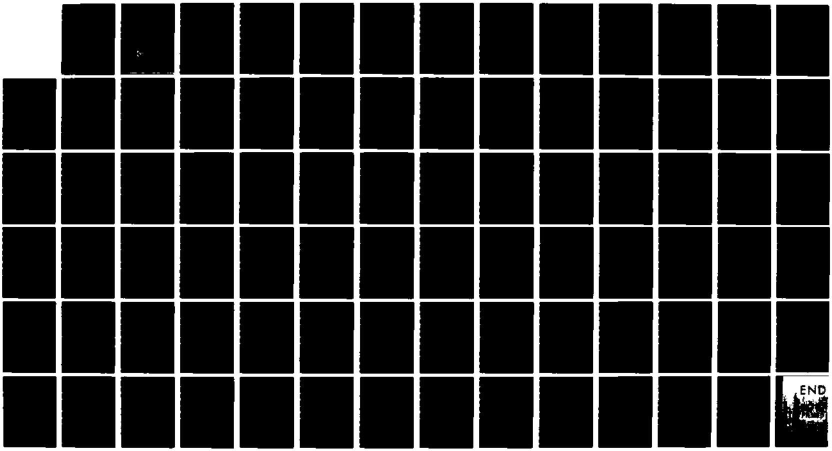
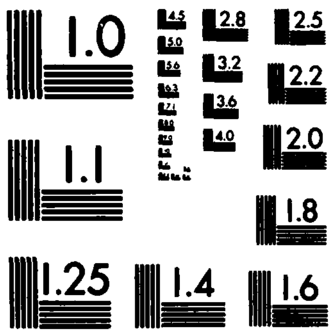
AD-A133 882 CHARACTERISTICS OF VARIOUS TYPES OF ABLATIVE MATERIALS WITH ASSOCIATED NAVAL APPLICATIONS(U) CHARLES STARK DRAPER LAB INC CAMBRIDGE MA J M LEARY MAY 83 1/1

UNCLASSIFIED CSDL-T-811 F/G 11/7 NL




1.0
4.5
5.0
5.6
6.3
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

AD-A133 882

CSDL-T-811

CHARACTERISTICS OF VARIOUS TYPES OF ABLATIVE MATERIALS WITH ASSOCIATED NAVAL APPLICATIONS

by

James Marcellus Leary

May 1983

Ocean Engineering/Master of Science Thesis
Massachusetts Institute of Technology

The Charles Stark Draper Laboratory, Inc.
Cambridge, Massachusetts 02139

Unclass

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A133882
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Characteristics of Various Types of Ablative Materials with Associated Naval Applications	5. TYPE OF REPORT & PERIOD COVERED Master's Thesis
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) James Marcellus Leary	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Code 031 Naval Postgraduate School Monterey, CA 93943	12. REPORT DATE May 1983
	13. NUMBER OF PAGES 79
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclass
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Evaluating thermal insulation materials for use in thermal protection of electronic packages exposed to low heat fluxes for short time durations.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

S/N 0102-LF-014-6601

Unclass

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entere

CSDL-T-811

CHARACTERISTICS OF VARIOUS TYPES OF ABLATIVE MATERIALS WITH ASSOCIATED NAVAL APPLICATIONS

by

James Marcellus Leary
Lieutenant Commander, U.S. Navy
B.S., United States Naval Academy
(1974)

Submitted to the Department of
Ocean Engineering in
Partial Fulfillment of the Requirements
for the Degrees of
Ocean Engineer

and

Master of Science in
Naval Architecture and Marine Engineering

at the

Massachusetts Institute of Technology

May 1983

Signature of Author: ________________________
Department of Ocean Engineering, May, 1983

Certified By: ________________________
Warren M. Rohsenow, Thesis Supervisor

Approved By: ________________________
A. Douglas Carmichael, Reader

Accepted By: ________________________
Chairman, Ocean Engineering Department

CHARACTERISTICS OF VARIOUS TYPES OF ABLATIVE

MATERIALS WITH ASSOCIATED NAVAL APPLICATIONS

by

JAMES MARCELLUS LEARY

Submitted to the Department of Ocean Engineering
on May 6, 1983 in partial fulfillment of the
requirements for the degrees of
Ocean Engineer and Master of Science
in Mechanical Engineering

ABSTRACT

This thesis discusses the thermal and mechanical properties of subliming, melting, charring, and intumescent ablative materials. The use of intumescent ablators as thermal protection in low heat flux environments is emphasized. Models for analysis of transient ablation are discussed. Naval applications of intumescent ablators are examined.

Thesis Supervisor: Dr. Warren M. Rohsenow
Title : Professor of Mechanical Engineering

ACKNOWLEDGMENTS

The author wishes to extend his sincere thanks to Professor Warren M. Rohsenow, for his support and encouragement during the preparation of this thesis.

A special measure of gratitude is reserved for Richard Martorana and the rest of the staff at The Charles Stark Draper Laboratory, Inc. for their support during this research.

The author is deeply grateful to his wife, Bunny, for her patience and understanding during the last three years.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

Symbol	Definition	Units
T	Fahrenheit temperature	°F
ΔT	Temperature rise	°F
k	Thermal conductivity value	Btu/ft-h-°F
ρ	Density value	$lbm/(ft)^3$
C_p	Specific heat value	Btu/lbm-°F
α	Thermal diffusivity value	$(ft)^2/s$
H	Effective heat of ablation	Btu/lbm
$\dot{q}$	Instantaneous heat flux	$Btu/(ft)^2$-s
$\dot{m}$	Mass loss rate	lbm/s
x	Penetration depth	ft
t	Time	s
t_{ss}	Time to steady state	s

CHAPTER 1

INTRODUCTION

Ablation is a complex energy dissipative process whereby a material undergoes combined thermal, chemical, and mechanical degradation accompanied with a physical change or removal of surface material. The material transformation can be in the form of sublimation, melting, char formation, or intumescence. As one researcher, D. L. Schmidt, wrote, "ablative materials are unique in that they can accommodate virtually any temperature or heat flux condition, automatically control the surface temperature, greatly restrict any internal flow of heat, and are able to expand up to thousands of Btu's of energy for each pound of material used."

The field of ablation was an area of extensive research during the preparation for manned space travel and the reusable space shuttle. As with much research that was done in conjunction with space travel, ablation theory has been applied to other areas. For instance, ablative materials have come to be recognized as very effective and practical fire retardant coatings. The U.S. Navy uses ablative materials as hull blast protection from the exhaust of ship-launched missiles. In some applications, ablative materials also contribute to the load-bearing capability of the substrate by adding structural strength. While these uses are varied, there are still further areas of application of ablative materials, and in this thesis the application of ablative materials to shipboard use will be discussed.

This thesis is the result of a combined research effort of myself, and two other researchers, Lieutenants Joseph P. Marques, USN, and Richard A. Schwarting, USN. Our study was concentrated on identifying, analyzing, and evaluating thermal insulation materials to be used for thermal protection of electronic packages exposed to low heat fluxes for short time durations. My thesis discusses the thermal and mechanical characteristics of the major classes of ablative materials. It also discusses the modeling of transient ablation and the naval applications of ablative materials. Lieutenant Marques' thesis, titled "Thermal Evaluation of Ablative Materials in Transient Low Heat Flux Environments", discusses and reports the results of experimental testing of various ablative materials. Lieutenant Schwarting's thesis was devoted to developing a computer simulation model of a particular type of ablator, and is titled "One Dimensional Model of an Intumescent Ablator".

CHAPTER 2

CHARACTERISTICS OF SUBLIMING AND MELTING ABLATORS

Subliming ablators were the orginal ablative material to be utilized in the U.S. space program. Early space reentry vehicles used metal heat sink thermal protection systems composed of copper or beryllium. These heat sinks were too heavy, and placed reentry velocity limitations on the spacecraft. To enlarge the performance envelope of the spacecraft, extensive ablative research was begun. This research effort, which extended for over twenty-five years, resulted in the development of the field of ablation. The first ablative material application to result from this research was the subliming ablator Teflon. Teflon offered reentry vehicle designers substantial weight savings and good insulating properties. Teflon and other subliming ablators were used on the early unmanned space vehicles. The time integrated heat loads experienced by these subliming heat shields were on the order of 10,000 Btu per square foot. The advent of manned space travel required different reentry procedures which resulted in the heat shield experiencing a heat load on the order of 100,000 Btu per square foot. This increased heat load resulted in excessive subliming ablator thickness, and hence the decision to use charring ablators.

