2-sec. The average spread was 1.8 mil/sec.

The surface temperatures measured with the infrared pyrometer were not highly dependent upon either environmental heat flux or material thickness.

TABLE II

ABLATION OF THERMOPLASTICS[a]

Material	Initial Density (gm/cc)[b]	Initial Thickness (in.)[c]	Heat Flux (Btu/ft^2-sec)[d]	Crater Depth (in.)	Exposure Time (sec)[d]	App Penetration[e] Rate (in./sec) x 10^3	Infrared Pyrometer Temp (°F)
Delrin	1.43 ± 0.01	0.064 ± 0.008	100		4.5	14.5	815
			300		2.5	24.8	770
			500[g]		3.0	25.3	750
		0.127 ± 0.009	100		9.5	13.3	810
			300		5.5	22.2	780
			500		5.0	25.1	760
		0.250 ± 0.006	100		19.8	12.6	810
			300		12.0	20.7	300
			500		10.0	25.0	770
Kel-F	2.14	0.062 ± 0.002	100		6.3	9.8	440
			300		3.8	16.2	520
			500[f]		3.0	20.3	490
		0.125 ± 0.001	100		14.0	8.9	460
			300		7.5	16.7	520
			500		6.5	19.2	530
		0.250 ± 0.002	100		31.7	7.9	470
			300		16.2	15.4	530
			500		13.0	19.2	460

TABLE II (CONTD)

Material	Initial Density (gm/cc)[b]	Initial Thickness (in.)[c]	Heat Flux (Btu/ft^2-sec)[d]	Crater Depth (in.)	Exposure Time (sec)[d]	App Penetration[e] Rate (in./sec) x 10^3	Infrared Pyrometer Temp (°F)
Polyethylene	0.955 ± 0.003	0.064 ± 0.004	100[g]		4.5	14.2	860
			300		3.0	21.2	840
			500		2.5	25.1	830
		0.126 ± 0.002	100[g]		9.5	13.3	840
			300[f]		6.0	21.0	835
			500[f]		5.0	25.2	830
		0.248 ± 0.004	100[g]		21.0	11.8	875
			300[f]		12.8	19.4	850
			500[f]		10.5	23.8	850
Teflon TFE	2.18 ± 0.01	0.063 ± 0.005	100	0.054	7.7	7.1	660
			300[f]		4.0	15.6	575
			500[f]		3.2	19.1	525
		0.126 ± 0.009	100	0.114	19.2	6.0	670
			300		8.7	14.3	580
			500		7.3	17.3	570
		0.249 ± 0.004	100	0.237	42.7	5.6	675
			300	0.245	18.5	13.2	575
			500		15.2	16.6	575

TABLE II (CONCLUDED)

Material	Initial Density (gm/cc)[b]	Initial Thickness (in.)[c]	Heat Flux (Btu/ft^2 -sec)[d]	Crater Depth (in.)	Exposure Time (sec)[d]	App Penetration[e] Rate (in./sec) x 10^3	Infrared Pyrometer Temp (°F)
Teflon FEP	2.16± 0.01	0.064± 0.001	100		8.5	7.6	600
			300		4.2	15.4	605
			500		3.5	18.4	585
		0.125± 0.003	100		18.3	6.8	630
			300		9.0	13.9	610
			500		7.0	18.0	575
		0.248± 0.002	100		38.7	6.4	635
			300		18.2	13.6	610
			500		14.7	17.0	610

