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A Review of Ablative Studies of Interest to Naval Applications

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SUMMARY

Ablative materials have been used widely by the Navy to protect both the internal and external surfaces of solid-propellant missile propulsion systems. Plastics and rubber-based ablators have been employed for this purpose because of their relatively low density and high thermal insulation performance. To aid in the development and selection of these materials, laboratory-scale thermal tests have evolved. An oxyacetylene burner test found to be useful for this purpose has gained widespread acceptance and is now a standard procedure known as ASTM 285-65T. Standardization of other test procedures and techniques is in process. These include a method for determining the total enthalpy of electric plasma arc heaters and recommended practices for installing thermocouples in ablative test specimens. An advanced technique in use at the Naval Ordnance Laboratory (NOL) known as the "alpha rod test" provides a continuous record of ablation rate and internal temperature. It also enables one to compute the effective thermal diffusivity as a function of temperature, which is suitable for predicting internal temperature histories in ablators. Under ideal conditions, agreement to within 5-10% of experimental data has been obtained. Using the concept of "constructive thermal degradation," NOL has also developed new, novel epoxide resin-curing agent systems equal to or better than phenolics in ablation performance.

INTRODUCTION

Due to the extensive use of solid propellants by the U.S. Navy, ablative materials have been employed quite liberally as thermal protection for both the internal and external surfaces of missile propulsion systems. Solid propellants are usually preferred because of the hazards associated with the handling of liquid propellants on shipboard and because of the instant tactical readiness of solid propellants. Solids, however, have the drawback that they do not provide liquid coolants for nozzles and combustion chamber walls, as is the practice for many liquid systems. While star-grained propellants provide a degree of insulation for a portion of the rocket motor, an efficient, lightweight, thermal insulation material is usually needed to protect the aft walls of the propulsion system to prevent failure during a mission. Over the past 8 or 9 years, organic plastics and rubber-based ablative materials have been used for this purpose because of their relatively low density and high thermal insulation performance [1]. In this paper, some of these ablative materials and the evaluation techniques used in their development and selection are discussed

INTERNAL INSULATION PROBLEMS

The interesting (and often discouraging) feature of missile propulsion systems is that no two systems are exactly alike, even in the instance where the same propellant is used. Chamber pressure, mass flow, gas velocity, local turbulence, gas chemistry and temperature, burning rate and time, physical dimensions, etc. all have a role in producing the desired performance of the propulsion system. They also affect the ablation performance of thermal protection systems, making it difficult to extrapolate ablative performance data from one application to another and from laboratory and subscale tests to full-scale applications. Thus, when one stops to consider the almost infinite combination of environmental conditions to which an ablator can be exposed, one can readily see the dilemma that faces us. This, together with the variation of conditions at different locations within a specific motor, and the usual high cost of propellants, has made testing and evaluation difficult. In some ways, the advancement of ablative technology for propulsion systems has been more difficult than for aerodynamic heating, since one must cope with a variety of combustion gas mixtures, high internal pressures, high shear stress, and an almost total lack of predictability in gas flow patterns.

As in the case of aerodynamic heating, the problem of simulation has been most difficult. For economic and other practical reasons, it is not possible for many development laboratories to use rocket motors for testing ablative materials. This is particularly true of nonrocket motor development laboratories that have neither facilities nor qualified people to operate them. To circumvent this problem, bench-scale laboratory tests are in use in order to gain some measure of the relative performance of insulation materials. These consist of chemical burners, small bottled gas burning rocket engines, and electric plasma arc heaters [2].