The reaction process of the subliming ablator is conceptually simple. The subliming ablator acts as a heat sink to the incident heat flux until the surface temperature reaches the sublimation temperature. At the reaction temperature, the virgin material endothermally sublimes, removing heat from the insulation material. An ablative material such as

Teflon provides very effective insulation due to its low reaction temperature, and high endothermic value for heat of reaction. The reaction process of the subliming ablator is easily modeled, and is often described in heat transfer textbooks.

A melting ablator acts essentially like a subliming ablator, except that instead of subliming at the reaction temperature, it melts. The most common type of melting ablators are quartz and nylon. Melting ablators generally have heat of reaction values similar in value to subliming ablators, but thermal conductivity values much higher than the subliming ablators. When compared to other types of ablators, the melting ablator offers little thermal performance advantage. Ablative literature lists very few uses for pure melting ablators. However, melting ablators are added to some charring ablators to improve the ablative performance of the charring ablator.

The next advance in ablative research was spurred by the development of the space shuttle orbiter. The shuttle designers needed a thermal protection system which would survive a minimum of 100 missions (the orginal target was for a 500-mission life). After a decade of extensive research, the decision was made to use a low erosion reradiating tile. The reentry path of the space shuttle orbiter results in a low heat flux, long duration pulse. The maximum heat load is generally modeled as an instantaneous heat flux of approximately 10 Btu per square foot per second lasting for about 2000 seconds. During this heat flux, the shuttle tiles reach a service temperature on the order of 2300 degrees Fahrenheit. This high temperature results in significant reradiation of heat providing effective insulation to the substrate. Despite this high temperature, the tiles experience very little erosion. The tile thermal protection system is very lightweight, and allows a large cargo load for the shuttle orbiter.

The space shuttle orbiter tiles are silica bricks, and are generally referred to as Reusable External Insulation (REI). The exact classification of these silica bricks is uncertain. Literature classifications of this material vary from nonablating ceramic to subliming ablators. Silica itself is sometimes referred to as a melting ablator. Because the silica tiles sacrifice material in thermally protecting the orbiter, and the fact that the material is generally sublimed due to the high temperature, the author feels that the silica bricks should be classified as a subliming ablator.

The silica bricks are not the only subliming ablator used on the orbiter. For the surfaces which have significant curvature, such as the leading edge of the wings, a subliming carbon composite ablator is used.

The thermal properties of subliming ablators are listed in Table 1. The evaluation of the thermal parameters of the subliming ablators will be discussed in Chapter 6. Basically though, due to the relatively high value of thermal diffusivity, subliming ablators are best suited to long duration heat fluxes. The space shuttle subliming ablators were selected with a design maximum instantaneous heat flux of 50 Btu per square foot per second. On the fuel tanks and rocket motor which accompany the orbiter during the space shuttle system launch, this maximum heat flux is exceeded, and charring ablators are used for thermal protection.

The major obstacle to the widespread use of subliming ablators is the form of application. Subliming ablators are usually produced in tiles. These tiles present bonding problems, vibration resistance problems, and substrate curvature problems. These problems have been demonstrated in the space shuttle program, by the bonding failure of tiles during the first few missions. Despite application limitations, nonspace vehicle uses for subliming ablators are beginning to be recognized. For instance, the U.S. Navy is interested in using subliming ablators as a supplement to an existing ablative blast protection system.

Table 1. Thermal properties of subliming ablators.

Material	ρ	c_p	$k \times 10^6$	$\alpha \times 10^6$
S-1	9	0.23	4.6	2.22
S-2	15	0.23	4.6	1.33
S-3	15	0.24	11.0	3.06
S-4	8	0.24	9.0	4.69

CHAPTER 3

CHARACTERISTICS OF CHARRING ABLATORS

Charring ablative material was the subject of a great amount of research prior to manned space travel. When conducting a literature search on ablation, the great majority of the reports are concerned with charring ablators. The reason for this interest is the wide range of heat fluxes, and environments for which charring ablators provide effective thermal insulation. While intumescent and subliming ablators have somewhat specialized areas of thermal performance, charring ablators are used in the remaining spectrum of heat fluxes and thermal environments. Charring ablators can provide insulation in situations with instantaneous heat fluxes greater than 100 Btu per square foot per second, and time integrated heat fluxes on the order of 100,000 Btu per square foot. Charring ablators also provide excellent insulation in the low heat flux medium pulse duration environments. Char former (synonym for charring) ablative materials have been utilized in numerous aerospace applications.

The physical aspects of the charring ablator decomposition process are illustrated in Figure 1. Initially, the material acts as a heat sink absorbing all of the incident heat flux. The low thermal diffusivity of the virgin material entrains the heat in the surface region causing the temperature of the surface region to rise rapidly. When the material temperature reaches the reaction temperature, an endothermic chemical decomposition occurs. Organic components present in the material are pyrolyzed into various low atomic weight gaseous products and residual carbonaceous material. These gases percolate through the surface of the

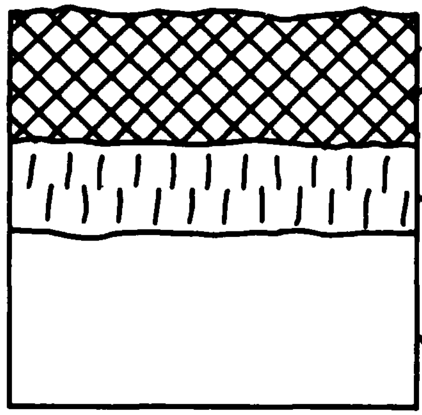


Figure 1. Physical model of a charring ablator.

material into the boundary layer. The temperature of the residual char will continue to increase under the influence of the incident heat flux. Maximum surface temperatures of the surface char can be as high as 2000 degrees Farenheit. If the incident heat flux is greater than 100 Btu per square foot per second significant surface recession will occur.

Charring ablators generally produce a char of sufficient mechanical strength to survive environments of high velocity flows. This strong char and the release of low atomic weight gases into the boundary layer, result in the charring ablator achieving a significant insulation mechanism. The injection of the decomposition gases increases the thickness of the boundary layer, and alters the temperature and velocity gradients. This gradient alteration results in a reduction of convective heat transfer from the environment to the ablating material. The pyrolysis gases provide further insulation by absorbing heat as they pass through the high temperature char material on the surface. The combined insulation effect of the boundary layer thickening, and the heat absorbed by the pyrolyzed gases is termed transpirational cooling.

The char of the charring ablative material can survive high temperatures which results in reradiation from the insulation material to the environment. The magnitude of this reradiation is less than the reradiation achieved by subliming ablators, but is still sufficient to help insulate the substrate.

In summary, the substrate is isolated from a major portion of the incident heat flux through the four mechanisms of the charring ablator. These four mechanisms are:

(1) The heat capacitance of the virgin and char material.

(2) The latent heat absorbed in the endothermic decomposition forming the pyrolyzed gases and the char.

(3) The reduced incident heat flux and cooling achieved via transpirational cooling.

(4) The reduction in the thermal energy of the material due to the reradiation from the surface of the charred material to the environment.

The effect of these four mechanisms are combined into a single term called effective heat of ablation (units of Btu per pound mass). The effective heat of ablation is generally the parameter of major importance when discussing charring ablators.

In equation form, the effective heat of ablation is expressed as

$$H = \frac{\dot{q}}{\dot{m}}$$

As the equation indicates, the magnitude of the effective heat of ablation is a function of the incident heat flux. The greater the incident heat flux, or more severe the thermal environment, the higher the value for effective heat of ablation. Convective heat fluxes also allow greater values for effective heat of ablation due to the insulating effect of transpirational cooling. Because the effective heat of ablation is environmentally dependent, it is difficult to predict the actual ablative performance of a charring ablator without testing.

The high value for effective heat of ablation makes charring ablative material well suited to the severe thermal environment associated with aerospace applications. The major portion of these heat fluxes are of a convective nature due to aerodynamic function. The U.S. Navy has also recognized the value of charring ablators, and is using these materials to thermally insulate the new shipboard missile launching system.