[a]Environmental parameters within limits of Table I

[b]27 sample average, limits

[c]9 sample average, limits

[d]3 sample average, unless noted

[e]Rate = thickness/time, or rate = crater depth/time for samples not penetrated

[f]2 sample average

[g]Single sample only

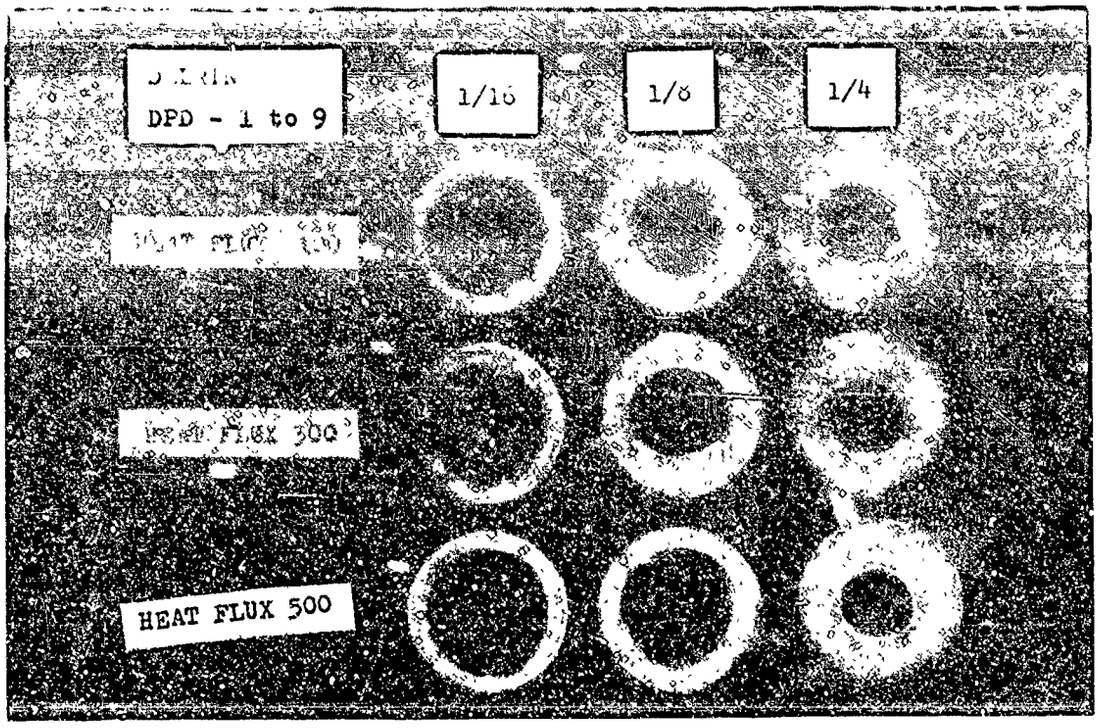

Figure 1. Delrin Sample Photographs

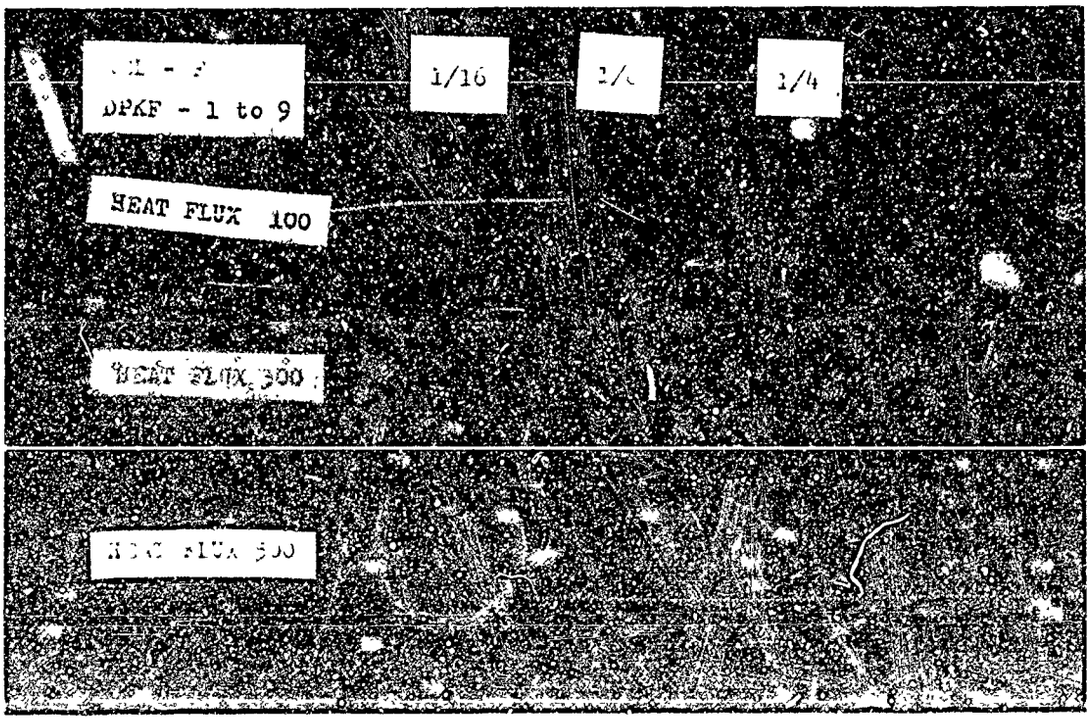

Figure 2. Kel-F Sample Photographs

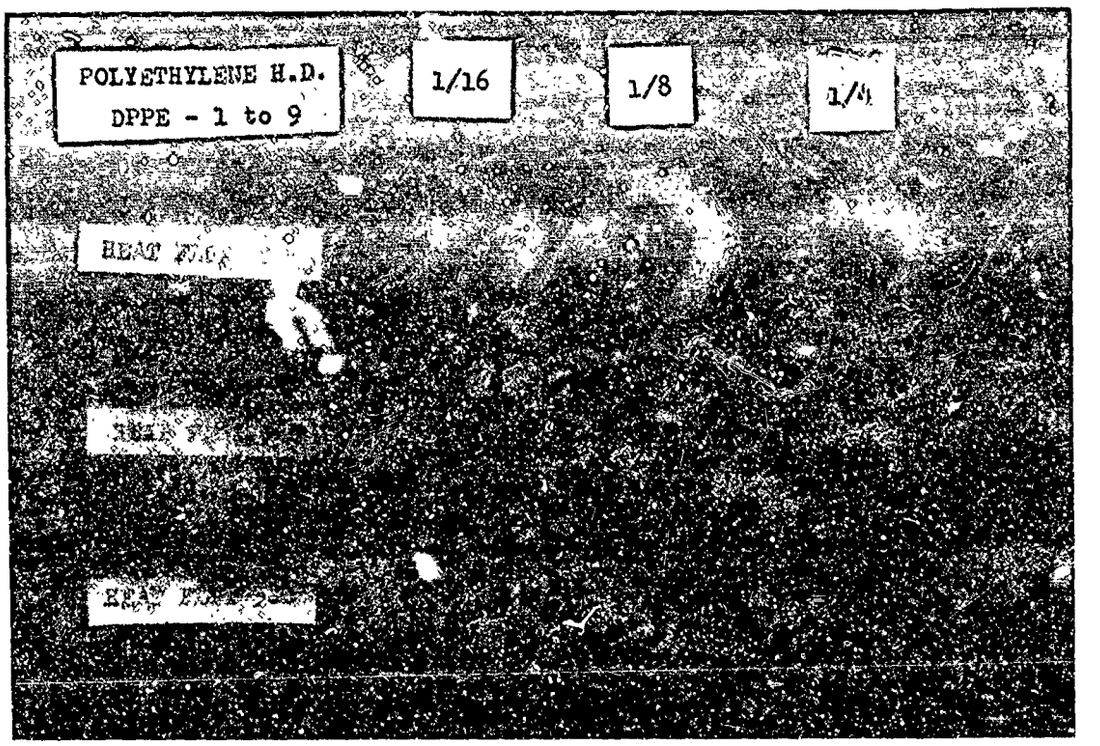

Figure 3. Polyethylene Sample Photographs

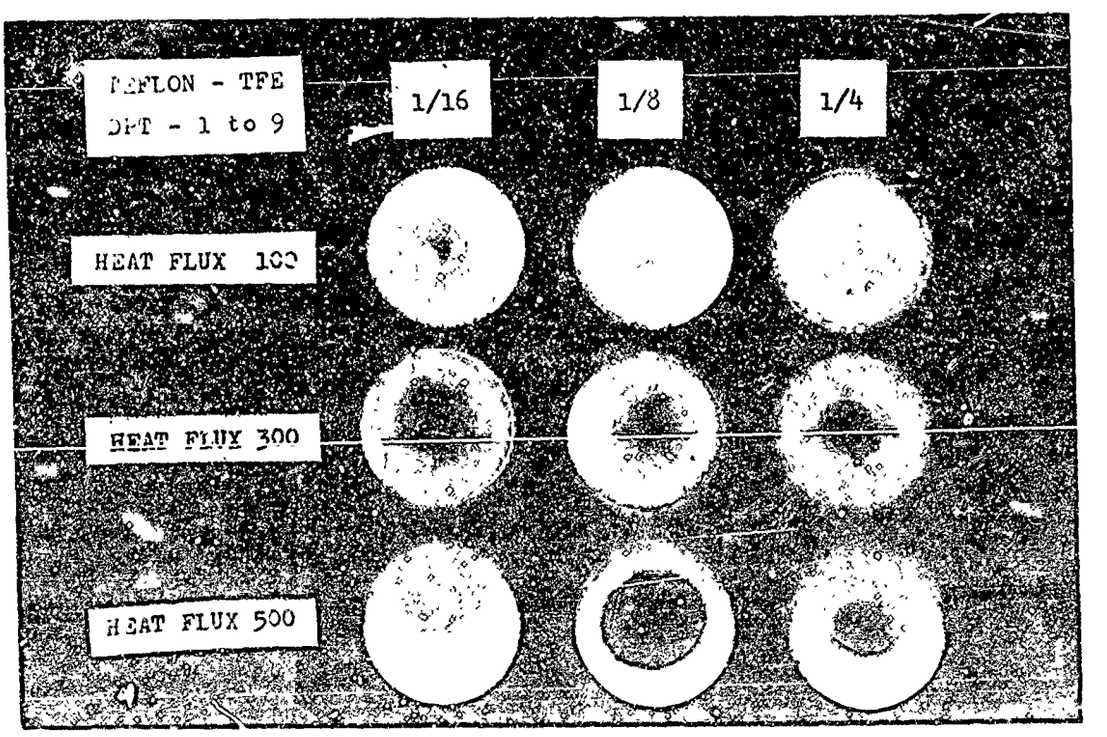

Figure 4. Teflon TFE Sample Photographs

While these "apparent" temperatures were not corrected for sample emittance, the results were relatively indicative of radiative emission within the 3.5 to 4.1 microns band. The values ranged from 440°F for 1/16 inch thick Kel-F at 100 Btu/ft^2-sec to 815°F for 1/16 inch thick Delrin at 100 Btu/ft^2-sec. At constant heat flux, the temperature tended to increase with increasing thickness. The total spread of this small and not necessarily real increase for the three thicknesses ranged from 5°F for several cases to 70°F for Kel-F at 500 Btu/ft^2-sec. The average spread was 30°F. At constant thickness, the temperature tended to increase with increasing heat flux for Kel-F and decrease for the remaining materials. The spread for the three heat fluxes ranged from 20°F for 1/16 inch thick Teflon FEP to 135°F for 1/16 inch thick Teflon TFE. The average spread was 70°F.

The relative decreasing order of apparent surface temperature was Polyethylene > Delrin > Teflon TFE > Teflon FEP > Kel-F. The observed order of apparent surface temperature for the three halohydrocarbons was identical to their order of decreasing penetration rate.

There were physicochemical aberrations for the ablation of the thermoplastics (Tables III and IV). Polyethylene underwent melting and shear removal of the molten layer. Several effects, although not resulting from melting, were due to physical softening and viscous flow. They included formation of a thin bubble opposite the exposed face, an outer rim of nearly unaffected polymer, or shrinking and warping near the disc center. In some cases the photocell circuit was tripped by an ablating sample or distorted sector radiative transmission prior to effluent penetration.