The bench-scale test that has been used by many laboratories associated with Navy and other Defense Department projects employs an oxyacetylene burner as the heat source. This device has been used extensively to aid in the development of improved ablators and to aid in their selection for specific applications. While this test does not simulate all of the conditions inside a rocket combustion chamber, in many cases materials performing well in the burner test have also provided excellent protection as rocket insulation. One of the test procedures used by the industry is now an American Society for Testing and Materials (ASTM) standard procedure [3]. The test, summarized in Table 1, consists essentially of impinging the hot gases from a large oxyacetylene cutting torch onto the face of a flat test specimen until burn-through to the back face is achieved. The average erosion rate (from the measured burn-through time) and the time to some specified back-face temperature is used as a measure of the thermal protection afforded by the insulator. Some typical performance data from a number of representative ablative materials are shown in Table 2. Many of the materials shown here have been used at one time or another, either singly or in combination, as motor liners or for rocket nozzle protection. Phenolic materials numbered 1 to 4 in the table are used extensively for nozzle approach and exit cones. In areas of very severe erosion, graphite or carbon cloth phenolics are frequently placed at the hot gas surface because of their resistance to erosion, while silica or asbestos phenolic is placed underneath to insulate the more conductive graphite. The butadiene-acrylonitrile- and styrene-based ablators (materials 6-10) have enjoyed outstanding success as motor liner materials, not only because of their excellent ablative performance and lower density but also because of their ability to elongate and maintain contact with the rocket case as it expands during chamber pressurization. The silicone rubbers (materials 11-13) have been used mainly as external insulation for aerodynamic heating and back-blast protection (along with cork materials), but they could become important competitors to the butadiene rubbers as formulations are improved and the need for low environmental temperature insulators increases.

Table 1. Synopsis of ASTM E285-65T, Tentative Method for Oxyacetylene Ablation Testing of Thermal Insulation Materials

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General

An oxyacetylene flame is impinged on a test panel until burn-through is achieved. Erosion rate is computed by dividing thickness by time to burn-through. The back-face temperature is monitored and insulation indices are computed by dividing times to temperature changes by the original thickness of the specimen.

Test conditions

Stand off distance, 1.905 cm (0.750 in.)
Angle of impingement, 90°
Heat flux, 200 cal/cm^2 sec (736 Btu/ft^2 sec)
Total gas flow, 6.37 SCMH (225 SCFH)
O_2/C_2H_2 ratio, 1.20

Specimen

Flat panel, 10.16 cm X 10.17 cm X 0.635 cm (4 in. X 4 in. X 1/4 in.)

Equipment

Torch tip: Victor, Type 4, No. 7
Thermocouple: No. 28, Chromel-alumel
Calorimeter: Transient type; copper slug, 1/4 in. diam mounted in copper plate, thermally insulated from sides. Heat flux computed by measuring linear rate of temperature rise.

The oxyacetylene burner test was used quite effectively to aid in the selection of a thermal protection for the aft end of a rocket engine developed by the Naval Ordnance Laboratory [4]. Because of severe erosion at the juncture of the motor walls and the aft closure and at the point where the nozzle is fastened to the aft bulkhead, a material having good erosion resistance was needed to prevent failure of the motor case at these points. Table 3 summarizes the test data taken on a number of candidate molding materials available (many of the materials in Table 2 were not yet developed). From these tests, several materials were selected for half-scale and full-scale solid rocket firings using the propellant for the intended application. Based on these firings, a final selection was made and it proved

Table 2. Oxyacetylene Panel Test[a] Data on Some Typical Ablators

No.	Organic binder	Filler	Density, g/cc	Erosion rate, mil/sec[b]	Insulation index[c] sec/in.
1	Phenolic	Graphite cloth	1.50	1.2	148
2	Phenolic	Asbestos mat	1.89	3.4	142
3	Phenolic	Asbestos fibers	1.80	3.6	180
4	Phenolic	Silica cloth	1.75	3.4	194
5	Phenolic	Nylon cloth	1.18	15.6	58
6	PBA[d]	Asbestos fibers	1.29	6.4	122
7	PBA-phenolic	K oxalate	1.26	3.2	225
8	PBA	Silica powder	1.23	11.6	64
9	PBA	Cork	0.75	14.1	62
10	PBS[e]	Asbestos fibers	1.40	3.6	165
11	Silicone rubber	Asbestos fibers	1.31	4.4	197
12	Silicone rubber	Silica powder	1.28	14.3	69
13	Silicone rubber	Cork	1.02	13.9	72
14	Phenolic	Pressed cork	0.49	20.5	48