Some charring ablators have very low values for thermal conductivity and thermal diffusivity. Table 2 lists the thermal properties of some charring ablators. Chapter 6 of this thesis discusses the value of these thermal properties of charring ablators. Figure 2 demonstrates the increase in the thermal conductivity value of a charring ablator as the material temperature increases. Figure 3 demonstrates the decrease in the specific heat value of a charring ablator as the material temperature increases. These temperature trends are typical of a charring ablator. Ignoring density effects, the result of these trends is an increase in the effective thermal diffusivity value as the temperature of the material increases.

In general, charring ablators are composite-reinforced organic polymers. The two most common varieties of polymer charring ablators are elastomers and plastics. To facilitate char formation, the charring polymer is of the thermosetting type, which means that it has a high degree of cross linking. The typical charring ablative material designed for high heat fluxes will be a composite of a char forming resinous matrix and a melting ablator. Melting ablators such as nylon are used as gas-generating components, and melting ablators such as silica, carbon, or graphite are used as reinforcing material.

Charring ablators have also been designed for mild heating environments and fire-retardant systems. The most common family of polymer charring ablators used in these environments is the silicone (siloxane) type.

Table 2. Thermal properties of charring ablators.

Material	ρ	c_p	$k \times 10^6$	$\alpha \times 10^6$	H*
C-1	34.0	0.47	11.9	0.75	--
C-2	62.0	0.38	18.6	0.80	2812
C-3	68.6	0.45	22.2	0.73	--
C-4	40.0	--	13.9	--	--
C-5	45.6	--	20.8	--	--
C-6	39.3	--	17.4	--	--
C-7	72.0	0.47	27.8	0.82	5000
C-8	54.0	0.30	23.1	1.43	8000
C-9	102.0	0.28	75.83	2.65	7500

*The effective heat of ablation values are for $\dot{q}$ = 100 Btu/ft^2-s at 1 atmosphere pressure

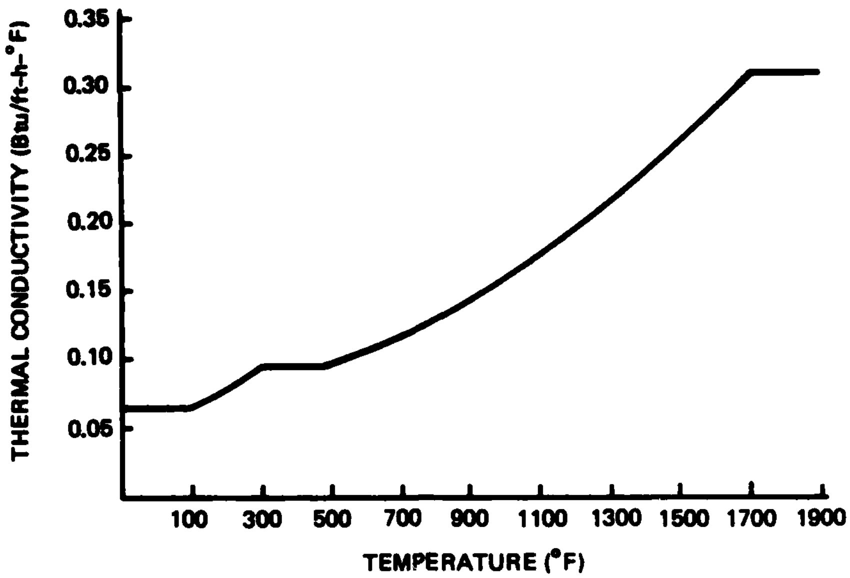


Figure 2. Effect of temperature on the thermal conductivity value of a charring ablator.

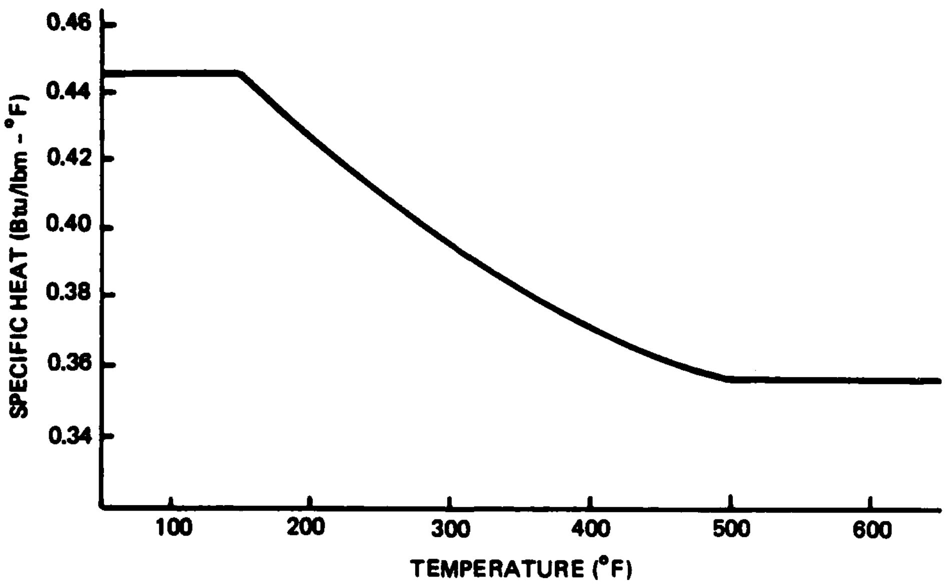


Figure 3. Effect of temperature on the specific heat value of a charring ablator.

Silicon elastomeric polymers have several advantages over other charring ablators. These charring ablators have low values for virgin thermal conductivity and thermal diffusivity. They are also lightweight with relatively good ablative performance. Further, when the silicon material melts it covers the char preventing further oxidation. The silicon elastomers, however, experience very rapid surface recession at heating rates in excess of 100 Btu per square foot per second. Additives including microballons and reinforcement materials are employed in attempts to improve the insulative and ablative efficiency of the silicone-based materials. Silicon rubber in fire-retardant systems provides excellent thermal protection for the substrate, generates very little smoke, and presents a low toxicity hazard. Silicone elastomers are generally limited by their low mechanical strength. The great expense of silicon elastomers is another limitation to their application use.

Recently, silicon elastomer cork has been the subject of much attention. The resulting cork composite has one of the lowest values for thermal conductivity and diffusivity commercially available. With a density value of only 6 pounds mass per cubic foot, the cork composite is a very appealing material for use in aerospace or naval vehicle design. A major drawback to this composite is that it presently has to be applied in sheets. For surfaces that are irregular with numerous appendages, the use of sheets presents an application problem. Some literature has recently been published describing molded cork ablators, but these descriptions are not specific concerning the range of applications of molding techniques.

The thermal performance of the cork composite appears to have limitations. In Lieutenant Marques's testing the cork material experienced a large temperature rise. Also, tests done by Mr. P.J. Schneider indicate that a diathermanous condition of cork allows radiative heat fluxes to pass through the cork causing rapid temperature rises on the surface of the substrate. Good thermal performance has been reported with cork material in time integrated heat fluxes less than 450 Btu per square foot in magnitude. These results are most likely due to the excellent pure insulative properties, rather than the ablative performance of the cork composite.

The mechanical strength of charring ablators vary as do the thermal characteristics. There are low-strength materials (silicone) and high-strength materials (blast protection material). The mechanical strength characteristics of charring ablators will be discussed more fully in Chapter 7. But the point to be made is that mechanical considerations generally do not limit the use of charring ablative material.

CHAPTER 4

CHARACTERISTICS OF INTUMESCENT ABLATORS

Intumescent materials are the most misunderstood ablative materials. In fact, vendor-provided material advertisements will often fail to explicitly state that a material is an intumescent ablator. Intumescence is a heat insulating mechanism where the insulator forms a foam-like material through enlargement, swelling, or bubbling of the virgin material under the action of heat. This type of ablative material is best suited to low heat fluxes and mild thermal environments. Intumescent ablative materials offer two advantages to the insulation designer. First, as the intumescent material expands, the thermal conductivity value decreases, providing excellent insulation for the substrate. Second, the ablative material forms a dense char which cuts off the oxygen supply to the substrate. The most common use of intumescent ablative materials is as a fire-retardant paint protection for metals, plastics, wood, and other materials.