The degree of the softening effects, found mainly for 1/16 inch thick samples, was ranked in decreasing order as Kel-F > Delrin > Teflon FEP > Teflon TFE. The polyethylene samples were relatively free of shrinkage and warpage.

TABLE III
POST-EXPOSURE CHARACTERISTICS OF THERMOPLASTICS - TERMS

Bubbling (B) - Viscous flow of center material formed a bubble opposite the exposed face. Transparency occasionally tripped the photocell circuit ending the run before penetration. Prevalent for thin samples.

Hardening (H) - Same visual appearance as for the original material but an apparent degree of brittleness and hardness perhaps due to repolymerization.

Rimming (R) - Ablation and/or viscous flow of material adjacent to the cold shoulder of the holder. The rim edge was often ragged and thin.

Rim Reaction (RR) - Heterogeneous material near the holder rim. Usually adherent and black in color implying carbon.

Shrinking (S) - Shrinking of center material, perhaps associated with bubbling, repolymerization, thermal stress, etc. Prevalent for thin samples; usually with warping.

Warping (W) - Localized twisting of center region in the sample plane. Prevalent for thin samples; usually with shrinking.

TABLE IV

POST-EXPOSURE CHARACTERISTICS OF THERMOPLASTICS - DESCRIPTIONS

Material	Initial Thickness (in.)	Heat Flux (Btu/ft^2-sec)	Descriptions*	Remarks
Delrin	0.064	100	B?, H, R, W?	Eroded surface smooth except for W. H always distinct; R distinct for 0.250 inch thickness. Translucent in all thicknesses.
		300	B, H, R, W	
		500	H, R, W	
	0.127	100	H, R	
		300	H, R	
		500	B?, H, R, W?	
	0.250	100	H, R	
		300	H, R	
		500	H, R	
Kel-F	0.062	100	H, R, S, W	Eroded surface smooth except for B, S, W. Difficult to isolate minor B, S,W; H decreased with heat flux increase. Nearly transparent in all thicknesses.
		300	H, R, S, W	
		500	B?, H, R, S, W	
	0.125	100	H, R, S, W	
		300	B, H, R, S	
		500	B, H, R, S	
	0.250	100	B, H, R	
		300	B, H, R	
		500	H, R	
Polyethylene	0.064	100	B, R, RR	Eroded surface smooth except for B. B distinct at 100 Btu/ft^2-sec. Translucent in all thicknesses.
		300	B, R, RR, S?, W?	
		500	B, R, RR	
	0.126	100	B, R, RR	
		300	B, R, RR, S?, W?	
		500	B?, R, RR	
	0.248	100	B, R, RR	
		300	B, R, RR, S?, W?	
		500	B?, R, RR	

TABLE IV (CONTD)

Material	Initial Thickness (in.)	Heat Flux (Btu/ft^2-sec)	Descriptions*	Remarks
Teflon TFE	0.063	100 300 500	R?, S, W R, S, W R, S, W	Eroded surface smooth and shiny except for B, S, W. R distinct for 0.250 inch; S, W distinct for 0.063 inch; slight RR for 0.250 inch. Translucent, transparent when thin.
	0.126	100 300 500	B?, R, W? R, S, W R, S, W	
	0.249	100 300 500	B, R, W? R, S, W R, S, W	
Teflon FEP	0.064	100 300 500	B, H, R, S, W B, R, RR, S, W B, R, RR, S, W	Eroded surface smooth except for B, H, S, W. R distinct for 0.250 inch; B, S, W distinct at 100 Btu/ft^2-sec; RR distinct at 300 & 500 Btu/ft^2-sec; H slight, usually at 100 Btu/ft^2-sec with B. Nearly transparent in all thicknesses, transparent when thin.
	0.125	100 300 500	B, H, R, S, W B, R, RR, S?, W? R, RR	
	0.248	100 300 500	B, H, R, S, W R, RR R, RR	

*B - bubbling, H - hardening, R - rimming, RR - rim reaction, S - shrinking, W - warping. ? Indicates very slight or questionable degree. See Table III for further definition of the terms.

Post-test sample inspection revealed chemical aberrations. They consisted of a surface increase in brittleness and hardness possibly due to repolymerization and evidence of secondary reactions near the holder rim yielding a carbon product. Hardening and rim reaction was relatively independent of heat flux level or sample thickness. Hardening was particularly noticeable for Delrin and Kel-F in about equal degrees. Rim reaction was especially evident for polyethylene and Teflon FEP.

For a given nominal heat flux level, the penetration rate was lower and the surface temperature was higher for thicker samples. The results for the 1/16 inch thick samples were partially biased by physicochemical effects. The 1/8 inch and 1/4 inch thick samples were partially biased by edgewise heat loss. For these thicknesses, a larger quantity of material was exposed for the longer penetration time. This unaffected material conducted into the sample holder. Edge cooling gave some suppression of penetration rate with little if any effect on the surface temperature (measured at the center of the disc). For example, the 1/4 inch thick samples generally had the smallest penetrated area. Further, a ragged and thin rim often remained. The maximum effect of cooling loss was the difference between the penetration rate for 1/8 versus 1/4 inch thicknesses. This did not exceed 1.5 mil/sec, a value slightly larger than the reproducibility for triplicate runs of the same material.