[a] ASTM E285-65T.
[b] Thickness divided by burn-through time.
[c] Time to reach back-face temperature (200°C) divided by thickness.
[d] Polybutadiene-acrylonitrile rubber.
[e] Polybutadiene-styrene rubber.

to be successful. An interesting sidelight on this project was that the material selected, a phenolic filled with granular graphite and aluminum silicate, was molded to shape using a unique modification of matched metal die molding. The dished aft end of the motor case was used as the female component of the die, and the material was molded directly in place. This was probably the first instance of this technique being used for this purpose, and it is now a standard manufacturing technique for this particular Navy missile.

Table 3. Oxyacetylene Screening Tests of Candidate Molding Materials for Aft Bulkhead Insulation

No.	Description of organic binder	Material filler	Erosion rate, mil/sec	Time to 200°C, sec
1	Phenolic	Asbestos fibers	3.8	36
2	Phenolic	Granular graphite, aluminum silicate	2.8	25
3	Phenolic	Quartz fibers	5.8	35
4	Phenolic	Quartz fibers	6.6	34
5	Phenolic	Ceramic fibers	4.6	20
6	Phenolic	Quartz fibers	5.7	22

STANDARDIZATION OF ABLATION TEST METHODS

The value of bench-scale chemical burners for materials development and selection has been a controversial issue and will probably remain one as long as they are in use. The fact remains, however, that these devices have proved to be quite helpful, especially to those laboratories which, for one reason or another, do not have more elaborate devices. As mentioned earlier, the flat panel test was made an ASTM standard because of its popularity. The need for standardization of this test became apparent during its use in the development of the Polaris missile. Due to the high cost of full-scale rocket motor testing, a number of bench-scale "screening tests" evolved among contractors, Navy laboratories, and materials suppliers. Since no two tests were the same, materials technologists could not compare data from different facilities, nor could they determine which would be the best candidates for an application.

At the request of the Navy's Special Projects Office (Polaris) and the Bureau of Naval Weapons, we coordinated the development of a standard screening test for rocket motor insulation materials using an oxyacetylene burner as the heat source [5]. The latter was selected because of its widespread use, low costs, and fair to good correlation with certain subscale rocket motor tests used in the Polaris development work.

Prior to standardization, however, there was no single, reproducible heat source (all sizes of oxyacetylene torches were used and gas flow rates varied), nor was there a standard specimen size or a common set of rules for test. To solve this problem, a working committee, affiliated with ASTM Committees D-20 on Plastics and E-21 on Space Simulation, was formed from various laboratories using some form of oxyacetylene test. Operating informally on a "volunteer" basis, the task group made a detailed study of the critical parameters influencing the usefulness and reproducibility of the oxyacetylene test and then recommended a procedure and apparatus that was found to be reproducible to about ±5% among six laboratories (see Table 4) [6]. To obtain this precision, the group found it necessary to specify a single commerical torch design and one specimen size. A method of measuring the heat flux or thermal output of the torch also had to be developed, and tolerances were set on test distance, angle of impingement, and gas flow rates. Other minor specifications were also developed. (See Table 1 and reference [3] for test details.)