The physical aspects of the intumescent reaction is illustrated in Figure 4. Initially, the material acts as a heat sink absorbing all of the incident heat. As in charring materials, the low value for thermal diffusivity causes the heat to be entrained close to the surface of the material resulting in a rapid rise in the temperature of the surface region. When the intumescent reaction temperature is reached, a pyrolysis generation zone forms. The hot pyrolysis gases produced by the decomposition reactions perculate toward the surface of the ablator.

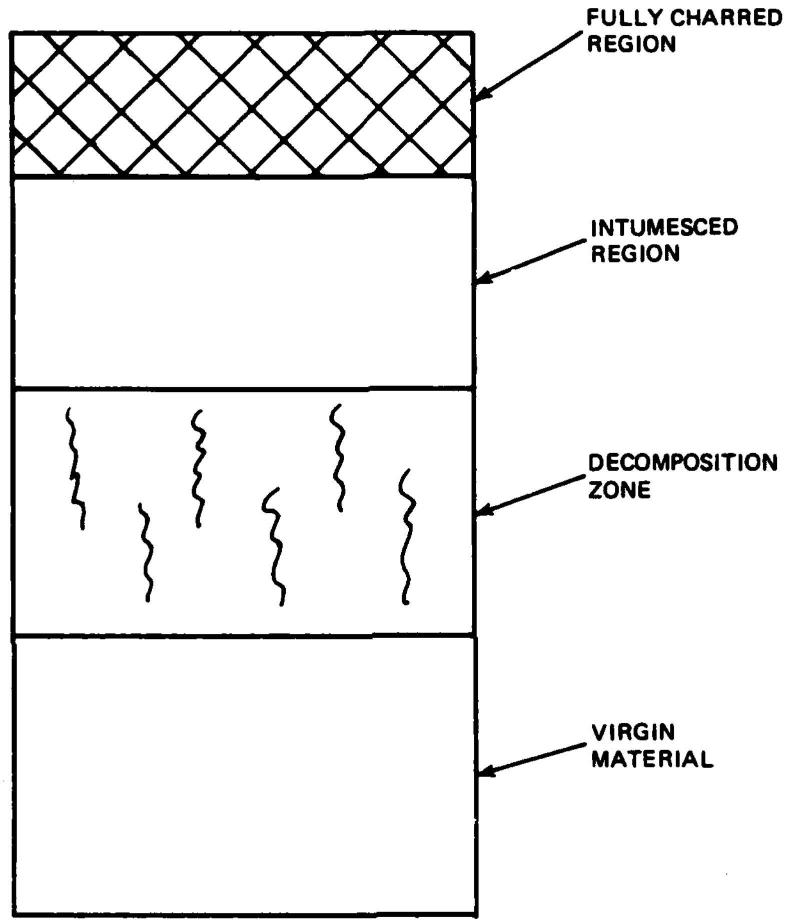
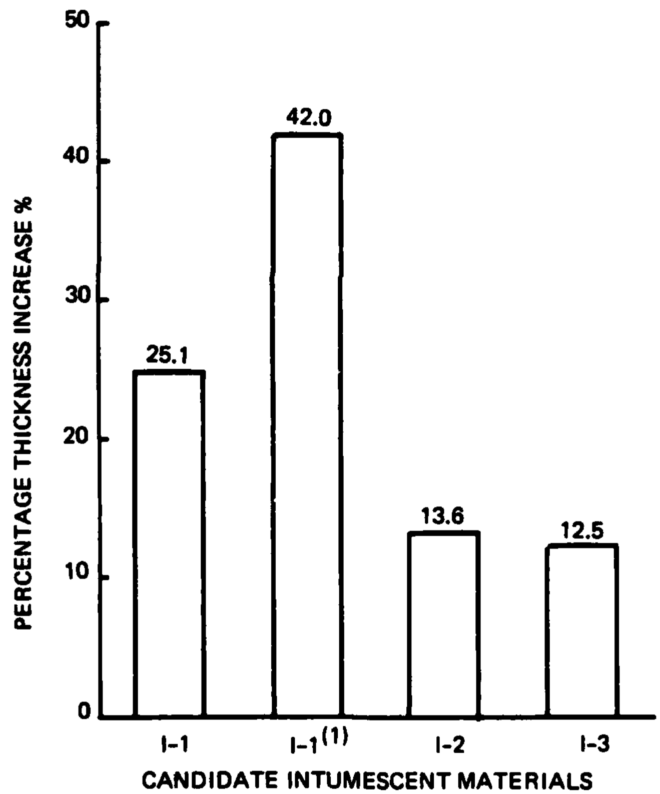


Figure 4. Physical model of an intumescent ablator.

As the gases come in contact with the virgin material, an expanded region of lower density foamy material is formed. This region of foamy material is called the intumesced region. The formation of the intumesced region causes an increase in the total thickness of the insulation material. This increase in thickness can be as much as fifty times the thickness of the original virgin material. Figure 5 shows the intumescent expansion which occurred during Lieutenant Marques' testing. The incident surface of the intumescent material will form a char with sufficient heat input.



NOTE: I-1(1) IS MATERIAL I-1 COATED WITH AN ENVIRONMENTAL VINYLOID TOPCOAT

Figure 5. Expansion of intumescent ablative materials.

The fact that intumescent ablative material forms a surface char results in intumescent materials often being categorized as charring ablators. But the intumescent ablator is much different than the charring ablator. The most striking difference between the two ablators is that the intumescent decomposition reaction is exothermic (heat releasing), while the charring decomposition reaction is endothermic (heat absorbing). The exothermic reaction could combine with the heat from the incident heat flux to reduce the substrate insulation protection. As discussed in Reference 11, the effect of the intumescent exothermic reaction can be counteracted by the addition of endothermic inorganic fillers. While the chemical compositions of commercial intumescents is proprietary, vendors must use endothermic fillers due to the net endothermic reaction of commercially available intumescent materials. Mr. P.M. Sawko and Mr. S.R. Riccitiello of NASA Ames Research Center have done extensive research on the use of the filler material to improve the thermal performance of intumescent ablative materials.

The second major difference between intumescent and charring ablators is the response of the thermal conductivity and specific heat values for the ablative materials to increasing temperature. As shown in Figure 6, the result of the intumescent reaction is a decrease in the value of thermal conductivity as the material temperature increases. As shown in Figure 2 in the previous chapter, the result of the charring reaction is an increase in the value of thermal conductivity as the material temperature increases. As shown in Figure 7, the result of the intumescent reaction is an increase in the value for specific heat as the material temperature increases. As shown in Figure 3 in the previous chapter, the result of the charring reaction is a decrease in the value for specific heat as the material temperature increases. Thus, as the material temperature increases, the thermal diffusivity value for an intumescent ablative material decreases, while the thermal diffusivity value for a charring ablative material increases.

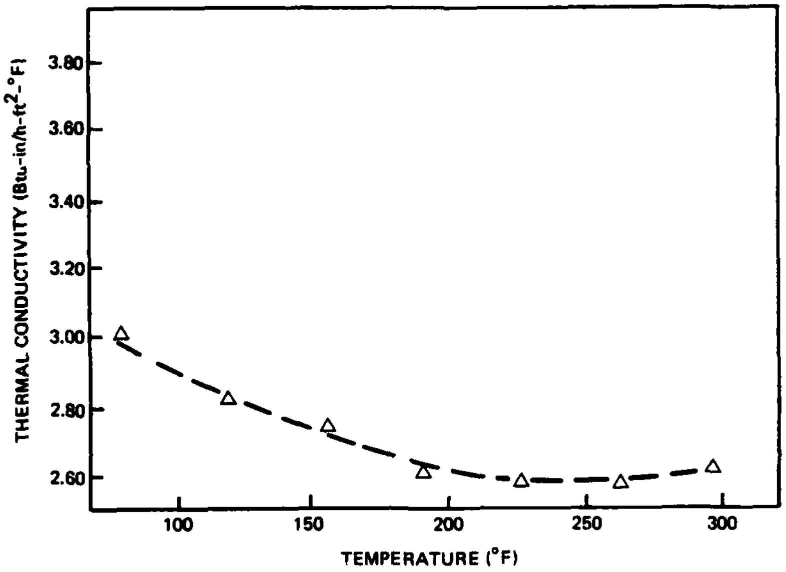


Figure 6. Effects of temperature on the thermal conductivity value of an intumescent ablator.