Surface temperatures were estimated using an infrared (3.5 to 4.1 microns), optical (0.65 micron), and total radiation (silica optics) pyrometer. The optical and total radiation pyrometric results were generally high. This was due to pickup of sample reflected arc heater radiation.

Although always low due to a low material emittance in the 3.5 to 4.1 micron range, the infrared pyrometer readings were more realistic (Table II). For example, the true surface temperatures for polyethylene and Teflon TFE over a wide range of environments have been reported as 915°F and 1340°F, respectively (Reference 2). The average infrared pyrometer results for 1/8 inch thick samples for the three conditions were 835°F and 610°F for polyethylene and Teflon TFE, respectively. The previous spectrophotometric results showed a fairly large emittance for polyethylene and a low emittance for Teflon TFE within the pyrometer spectral region. The emittances, as well as the measured temperatures in the present work, were perhaps slightly biased by sample diathermancy and transmittance. The apparent surface temperatures were higher for thicker samples. This was believed partially due to diathermancy with transmittance giving a low reading for the 1/16 inch thick discs. These two effects, if present, did not exceed about 70°F, the maximum difference between 1/16 inch and 1/4 inch thick discs at any heat flux level.

Initial growth for several 1/16 inch thick samples due to softening and viscous flow altered the penetration rate. Other transient states were not important other than initial growth, limited edge cooling, or odd physicochemical influences. For example, a conservative estimate for the time for a semi-infinite body of Teflon TFE to reach an ablation temperature of 1400°F was a small fraction of a second for a heat flux of 100 Btu/ft^2-sec. This was largely due to the low thermal conductivity and low ablation temperature of the material.

Post-run inspection revealed that 1/8 inch thick discs were least susceptible to edge loss or physicochemical effect and gave the more reliable apparent surface temperature. For the more useful 1/8 inch thick samples, the order of decreasing erosion resistance at all heat flux levels was Teflon TFE > Teflon FEP > Kel-F with Delrin and polyethylene being nearly identical. The order of decreasing apparent surface temperature at all heat flux levels was polyethylene > Delrin > Teflon TFE > Teflon FEP > Kel-F. The observed order for the three halohydrocarbons was identical to their order of decreasing penetration rate.

A basis for comparing the erosion resistance of the materials with past results was the cold-wall effective heat of ablation, a ratio of calorimetric heat flux to mass loss flux at steady-state conditions

$$q_c^* = q_c / v\rho \qquad (1)$$

The order of cold-wall heats of ablation reported in the literature was identical to the penetration rate ranking of the halogen-substituted materials of similar density (Reference 3). The heat of ablation of polyethylene was reported as being higher than for these polymers, a result of a lower density and different energy rejection mechanisms perhaps associated with melting. The situation for polyoxymethylene proved obscure.

The intrinsic thermal stability of the polymer was important during ablation. For example, a theory for the surface recession of a semi-infinite body with an in-depth reaction of the pseudo-first order type gave the following relation for the cold-wall effective heat of ablation

$$q_c^* = q_c / (\beta A X^{-1} e^{-X})^{1/2} \quad (2)$$

$$\beta = kp/(C\gamma - \Delta HR/E\gamma + \Delta HRX/E) \quad (3)$$

This was a simplified model for Teflon TFE (Reference 4). Major assumptions included constant properties and the neglect of such heat and mass transfer mechanisms as combustion, internal gas convection, radiation, and viscous solid flow. Although the model probably failed for melting, it was interesting to note validity for idealized cases. The restrictions were an absence of gas or liquid convection, no evaporation, a zero heat of fusion, and immediate removal of the melt layer upon formation or a constant melt thickness with identical properties for the melt and solid.

The important thermal stability terms in Equation 2 were A and E, a low A and high E yielding both a high order of stability and a low surface recession rate. The ranking of the thermoplastics with respect to penetration rate was identical to a ranking for relative thermal stability (Reference 5). Stability was based upon constant heating rate thermogravimetry of a few milligrams of powder in a nitrogen atmosphere at 2.5°C/min.

2. BORON-NITROGEN MATERIALS

The ablative mechanisms of boron nitride (BN) were dependent upon calorimetric heat flux (Table V, Figure 6). At 100 Btu/ft^2-sec, the run was stopped after 180 seconds due to only minor erosion. The only visually detectable sample change was a slight surface roughness and newly