Table 4. Round Robin Data, October 1963 (Final Results), Oxyacetylene Panel Test Standardization

	Erosion rate, (cm/sec) × 10^3		I_I, insulation index (sec/cm) (time to temp. ÷ specimen thickness)			
			I_I, 200°C		I_I, 400°C	
	for material[a]		for material[a]		for material[a]	
Laboratory	1	2	1	2	1	2
A	5.77	10.8	159	70.5	168	86.2
B	5.08	10.4	139	66.7	162	81.1
C	5.05	9.1	149	65.0	180	81.7
D	5.40	10.1	130	63.2	166	79.1
E	5.04	10.2	149	66.4	180	No data
F	4.80	9.6	71.4[b]	58.5	182	88.5
Average (K)	5.19	10.0	145	65.1	173	83.3
Mean deviation (M)	±0.26	±0.47	±8.60	±2.82	±7.67	±3.22
% Mean deviation (M) × 100 ÷ (K)	±5.0	±4.7	±5.9	±4.3	±4.4	±3.9
Average of two materials	±4.9		±5.1		±4.2	
Overall average % (M)			±4.7			

[a] Material 1: phenolic, polyamide resin, asbestos laminate; material 2: asbestos-filled polybutadiene, styrene rubber.

[b] Not used in average.

To assure widespread acceptance and to get maximum feedback of constructive criticism, the recommended test method was letter-balloted and processed by the usual ASTM procedures. It is estimated that more than 150 organizations and perhaps 200-300 people perused the method prior to its acceptance by ASTM. Comments were carefully considered for possible improvements to the test prior to its publication in final form.

Near the close of the oxyacetylene work, the committee (now grown to over 100 members) turned its efforts to the overall field of ablation testing to see what other procedures needed attention. A quick look at the large variety of applications, test equipment in use, and the infinite combinations of environmental parameters showed that standardization of specific tests should not be attempted. Instead, a policy was adopted to concentrate on subprocedures common to many, if not all, ablation tests and to improve these to the point where anyone using these standard procedures will get maximum accuracy and reproducibility. For example, in measuring ablation performance in an electric plasma arc heater, the tester reports the total enthalpy (thermal input energy) of the arc heater. Since this parameter figures into the use of ablation data in heat shield and in determining reproducibility of test conditions, it is important that it be measured accurately. Thus, the ASTM committee considered it desirable to have a standard procedure for determining total enthalpy. The proposed method was favorably balloted through Committee E-21 level, and it is anticipated that it will be published as a tentative method of test in the 1968 book of ASTM standards. Other areas in which the committee is active include heat flux-calorimetry measurements, thermocouple instrumentation for internal temperature measurements (a proposed recommended practice is ready for publication), surface temperature measurements by optical pyrometry, enthalpy probes for plasma arcs, char and surface recession rate measurements, and definitions and nomenclature. The work of this committee represents a start in a highly complex technology where standardized procedures are badly needed to further the interchange of reliable data between materials scientists and heat shield designers and between various organizations active in the field of ablation technology.

NOL ALPHA ROD TEST

During the evolution of the oxyacetylene panel test, we began the development of an improved ablation test which has come to be known as the

NOL alpha rod test [7]. This procedure consists of subjecting the flat end of a cylindrical specimen to the hot gases of an oxyacetylene burner. The sides of the specimen are isolated from the hot gases by a water-cooled guard ring and the specimen is moved toward the heat source as it ablates. This is shown schematically and pictorially in Figs. 1 and 2, respectively. A small signal is impressed across two concentric electrodes surrounding the specimen. A servo mechanism monitors this signal and maintains a constant voltage across the electrodes by advancing or withdrawing the specimen [8]. Since the position of the char zone has been found to directly influence the ion population in the vicintiy of the electrodes, the servo system moves the specimen at the rate of char progression into the specimen. With the alpha rod test, it is possible to measure the char rate and internal temperature continuously during an ablation test under conditions of one-dimensional heat flow and constant heat flux. This is not possible with other tests, for even with shrouded cylindrical specimens, the test material is stationary and the heat flux at the receding front face varies (with most heat sources, heat flux usually varies down the central axis), and it also is not possible to monitor char rate continuously.