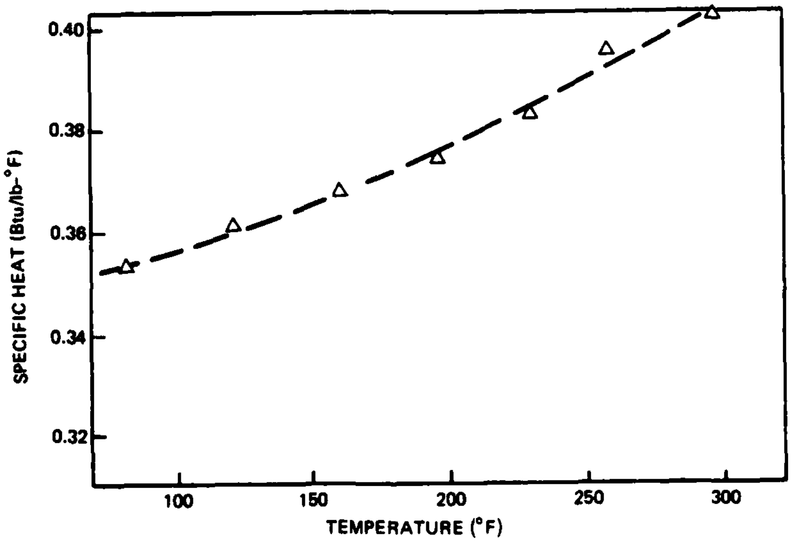


Figure 7. Effects of temperature on the specific heat value of an intumescent ablator.

As mentioned in the previous chapter, charring ablators provide effective insulation due to their high values for effective heat of ablation. However, effective heat of ablation is generally not discussed as a parameter of major importance when considering intumescent ablators. Due to the low net endothermic reaction for the intumescent material reaction, intumescent materials would not survive high heat fluxes or severe thermal environments. The char of the intumescent material does have poor mechanical strength, and the char is generally able to remain intact in environments of only low flow velocities. Thus, intumescent ablators are usually applied to surfaces which will experience primarily a radiant heat flux. Thus, little transpirational cooling is achieved with intumescent ablators. The char of the intumescent ablator will melt at a temperature level of approximately 1000 degrees Fahrenheit, thus, significant reradiation from the surface will not occur.

The value of intumescent ablators lies in their pure thermal insulation properties which become most evident and valuable in low heat fluxes. Thermal properties for various intumescent materials are listed in Table 3. Intumescent ablators are relatively dense, and have high values for heat capacitance. The virgin intumescent materials have low values for thermal diffusivity, and as mentioned before, the value for thermal diffusivity decreases as material temperature increases. The expansion of the material thickness due to intumescence, increases the heat penetration depth to the substrate. For insulation used in transient heat conduction situations, the two most important parameters are a large penetration depth and a low value for thermal diffusivity. The intumescent reaction provides both of these parameters. Transient ablation will be discussed in more detail in Chapter 5, however, in general, the low heat regimes in which intumescent ablators are used are situations of transient heat conduction through the insulation material.

Another value of the use of intumescent ablative materials for use in low heat flux environments is the relatively low temperature at which

Table 3. Thermal properties of intumescent ablators.

Material	ρ	c_p	$k \times 10^6$	$\alpha \times 10^6$	H
I-1	77.8	0.47	37.5	1.03	--
I-2	75.0	0.20	30.5	2.03	--
I-3	85.5	0.35	69.4	2.32	2130
I-4	55.0	0.46	35.5	1.40	--
I-5	87.3	0.42	64.0	1.75	--

intumescence begins. As shown by Figure 6, the intumescence reaction has generally occurred by the time the insulation material temperature reaches 250 degrees Fahrenheit. For charring ablators, the reaction temperature is generally in the range of 400 to 500 degrees Fahrenheit. Thus, while an intumescent ablator has a lower net endothermic heat of reaction than a charring ablator, the intumescent reaction occurs at a lower temperature. For low heat fluxes, this lower temperature of reaction is of insulation value, but for higher heat fluxes, the large value of the charring heat of reaction outweighs the fact that it occurs at a higher temperature.

Lieutenant Marques tested the thermal insulation performance of intumescent and charring ablators during his thesis research. He exposed the ablative materials to a radiant instantaneous heat flux of magnitude 10 Btu per square foot per second for periods of 45 to 200 seconds. These tests demonstrated that insulation performance of the ablative materials is sensitive to total heat load. As shown in Table 4, during the 45-second heat flux the two best insulators were both intumescent ablators. However, during the 200-second heat flux, one intumescent and one charring ablator were the two best insulators. In practice, intumescent ablative materials are used in applications where the time integrated heat flux is less than 1000 Btu per square foot. The results and implications of Lieutenant Marques's testing will be more fully discussed in Chapter 6.

Intumescent ablative materials possess good mechanical strength properties. The ablative coating is capable of adding structural strength to a structure and surviving the blast from a missile rocket. The range or mechanical properties of the intumescent material, which are discussed in Chapter 7, give this ablative material a wide range of applications. One physical parameter that does limit the use of intumescent material is density. Due to the high density value of this ablative material, there is a weight penalty associated with its use.

Table 4. Results of thermal testing.

Material	ΔT 45 s	Ranking*	ΔT 200 s	Ranking
I-1	149.7	1	158.8	1
I-2	194.5	2	243.4	3
I-3	276.9	9	280.2	4
C-1	229.0	6	N.T**	-
C-2	240.3	7	340.0	5
C-3	225.6	5	225.6	2
C-4	216.9	4	N.T.	-
C-5	208.8	3	369.0	7
C-6	250.9	8	350.4	6

*The lower the ranking, the lower the temperature rise.

**N.T. means not tested.

Most commercial applications of intumescent materials are as a paint or trowelable coating for fire-retardant purposes. As a paint coating, intumescent material is used in the fields of civil engineering, aerospace and aviation vehicles, and naval architecture. Intumescent ablative materials are being increasingly used in composite insulators. The intumescent material is applied as a paint over foam material. The result is a very effective, inexpensive, and lightweight insulator. Another significant value to the use of intumescent ablative paints is that they generate only small amounts of toxic combustion gases when exposed to a heat flux.

CHAPTER 5

MODELING OF TRANSIENT ABLATION

As in most physical processes, ablation processes have both a transient and steady-state regime. While there is no definitive transition time, D.L. Schmidt has expressed the time for steady-state ablation to occur in the following equation

$$t_{ss} = \alpha\left(\frac{\rho H}{\dot{q}}\right)^2$$

The transition time for steady-state ablation varies for the different ablative environments. For the high heat flux situation where charring ablators are used, the transition time can be less than one second. For the long duration heating situations encountered by the space shuttle orbiter, the transition time is on the order of 80 seconds. For fire-retardant situations where intumescent ablative material is used, the transition time is on the order of 200 seconds.

In modeling the ablation process that will occur in high heat flux environments, the thermal and chemical reactions that occur during the transient period are generally assumed to be insignificant in relation to the reactions that occur during steady-state ablation. This same assumption can be made in modeling the ablation process that the space shuttle orbiter tiles experience. With the transition time for steady-state ablation being less than 5 percent of the flux duration experienced by the subliming ablators, the aforementioned assumptions appear logical. Thus, by considering only the steady-state regime, these ablation processes can be modeled by closed form solutions to integral equations. These solution techniques are generally similar to the Goodman Integral Technique. These techniques minimize computer cost and time consumption in performing studies of the complex problem of the coupled phenomena of conduction and ablation. Using assumed exponential profile approximations (which have been refined with experience) surface recession and in-depth temperature response have been accurately predicted.

In low heat flux environments of short or medium duration, the transient ablation process can not be ignored. This is the modeling situation of intumescent and some charring ablators. In Lieutenant Marques's testing program, the pulse duration of 45 seconds was of major concern. This pulse duration was well less than the time required to reach steady-state ablation. Also, ablative materials intended for use in fire-retardant systems, where the heating duration is on the order of 3 to 5 minutes, require transient analysis.