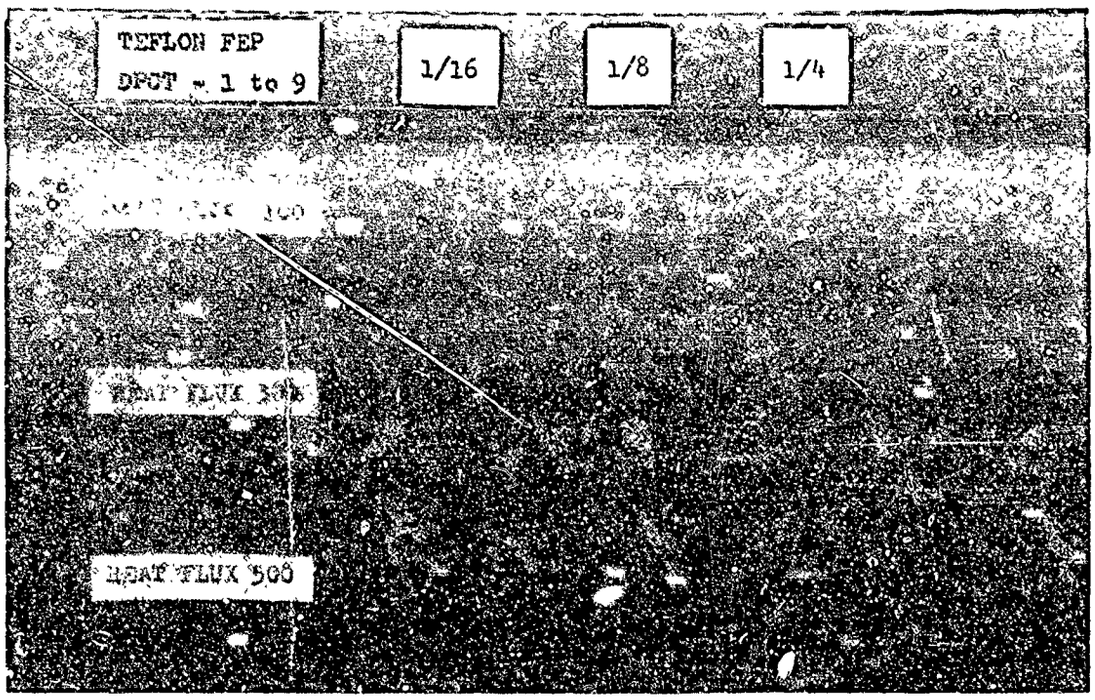

Figure 5. Teflon FEP Sample Photographs

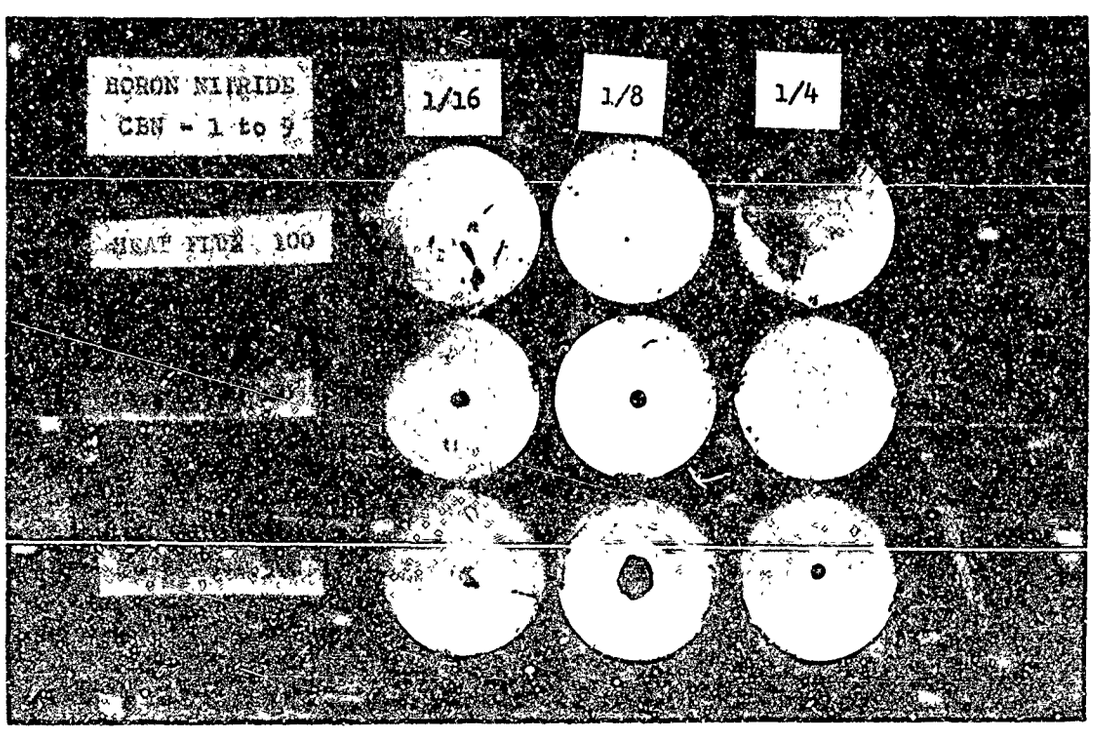

Figure 6. Boron Nitride Sample Photographs

TABLE V

ABLATION OF BORON NITRIDE

Initial Density (gm/cc)[b]	Initial Thickness, (in.)[c]	Heat Flux (Btu/ft^2-sec)[d]	Crater Depth (in.)	Exposure Time (sec)	App Penetration Rate (inch/sec)[e] x 10^3	Pyrometric Surface Temperatures (°F)[f]		
						Optical	Total Radiation	Infrared
2.06 ± 0.03	0.062 ± 0.0002	100[g]	0.001	180	nil	2310	1550	1925
		300	0.064	41.8	1.5	3415	2965	4000
		500[g]	0.062	17.5	3.6	4085	3975	4000
	0.124 ± 0.009	100	0.001	180	nil	2290	1400	1600
		300	0.090	261	0.3	2850	2315	3280
		500	0.123	50	2.5	4075	3725	4000
	0.247 ± 0.002	100	0.001	180	nil	2260	1400	1495
		300[g]	0.019	180	0.1	2655	2120	2825
		500	0.247	147	1.7	3655	3000	4000

[a]Environmental parameters within limits of Table I

[b]27 sample average, limits

[c]9 sample average, limits

[d]3 sample average, unless noted

[e]Rate = crater depth/time

[f]Optical pyrometer - 0.65 microns; total radiation pyrometer - silica optics; infrared pyrometer - 3.5 to 4.1 microns

[g]2 sample average

formed pale green and light gray surface residue; the green material likely a copper product, the gray likely $B_{13}O_2$.