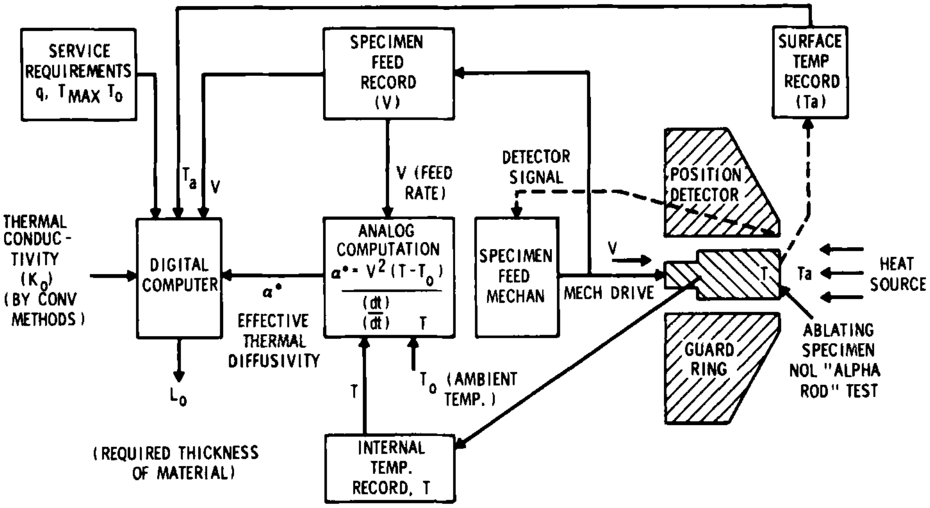

Fig. 1. High-temperature materials program (schematic).

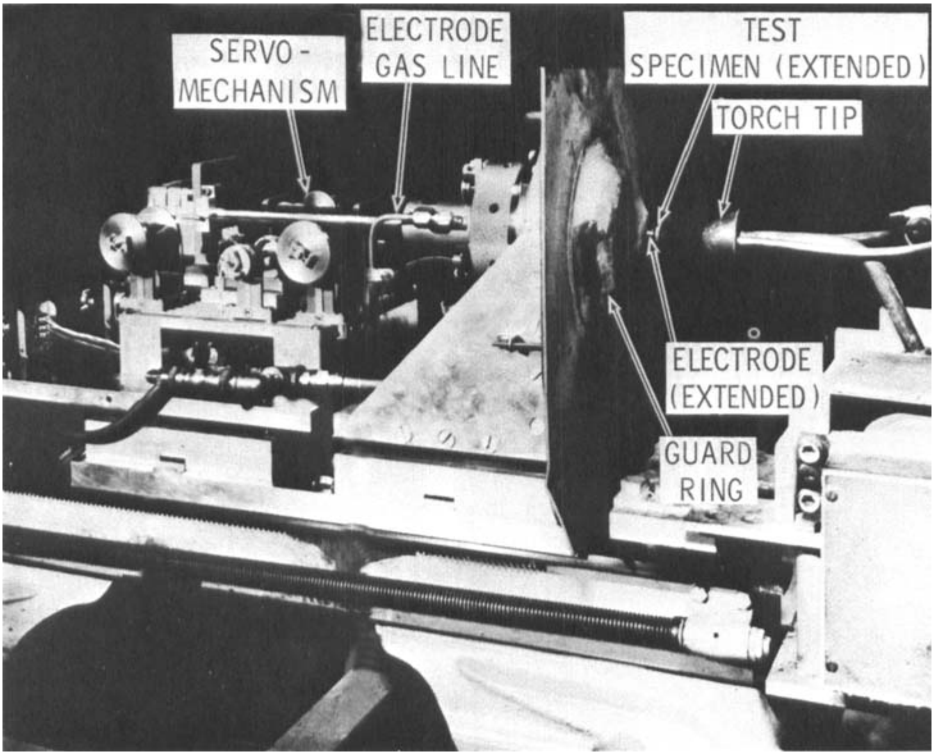

Fig. 2. General view of automatic feed device and oxyacetylene burner.