The transient response of an ablative material is extremely complex, and the mathematical models to describe this response require more simplifying assumptions and approximations than in steady-state ablation to achieve even a numerical solution. For transient ablation, implicit finite difference techniques are generally employed to solve the energy equation and the transient heat conduction equation. These sophisticated techniques use computer simulation of the governing differential equations, and allow designers to vary boundary conditions and properties of the ablative material. The complete transient solution will include the decomposition in depth with the attendant density variations and temperature profiles.

In his thesis, Lieutenant Richard A. Schwarting, USN, modeled one-dimensional transient ablation of an intumescent material under the influence of a low heat flux. With an extensive literature search, he found a very efficient finite difference ablation computer program written by Donald M. Curry of the Manned Spacecraft Center located in Houston, Texas. The report detailing this computer program is titled

An Analysis of a Charring Ablation Thermal Protection System, while the computer program itself is titled "Standard Ablation Program (STAB II)". This analytical model determines the transient one-dimensional ablation thermal response of a charring ablative material and substrate structure. The charring ablator is assumed to be composed of three distinct regions or zones. These zones are:

(1) The charred material zone.

(2) The zone where the ablation reaction occurs.

(3) The zone consisting of the virgin or unaffected material.

While specifically designed to model a charring ablator, the reaction zone of the STAB II program can be modeled as an intumescent layer through the user's input of conductivity and heat of reaction values. The STAB II program does not accept a "negative" surface recession, or in other words, the expansion of an intumescent material.

The STAB II program is a sophisticated design tool which permits a variety of environmental conditions and thermal boundary conditions. The range of application of the model is increased by its ability to accept up to twelve separate backup materials with or without air gaps between the individual materials. Thermophysical properties of the ablative material may be constant or functions of one or two variables. When heated, the rate of decomposition of the ablating material is modeled by the Arrhenius kinetic rate expressions. This allows the ablation process to be sensitive to variations in pressure and temperature. The surface heat inputs can be in the form of incident heat flux (convective or radiative), or in the form of in-depth temperature time histories. The output of the model includes in-depth temperature response of the ablative material and substrate structure and instantaneous and time-integrated heat flux information.

Ablation modeling similar to Lieutenant Schwarting's thesis has been performed at the National Aeronautics and Space Administration Ames Research Center (NASA Ames). The Chemical Research Projects Office of NASA Ames has pioneered in the development of intumescent paints, and rigid and semirigid foams for application as thermal protection systems. These researchers have also modified an existing charring ablation simulation program (Aerotherm Charring Material Thermal Response and Ablation Program) to treat both charring and intumescing materials. The modified program is titled Aerotherm Transient Response of Intrumescing Materials (TRIM). This program is tailored specifically to a certain intumescent coating developed by NASA Ames. The authors of the program, in the article "Analytical Modeling of Intumescent Coating Thermal Protection System in a JPS Fuel Fire Environment", discuss the sensitivity of the program to thermophysical data of the ablating material. The ablation modeling done at NASA Ames was supported by the thermal testing of Mr. P.M. Sawko and Mr. S.R. Riccitiello.

As highlighted by the NASA Ames work and verified by Lieutenant Schwarting's work, the accuracy of the finite difference computer solutions is a direct function of the ability of the designer to describe the temperature and time variations of the thermophysical properties of the ablating material. This limitation requires that thermal testing be done in concert with computer modeling to allow the adjustment of the model to reflect the actual ablation phenomena. Lieutenant Marques's thesis study was the thermal testing to support Lieutenant Schwarting's computer modeling.

The work of Lieutenants Schwarting and Marques was a form of a technique for determining thermophysical properties called nonlinear parameter estimation. With this technique, a researcher first conducts an experiment measuring the thermal response to a known heat flux. Concurrently, an accurate computer simulation is developed. Next, a nonlinear parameter estimation computer algorithm is used to determine the thermal properties of the material. This algorithm derives the thermal properties of interest that result in the final simulation predicted thermal response duplicating the actual experiment result. The thermal properties thus derived are those which must have existed in order for the measured response to have occurred. While Lieutenant Schwarting's program did not have a nonlinear parameter estimation algorithm, by manually varying thermal properties, he was able to match Lieutenant Marques's test data. Lieutenant Schwarting's analysis resulted in the determination of an "effective" thermal conductivity value for the ablating material which compensated for the inability of the computer model to handle the intumescent swell.

The Naval Surface Weapons Center located at Dahlgren, Virginia has begun a testing program using nonlinear parameter estimation techniques to determine thermal conductivity values of virgin and intumescent ablative material, the intumescent reaction temperature range, and the proper coefficients of the Arrhenius expressions. Lieutenant Schwarting's work indicated that these quantities were of major importance in matching actual ablation performance. The purpose of the Navy Surface Weapons Center work was to conduct a parametric study of a generic class of intumescent ablative materials. The result of this study would be the identification of the most important thermal characterisitics which contribute to the thermal insulation performance of the ablative material. The knowledge of these characteristics is hoped to be used to design new more efficient intumescent ablators.

In this chapter, the modeling of conductive heat transfer has been primarily concerned with one-dimensional heat flow. Because the work motivating this thesis was in low heat flux regimes for short time durations, two- or three-dimensional effects were assumed to be insignificant. The accuracy of this assumption was verified by Lieutenant Marques's testing. However, in many ablative material applications, such as reentry heat shields, multidimensional heat transfer and ablation are of major importance. For these applications, the influence of the multidimensional heat fluxes on the time-dependent surface and internal temperature responses must be ascertained.

CHAPTER 6

PREDICTING THERMAL PERFORMANCE OF ABLATIVE MATERIALS

More often than not, when selecting an ablative material, designers do not always have clear cut selection criteria. While some thermal properties of the ablative materials are known, there are generally more unknown properties than known. For instance, when evaluating an intumescent ablative material, the virgin properties are known, but the properties of the intumesced and char material are generally unknown. Also, the parameter effective heat of ablation is environmentally dependent requiring testing under operating conditions to determine its numerical value. The purpose of this chapter is to provide some insight for the evaluation of the thermal properties of ablative materials, with particular emphasis on intumescent ablators.

There does appear to be a usable selection criterion for the evaluation of subliming ablators for use on the space shuttle orbiter. As discussed by Mr. P.J. Schneider (Reference 8), in weight-critical designs with low but prolonged heating, the overal thermal effectiveness of an ablating material can be evaluated by the following parameter

$$\rho \frac{k}{c_p}$$

The subliming ablators are assumed to achieve the same degree of reradiation, therefore relative thermal performance is determined by pure thermal conduction properties. The above parameter resembles thermal diffusivity, except that the parameter density is the numerator vice the denominator of the ratio. The lower the numerical value for this parameter, the more thermal insulation the ablative material will provide. Table 5 lists various subliming ablators, and the associated values for this evaluation parameter.

For melting and the other types of subliming ablators, the parameter (ρkTH) is an index to steady-state thermal performance. Ablative materials with the lowest value of the parameter will have the lowest ratio of heat flux conducted through the material to heat flux incident to the surface of the material. The use of this parameter is limited to the few applications of melting and nonreradiating subliming ablators.

The two aforementioned evaluation parameters are the only two indices that are discussed in ablation literature. The vast majority of the evaluation of ablative materials is done via specific thermal testing. For the space program various charring ablators were tested under simulated flight environments. While the results of these tests give designers precise performance information, the cost of this evaluation approach is extremely high.

The purpose of the research that motivated this thesis was to identify the material which provided the most effective thermal insulation for an electronic package. This package would be exposed to a radiant heat flux with a time-integrated heat flux equal to or less than 1000 Btu per square foot, and an instantaneous heat flux approximately equal to 10 Btu per square foot per second. The current material in use is an intumescent ablator, but opinions had been offered that silicon-based charring ablators would thermally perform better than the present material. For this insulation task, weight was not of primary concern. This research was considered a preliminary investigation or survey, which was to be supported with nonsimulation laboratory testing.

To select the candidate materials to be included in the test program, the various ablative materials were ranked according to the

Table 5. Thermal performance parameter for reradiating subliming ablators.