At 300 Btu/ft^2-sec, the penetration rate and surface temperature were higher for BN than for the low flux case. In addition to some BN powder, there was a small quantity of gray product with some viscous glassy residue around the holder rim that was presumed to be amorphous B_2O_3. Both $B_{13}O_2$ and B_2O_3 were well known to inhibit the oxidative rate of sublayer BN.

The BN penetration rate and surface temperature were highest for the 500 Btu/ft^2-sec runs. There was an extensive accumulation of glassy residue over the exposed face. A fine white residual powder suggested some thermomechanical spallation for all runs at both 300 and 500 Btu/ft^2-sec. For larger pieces with free edges or for more severe environments, BN was well known to be susceptible to localized spallation possibly due to impurity inclusion (as water) or thermal shock.

For a given heat flux level, the penetration rate was lower and the surface temperature higher for the thinner BN samples. The thermal conductivity of BN was high normal to the molding direction -- roughly 0.1 that of copper near 600°F. The molding plane was probably oriented normal to the effluent stream and holder. Edge cooling losses due to the high conductivity were highest for the thinner discs and suppressed both penetration rate and surface temperature.

For all thicknesses of BN at any heat flux level, the highest apparent surface temperatures were registered by the optical pyrometer rather than the infrared or total radiation pyrometer. This was probably due to a high emittance near 0.65 micron.

The penetration rate and surface temperature of the polyaminoborane (PAB-5)samples increased with an increase in heat flux (Table VI). The high surface temperature and its wide variation with pyrometer type implied both intense and wavelength dependent emission. For example, the blackbody source values for irradiances of 100, 300, and 500 Btu/ft^2-sec were about 3120°, 4270°, and 4800°F, respectively. These temperatures were comparable to the maximum PAB-5 optical pyrometer readings. While radiation from sample combustion, pyrolytic gas, minute spalled (or coalesced) particles, or surface reflection may have been prevalent, these factors were likely secondary in nature. Gaseous B-O species, suggested by an intense green flame for both PAB-5 and QMB-3, were believed to be the source of the high pyrometric readings.

All samples of tetramethylammonium hydrotriborate (QMB-3) were penetrated within 2.5 to 3.5 seconds. This was the poorest erosion resistance found for any material. The apparent surface temperatures of 1800 to 4000°F were low compared to PAB-5. The QMB-3 temperatures showed little dependence upon either heat flux level or type of pyrometer.

All PAB-5 and QMB-3 exposed samples were friable and more brittle than the normally soft materials. The samples could not be removed from the holder without fracturing into small particles. The particles were

TABLE VI

ABLATION OF BORON-NITROGEN MATERIALS[a]

Material/ Molecular Formula	Initial Density (gm/cc)[b]	Initial Thickness (in.)[b]	Heat Flux (Btu/ ft^2-sec)[c]	Crater Depth (in.)	Exposure Time (sec)	App Penetration Rate (inch/ sec) x 10^3	Pyrometric Surface Temperatures (°F)[d]		
							Optical	Total Radiation	Infrared
Boron Nitride BN	2.06	0.124	100	0.001	180	nil	2290	1400	1600
			300	0.090	261	0.3	2850	2315	3280
			500	0.123	50	2.5	4075	3725	4000
Polyaminoborane $(BH_2NH_2)_n$	0.907	0.135	100		7.8	7.4	3000	2840	2570
			300		11	12.4	4100	3880	3970
			500		9.5	14.2	4280	4260	4000
Tetramethylammonium hydrotriborate $(CH_3)_4NB_3H_8$	0.757	0.135	100		3.5	38.3	2340	1640	2290
			300		2.5	53.6	----	1800	2120
			500		3.0	46.0	3000	----	4000

[a]Environmental parameters within limits of Table I

[b]3 sample average

[c]Performance values 3 sample average for BN; single sample only for all others

[d]Optical pyrometer - 0.65 microns; total radiation pyrometer - silica optics; infrared pyrometer - 3.5 to 4.1 microns

similar in physical appearance and were speckled with light to dark brown flakes of an unknown contaminant.

PAB-5 and QMB-3 particles were crushed in a mortar and subjected to x-ray diffraction. Compounds particularly sought but not found were B_2O_3 and BN for both PAB-5 and QMB-3, and B_4C for the carbon-containing QMB-3. Vague and well-defined diffraction patterns were respectively noted for relatively unordered PAB-5 and well crystallized QMB-3. The brown impurities could not be identified. BN, B_4C, or B_2O_3 (crystalline) were possibly present but in concentration below the threshold of instrument sensitivity.

A summary of penetration rates and surface temperatures of typical charring ablators was prepared to give an idea of their relative behavior (Table VII). These materials were run at 1/8 inch thickness in the macro test for a heat flux of 500 Btu/ft^2-sec.