With the readout from the alpha rod test, it is also possible to calculate the effective thermal diffusivity from the relationship [7]:

$$a^* = \frac{V^2 (T - T_0)}{(dT/dt)_T}$$

where a^* is the effective thermal diffusivity (alpha); V, the feed rate of specimen at steady-state ablation; dT/dt, the slope of internal temperature time record at temperature T; and T_0, ambient temperature.

For the materials developer, the advantages of the alpha rod test are that the data are generated under controlled conditions of constant heat flux and one-dimensional heat flow that cannot be readily obtained in a flat panel specimen or any stationary specimen. Moreover, a continuous measurement of ablation rate and internal temperature is obtained. With this information, a much more reliable indication of ablation performance is afforded the materials scientist to aid him in his efforts to develop superior ablators. While the construction cost is higher and its operation is more complicated than the simpler panel test, the information obtained from the alpha rod test far outweighs this drawback. Some typical alpha rod test data measured on a number of representative ablative materials are summarized in Table 5 [9, 10]. A typical internal temperature-time record measured by a thermocouple placed in a test specimen is shown in Fig. 3. Effective thermal diffusivity data as a function of internal temperature for phenolic nylon are shown in Fig. 4. The general trends of the curves on this graph are typical for many of the materials tested in that the effective thermal diffusivity is minimum (greatest thermal protection) in the range of 200-600°C, the region where most thermal degradation occurs.

Table 5. Alpha Rod Test[a] Data on Some Typical Ablators

No.	Organic binder	Filler	Ablation rate, 10^{-3} cm/sec	Effect. ther. diff. (400°C) 10^{-4} cm^2/sec	Heat of ablation, cal/gm
1	Phenolic	Nylon cloth	19.8	6.3	3,420
2	Phenolic	Silica cloth	1.80	2.0	12,700
3	Phenolic	Asbestos fibers	3.52	8.5	7,950
4	Phenolic	Asbestos mat	3.77	8.2	8,400
5	PBA[b]	Asbestos fibers	6.66	3.3	5,860
6	PBA-phenolic	K oxalate	3.05	1.6	9,015
7	PBA-phenolic	Boric acid	4.31	4.3	6,640
8	Silicone rubber	Cork	15.0	5.8	4,120
9	Phenolic	Pressed cork	13.8	4.0	5,970

[a] Heat flux, 64 cal/cm^2 sec (235 Btu/ft^2 sec); torch design and gas flow conditions as set forth in ASTM E285-65T.

[b] Polybutadiene-acrylonitrile rubber.

In addition to use for materials evaluation, alpha rod test data have been used successfully to predict internal temperature histories in ablating bodies [10, 11]. As shown schematically in Fig. 1, effective thermal diffusivity, a key parameter in heat transfer analysis, is put to use along with ablation rate, surface temperature, material thickness, and heat flux to compute the