Material	$\sqrt{\frac{\rho k}{c_p}}$	$\alpha \times 10^6$
S-1	0.0134	2.22
S-2	0.01730	1.33
S-3	0.0263	3.06
S-4	0.01732	4.69

thermal conduction properties of their virgin material. Based on the scarcity of ablative literature concerning the low heat flux, short duration thermal environment, the researchers felt that insulation properties would be of more importance than ablative properties. Also, this selection criterion favored silicon-based charring ablative material. The equation for temperature rise in a semi-infinite body due to a constant heat flux from the text, Conduction of Heat, was used to rank the various ablative materials. This equation is

$$\Delta T = \frac{2\dot{q}\sqrt{\alpha t}}{k} \text{ ierfc } \frac{x}{2\sqrt{\alpha t}}$$

Based on this initial analysis, the research team decided to select nine materials for evaluation. The selected materials included three intumescent ablators, three silicon charring ablators, one epoxy resin charring ablator, one silica fiber charring ablator, and one silicon-filled cork charring ablator. The ranking of these materials based on the above equation is included as Table 6.

The thermal testing that was conducted is detailed in Lieutenant Marques's thesis (Reference 16). The materials were exposed to an instantaneous radiant heat flux of 10 Btu per square foot per second for durations of 45 and 200 seconds. The materials were evaluated by the maximum amount of temperature rise experienced at a selected depth in the material sample. Table 7 lists the results of these tests.

There are many interesting results from this thermal testing. The most important result from this work is the verification that the presently used intumescent material (I-1) provides the most effective thermal insulation for both the short and long heat flux pulse. Another important observation of these test results is that thermal ranking is heat-load dependent. As the pulse duration changed, so did the ranking.

Table 6. Initial ranking of the candidate ablative materials.

Material	Ranking*
C-1	1
C-2	2
C-3	3
C-4	4
I-1	5
C-5	6
C-6	7
I-2	8
I-3	9

*The lower the ranking, the lower the expected temperature rise.

Table 7. Results of thermal testing.

Material	ΔT 45 s	Ranking*	ΔT 200 s	Ranking
I-1	149.7	1	158.8	1
I-2	194.5	2	243.4	3
I-3	276.9	9	280.2	4
C-1	229.0	6	N.T**	-
C-2	240.3	7	340.0	5
C-3	225.6	5	225.6	2
C-4	216.9	4	N.T.	-
C-5	208.8	3	369.0	7
C-6	250.9	8	350.4	6

*The lower the ranking, the lower the temperature rise.

**N.T. means not tested.

While the intumescent material I-1 performed consistently well on both pulse duration tests, the performance of all the intumescent materials was not as consistent. The intumescent material I-2 performed relatively well on the short duration pulse, but its relative performance was degraded by the longer pulse duration. Conversely, the intumescent I-3 performed poorly during the short duration pulse, and its relative performance improved during the long duration pulse. The performance trends of the intumescent ablative materials I-2 and I-3 match their applications. The I-2 material is used primarily in low heat flux fire-retardant applications. The I-3 material is used in higher heat flux environments, such as blast protection from ship-launched missiles.

The intumescent material thermal performance ranked according to the thermal diffusivity value of the virgin intumescent material. The lower the thermal diffusivity value, the lower the temperature rise experienced by the ablative material. Table 8 shows the thermal performance ranking, and the thermal diffusivity values of the intumescent materials. The ranking did not change with the change in pulse duration. These results indicate that possibly the virgin thermal diffusivity is a reasonable performance measure of intumescent ablative materials. Only three materials were tested, thus the sample size is too small to make a significant conclusion. There does appear to be value though, in conducting a thermal testing program similiar to Lieutenant Marques's to check the validity of the virgin thermal diffusivity ranking.

While the thermal performance of intumescent ablative materials ranked according to a quantitative parameter, the thermal performance of the charring ablators did not. Further, there was no quantitative measure with which to distinguish between the thermal performance of an intumescent and charring ablator. Before beginning the testing program, the researchers had hoped that vendor-provided thermal data could be used to rank the thermal performance of the ablative materials. Table 9 lists the thermal test ranking, and thermal conductivity, thermal diffusivity, and heat capacitance of the virgin ablative materials. Effective heat of ablation values, and reaction temperatures of the materials could not be used, due to the fact that these pieces of data are not provided by each vendor. Table 9 demonstrates that there does not appear to be a parameter with which to predict thermal performance. This indicates that thermal testing appears to be the only method of evaluating the suitability of an ablative material for a specific insulation task.

The ablative literature indicates that there will be an eventual performance crossover between intumescent and charring ablators as the heat load increases. While there was an improvement in the ranking of one charring ablator (C-3) during the longer pulse duration, a significant crossover in performance was not evident. It would be of interest to continue the testing program at higher heat loads to find the performance crossover point. However, based on this testing, the general use of intumescent ablative material in applications with heat loads less than 1000 Btu per square foot appears to be sound.

The author believes the value of intumescent ablative materials in low heat loads lies in the low effective thermal diffusivity of the material. As shown by Table 10, intumescent materials experience a relatively small mass loss during the heat flux exposure. Combining this small mass loss with the increase in specific heat value of the ablative material as temperature increases, causes the intumescent material to have a mugh higher "effective" heat capacitance value than the charring ablators. Also, the intumescent materials show a decrease in thermal conductivity values as temperature increases, while a charring ablator has an increase in thermal conductivity values as temperature increases. The combined effects of heat capacitance, and thermal conductivity with increasing temperature causes some intumescent materials to have lower thermal diffusivity values than charring ablators. This lower "effective" thermal diffusivity appears to be the reason that the intumescent material performs well in low heat loads.

Table 8. Thermal performance of candidate intumescent ablative materials.

Material	ΔT 45 s	ΔT 200 s	$\alpha \times 10^6$
I-1	149.7	158.8	1.03
I-2	194.5	243.4	2.03
I-3	276.9	280.2	2.32

Table 9. Ranking of thermal test results and themal property values of candidate ablative materials.

Material	Test Ranking*			Thermal properties**	
	45 s	200 s	$k \times 10^6$	$\alpha \times 10^6$	ρc
I-1	1	1	8	4	6
I-2	2	3	7	5	1
I-3	9	4	9	6	4
C-1	6	-	1	2	2
C-2	7	5	4	3	3
C-3	5	2	6	1	5
C-4	4	-	2	-	-
C-5	3	7	5	-	-
C-6	8	6	3	-	-

*For test ranking, the lower the ranking, the lower the temperature rise.

**For thermal properties, the lower the ranking, the lower the numerical value of the property.

Table 10. Percentage mass loss of candidate ablative materials during thermal testing.

Material	Percentage Mass Loss
I-1	4.2
I-2	2.4
I-3	7.7
[illegible]-1	19.7
-2	11.5
3	3.6
[illegible]	0.4
	18.9
	0.2
	7.6

CHAPTER 7

MECHANICAL PROPERTIES OF ABLATIVE MATERIALS

While most ablative materials are not used as structural members of the substrate, the mechanical properties of an ablative material contribute to the range of applications. Some ablative materials are used isolating the substrate from impinging jet blasts, while other ablative materials are used in fire-retardant systems with little associated mechanical stresses. The required mechanical properties of an ablative material are generally described in a qualitative sense. While the thermal or heat requirements of an ablative material are generally precisely delineated in terms of temperature rise of the substrate, designers can not usually describe accurately the mechanical stresses that an ablative material will require. The mechanical acceptance of an ablative material is then usually based on the designer's experience and testing.

Table 11 lists the mechanical properties of various ablative materials. This list demonstrates that charring ablators have a wide range in values of mechanical properties. Charring ablators have been used as lightweight thermal protection for missiles and as flash protection for missiles and as flash protection also have a variety of application techniques.

This research effort was mostly concerned with the mechanical properties of silicon-based charring ablators. As shown in Table 11, the silicon-based materials have low values for tensile strength, lap shear, and hardness. Additionally, there has been mention of a

Table 11. Mechanical properties of some ablative materials.