TABLE VII

ABLATION OF REINFORCED PLASTICS AT 500 Btu/ft^2-sec

Material	Initial Density (gm/cc)	Initial Thickness (in.)	Exposure Time (sec)	App Penetration Rate (inch/sec) x 10^3	App Surface Temp (°F)[a]
Phenolic/Asbestos Felt	1.70	0.120	11.0	10.9	3670
Phenolic/Carbon Fabric	1.44	0.145	30.3	4.8	4600
Phenolic/Glass Fabric	1.80[b]	0.108	9.0	12.0	3920
Phenolic/Graphite Fabric	1.32	0.132	31.0	4.2	4340
Phenolic/Nylon Fabric	1.10[b]	0.128	5.0	25.6	2800

[a]Optical pyrometer

[b]Estimated value

SECTION V
SUMMARY AND CONCLUSIONS

High density polyethylene and four thermoplastics were screened in an air arc heater. Polyethylene and polyoxymethylene, the latter structurally analogous to polyethylene but with alternate oxygen atoms in the chain backbone, gave similar penetration rates. The replacement of polyethylene hydrogen atoms with alternate halogens, analogous to a polychlorotrifluoroethylene, moderately increased erosion resistance. Complete fluorine substitution for polymer backbone hydrogen (polytetrafluoroethylene) gave an additional improvement. The effect of a pendant fluorocarbon group for the tetrafluoroethylene-hexafluoropropylene copolymer was erosion resistance intermediate between polychlorotrifluoroethylene and polytetrafluoroethylene. The penetration rate and relative thermal stability (thermogravimetry) rankings of the materials were essentially the same.

A novel boron-nitrogen pseudoanalog of polyethylene underwent ablation at high apparent surface temperature. The erosion resistance of the inorganic polymer, which contained about five monomer units, was poor. Higher molecular weight versions were available. A higher percentage of nonvolatile residue with some increase in erosion resistance seemed probable for these materials. A compatible reinforcement, perhaps carbon cloth or high purity silica cloth with a resin binder, appeared necessary to impart high erosion resistance and reduce surface brittleness. The brittleness was likely due to amorphous boric oxide.

A crystalline boron hydride derivative, tetramethylammonium hydrotriborate, underwent ablation at rapid rates with moderately high surface temperature.

The ablative micro test, although permitting the 175 or so samples to be run with rapid efficiency, was not entirely satisfactory. The 1/8 inch thick samples were least affected by procedural artifacts and gave reasonably good data for a screening test. The artifacts, which varied in degree with both material and condition, included edge cooling loss to the holder; low sample emittance over pyrometer effective wavelengths; sample transmission actuation of the photocell timing circuit prior to effluent penetration; softening or secondary chemical reactions for the sample; and variations in major heat transfer mechanisms for different sample thicknesses.

The study showed that sophisticated analytical models for the ablation of thermoplastics could require appropos accounting for repolymerization, softening, and viscous flow, especially for corners, gaps, protuberances, or tips.

APPENDIX

PAB-5 AND QMB-3 SAMPLE PREPARATION

The polyaminoborane (PAB-5) and tetramethylammonium hydrotriborate (QMB-3) materials were submitted in the form of fine powders by the Callery Chemical Company (Reference 6). PAB-5 was identified as 10 grams of Lot #2629-151-1 and QMB-3 as 9 grams of Lot #2693-79-2.

PAB-5 samples were made by weighing out 1.7 grams of powder into a one-inch diameter metallurgical mold. The mold was enclosed in a Teflon TFE vacuum bag and evacuated to about 29 in. Hg pressure. The bag assembly was then placed upon a Universal test machine and loaded at 5000 lb/min to 25,000 psi, the allowable mold strength. The sample was then crushed in a mortar to a coarse powder which was repressed by the same procedure.

For the QMB-3 samples 1.2 grams of powder were used with the above procedure excluding a second processing cycle. Both PAB-5 and QMB-3 samples were pressed at room temperature.

The average densities for PAB-5 and QMB-3 samples were 0.907 and 0.757 gm/cc, respectively. These were lower than Callery reported values of 0.93 to 0.94 for PAB-5 pressed at 80,000 psi, and 0.774 for QMB-3 at 11,500 psi. The low density for PAB-5 was probably due to inadequate pressure and contamination by absorbed gases or solid impurities. The low density of QMB-3 samples could not be explained; a second processing cycle, which normally tended to drive off absorbed gases, failed to increase the density of one sample.

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13. ABSTRACT The ablative characteristics of polyethylene and four substituted hydrocarbons were examined in arc heated air. The order of increasing penetration rates was polytetrafluoroethylene, a tetrafluoroethylene-hexafluoropropylene copolymer, polychlorotrifluoroethylene, polyethylene, and polyoxymethylene. Penetration rate was related to melting, softening, and viscous flow; molecular structure; sample thickness; secondary reactions; and surface temperature. A polyaminoborane analogy to polyethylene and a tetramethylammonium hydrotriborate derivative of boron hydride underwent penetration at rapid rates. Boron nitride was an efficient conducting heat sink. There was intense, wide-band radiative emission for all three boron-containing, noncharring materials. Three nominal heat flux conditions of 100, 300, and 500 Btu/ft^2-sec were employed with effluent air enthalpies of 1090 to 3350 Btu/lb, stagnation pressures of 0.29 to 0.78 psig, and test times to 180 seconds. The macro test used a one-inch diameter sample and water-cooled copper support. The major evaluation variables included effluent penetration time, exposure time, heat flux, sample thickness, sample features and surface temperature.

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