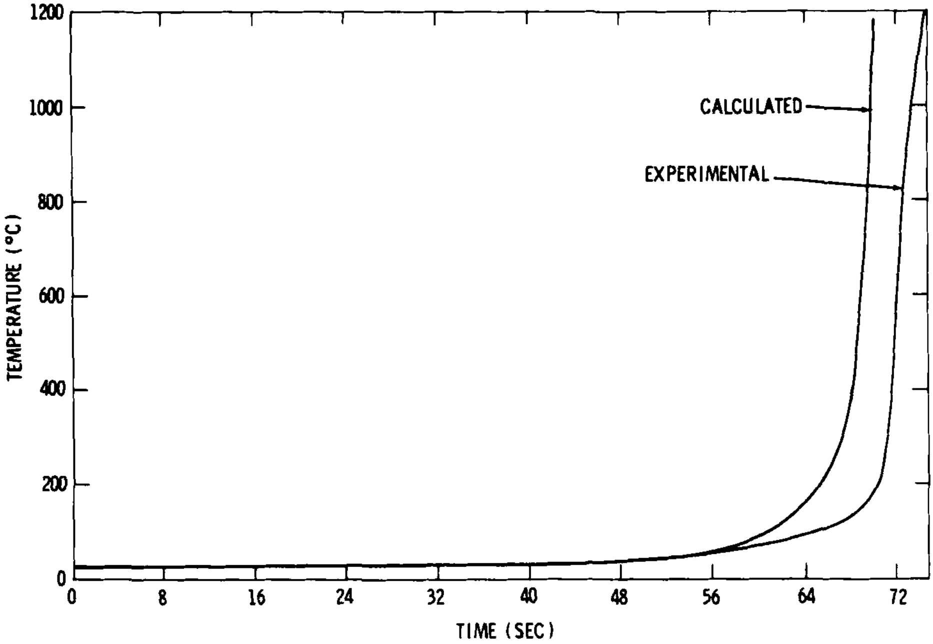

Fig. 3. Experimental and calculated temperature profiles for phenolic nylon (A material) oxyacetylene burner.

internal temperature of an ablating body under conditions of one-dimensional heat flow [12]. The following relationships are used:

$$\delta T/\delta t = a^* \ (\delta^2 T/\delta x^2)$$

$$-K_0(\delta T/\delta x) = \dot{q} \text{ (initial heat-up of front face prior to ablation)}$$

$$x = x_0 - \int_0^t u dt \text{ (after onset of ablation)}$$

$$\delta T/\delta x = 0 \text{ (on the back face)}$$

where T is the temperature; t, the time; a^*, the effective thermal diffusivity; x, the thickness of specimen at time t; K_0, the thermal conductivity at ambient temperature; $\dot{q}$, heat flux; x_0 = initial thickness of specimen; and u = ablation rate.

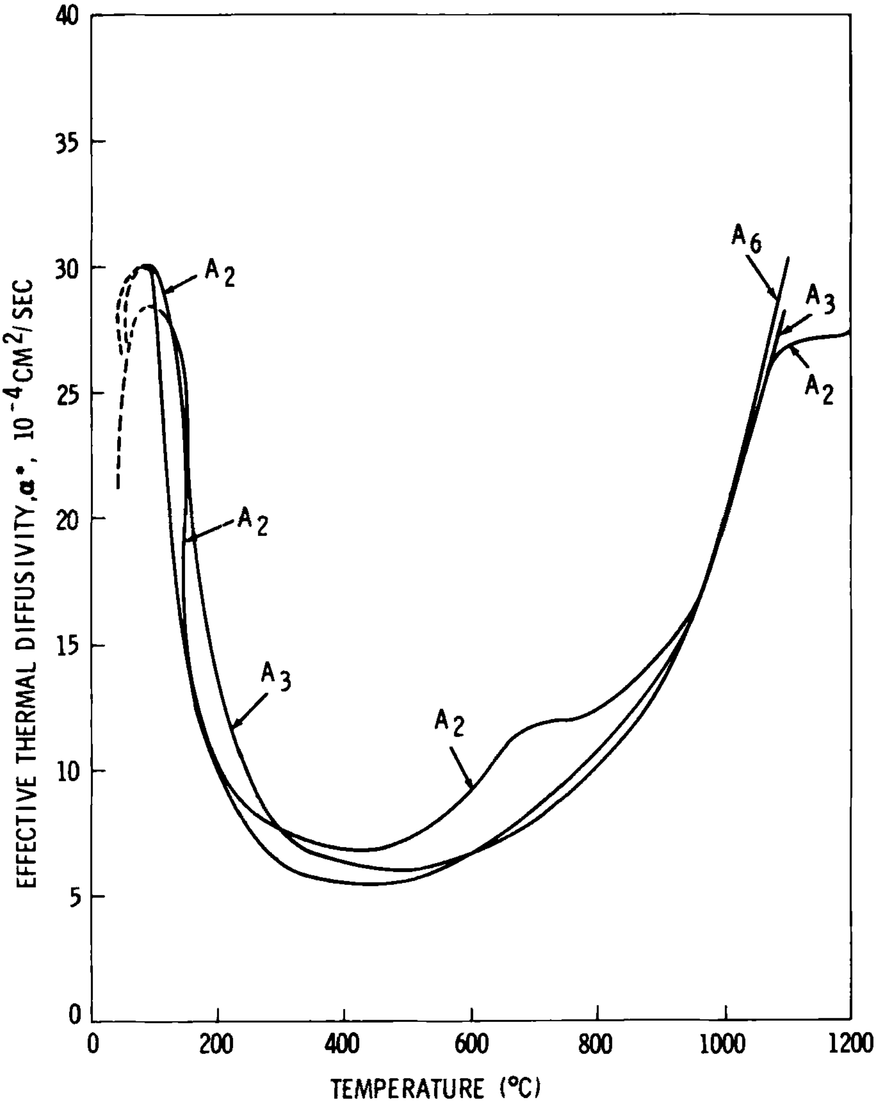

Fig. 4. Effective thermal diffusivity vs. temperature for material A (phenolic-nylon laminate) NOL oxyacetylene burner, 54 cal/cm^2 sec.

This information was programmed on a digital computer and internal temperatures were calculated and compared with those obtained experimentally in the alpha rod test. The results of calculations made for a number of different materials show that it is possible to predict temperatures to within 5-10% of the experimental values. To obtain these accuracies, it was found that it was necessary to measure effective thermal diffusivity and ablation rate under conditions of steady-state ablation. In cases where it was not possible to obtain steady state under the usual test conditions, increasing the heat flux and/or specimen length made it possible to obtain the data under steady-state conditions. A comparison of calculated internal temperature with measured data for phenolic nylon is shown in Fig. 3.

The above technique for computing internal temperature may have direct application in predicting materials thickness requirements for ablative heat shields for both aerodynamic heating and for rocket motor insulation. Present alpha data, however, have been generated for the limited environment of the oxyacetylene burner only. For more practical applications, information is needed with regard to how effective thermal diffusivity varies over a wider range of parameters. The above technique is nevertheless a much simpler procedure than some of the more cumbersome analytical techniques used for predicting ablative performance. It does not, unfortunately, offer a solution to the problem of predicting mechanical or chemical erosion, since this must be measured experimentally. At present, studies are under way at the Naval Ordnance Laboratory to learn if the effective thermal diffusivity technique can be used to predict internal temperatures in ablative liners placed inside the combustion chamber of small-scale rocket motors. If successful, this technique might be gainfully employed to reduce, if not eliminate, the large number of rocket motor tests needed in the design and selection of motor liners.

DEVELOPMENT OF ADVANCED ABLATIVE MATERIALS

Using the concept of "constructive thermal degradation," we have developed a family of new, novel epoxy resin systems equal to or better than conventional phenolic resins in ablative performance [13]. These systems are described in this symposium by G. J. Fleming [14].

SUMMARY AND CONCLUSION

During the past decade, it has become accepted practice to use ablative materials for protecting the structural surfaces of missile propulsion systems. More effective materials formulations have been developed during this period, and methods for test and evaluation have evolved. While this is commendable, it should not be construed as an indication that there is no room for improvement. To reduce the often severe weight penalty imposed by ablative liners, there is a need for lower-density ablators having higher ablation efficiency. Materials resistant to chemical erosion from exotic exhaust gases generated by advanced propellants are also needed. The possibility of higher flame temperatures and combustion chamber pressures also imposes more severe operating conditions. For test evaluation, standard methods should be established for those procedures common to testing, such as measurement of char and recession rate, calculation of heat of ablation, internal temperature measurement, heat flux determination, etc. Finally, effective analytical methods for selecting and predicting the behavior of ablators are needed to reduce the costly and time-consuming practice of rocket motor testing.

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