Ablative Material	Specific Gravity (lb/in^2)	Tensile Strength (lb/in^2)	Lap Shear	Hardness D Scale	Cure Time at Room Temperature (h)	Pot Life (min)	Contains Silicone
S-1	0.144	70	-	-	-	-	NO
C-1	0.55	330	-	-	-	-	YES
C-2	1.00	3000	2000	60	24	120	NO
C-3	1.10	240	360	50	24	120	YES
C-5	0.73	40	100	40	24	120	YES
C-6	0.63	40	100	40	24	120	YES
C-7	1.15	6100	-	-	-	-	NO
C-8	0.865	315	-	50	-	-	NO
C-9	1.44	12,600	-	-	-	-	NO
I-1	1.25	810	680	65	24	30	NO
I-2	1.20	960	1740	68	24	30	NO
I-3	1.37	900	1350	77	24	30	NO
I-5	-	-	1230	69	-	-	NO
I-6	-	-	1570	69	-	-	NO
I-7	-	-	1740	60	-	-	NO

piezoelectric effect that occurs when silicon-based materials are subjected to a compression-decompression cycle. Some of the silicon- and nonsilicon-based charring ablators failed to properly bond to aluminum plates during the preparation for thermal testing. The reader is encouraged to read Lieutenant Marques's thesis (Reference 16) for details on the bonding problem. Other applications of silicon-based charring ablators use reinforcing filler material of honeycomb metallic structures to improve mechanical strength. However, these reinforcements substantially degrade the thermal insulation property of the silicon-based materials.

When compared to silicon-based charring ablators, intumescent ablative materials have relatively high values for mechanical strength. The larger mechanical strength values correlate with the intumescent material having greater density values than the silicon-based charring ablators. The candidate intumescent materials were easily bonded to aluminum plates for thermal testing. In some applications, though, bonding problems have occurred with intumescent ablators due to porosity from entrained solvent or improperly prepared metallic surfaces. Intumescent materials have a wide range of application methods. These methods include spraying, troweling, and injection molding. It is interesting that in the low heat flux regime, intumescent ablative materials not only provide good thermal capabilities, but also good mechanical properties.

Some values of mechanical properties of subliming ablators are included in Table 11. These low density materials are chosen to provide lightweight thermal protection. Strength considerations are not the primary concern with subliming ablators for applications such as the space shuttle orbiter.

When evaluating the suitability of an ablative material for a particular application, mechanical testing is generally required. Bondability is a major acceptance criterion which should be evaluated. Unfortunately, bondability is extremely sensitive to environment and temperature. Therefore, the test environment should simulate the actual operating environment as much as possible. Probably the most informative bondability tests are the lap shear and peel test. Ease of application and curability of an ablative material should also be evaluated. Degradation of ablative material performance has been reported for some application due to water saturation, oil contamination, ultraviolet radiation, or fungus attack.

Once an ablative material, especially a polymer, is selected, the mechanical values of hardness, tensile strength, and lap shear strength become production quality indices. While it is difficult to determine when the mechanical values become unacceptable, a significant difference from the normal values acts as a possible indication of loss in production quality and control. Using the relatively simple and straightforward tests for the mechanical properties users can be generally assured that an ablative material will perform its required function.

CHAPTER 8

USE OF ABLATIVE MATERIALS IN PROTECTING SHIPBOARD STRUCTURES FROM MISSILE EXHAUST GASES

The major advancement in naval weaponry since World War II has been the development and deployment of ship-launched missiles. While the size and weight of missile systems is roughly equivalent to the size and weight of naval gun systems, the extremely hot gases flowing at supersonic velocities from ship-launched missiles posed a unique design problem to naval architects. Ship designers, now, had to contend with the problems of thermal expansion causing possible failure of the missile launching mechanisms, thermal fatigue of heated hull structure, and unwanted heat transfer through decks and bulkheads to various spaces in the ship. Since the early 1960's the Navy has used ablative materials to achieve the blast and thermal protection necessary to allow missile systems to be successfully integrated into ship designs.

Before 1975, the Navy used a charring ablator with asbestos fillers as the primary thermal coating for missile launchers and deck areas. This coating performed adequately for normal missile launching exercises, and had a reasonable degree of tolerance to sea and shipboard environments. Two major deficiencies with this charring ablator became evident. First, the asbestos filler was a carcinogenic material, and hence its removal was required by a 1975 Navy policy guideline. Second, the Navy began to develop sophisticated anti-aircraft weapon systems which required rapid launching of missiles. This rapid or "ripple" launch had been shown by fleet exercises to place too great a heat load on the charring ablator. Missile launchers protected with the charring ablator were shown to experience too much thermal expansion, and jammed or failed during rapid launches.

Due to the aforementioned two deficiencies with the charring ablator, the Navy began two replacement research efforts. One research effort was to find a commercially available ablative material which could be applied via troweling to existing missile launchers, and could thermally perform at least as well as the present charring ablator. The second research effort was much more extensive, and is an on-going program. This research effort required testing and modeling of various ablative materials to determine their thermal response. The object of this effort was to identify the ablative materials that should be used in a new missile launching system being developed by the Navy. Both of the research efforts were performed at the Naval Surface Weapons Center located at Dahlgren, Virginia.

Mr. John Shea of the Naval Surface Weapons Center was responsible for the selection of the alternate material for the previously used charring ablator. His ablative material candidates included both intumescent and charring ablators. For the thermal testing, each candidate material was exposed to a rocket motor exhaust with an associated time integrated heat flux of less than 1,000 Btu per square foot. This rocket motor exhaust plume did contain aluminum oxide, an especially erosive material. For mechanical property evaluation, the candidate materials were exposed to various severe environments. In addition, candidate materials were evaluated on: ease of mixing, substrate surface preparation for bonding, storage life, trowelability, cure time, survivability to deck traffic, cost, and repairability.

The candidate material which performed well in all areas was an intumescent ablative material called Flexfram 605. The intumescent coating was somewhat expensive, but not prohibitive. The selection of an intumescent coating is not surprising. The heat transfer rate of less than 1,000 Btu per square foot is in the normal range for intumescent ablative material. Mr. Shea stated in his report that as the heat flux was reduced, the ablative performance advantage of the intumescent material was increased. Also, as discussed in Chapter 7, the mechanical strength of an intumescent material is generally greater than charring ablative materials used in low heat flux environments. There was an added weight penalty due to the higher density of the intumescent material, but it was felt that the added weight would not degrade the performance of the ablative material. As a result of Mr. Shea's work (references 18 and 27) Flexfram 605 has become the standard ablative coating for use on conventional "above main deck" shipboard missile launchers.

While the selection of an intumescent coating did solve the asbestos contamination problem, and did improve the thermal performance of the launcher coating system, some serious limitations to missile operations did still exist. Through testing it was found that using only trowelable ablative materials, that even an intumescent coating would survive only one full magazine missile launch. Also, the rapid missile launch would still cause launcher failure. Due to the design and movement of the conventional missile launchers, and the ship hull movement in seaways, it was felt that a trowelable material would be the only material capable of covering all the required areas, and at the same time have the necessary strength. These limitations indicate that the conventional launcher, and associated intumescent coating, are inappropriate for use in a dense anti-aircraft warfare scenario where rapid missile launches are expected. However, for the scenarios of the launch of some short-range cruise missiles, antisubmarine missiles, and self-defense anti-aircraft missiles, the conventional missile launcher protected with an intumescent coating is indeed appropriate. For the latter scenario, the limitations of the intumescent coating system result in virtually no degradation of normal missile operations.

In concert with the heat transfer problems associated with rapid launches, weapon designers had become aware of the susceptibility of conventional missile launchers to fragment damage. In an anti-aircraft scenario, a ship might not suffer a direct hit from a missile, but the fragments from an exploded missile might strike a launcher, rendering it nonoperational. This situation became apparent during the Vietnam War, when a cruiser was struck by only fragments from an exploded missile. Pierside, the cruiser appeared undamaged; however, the entire anti-aircraft suite was severely degraded by pierced radars, and pierced hydraulic and electrical lines to the launcher. To reduce this so called "cheap kill" possibility, the Navy decided to develop a missile launching mechanism which would be entirely within the skin of the hull with no protrusions above the main deck. This launching device is called the Vertical Launching System (VLS) due to the vertical launching orientation of the missiles.

The heat transfer situation in the VLS is much different than in the conventional missile launcher. The rapid launch requirement, and the development of a longer range cruise missile increased the heat load by at least an order of magnitude. The use of intumescent ablative material was not even considered due to this high heat load. As mentioned previously, a second research effort was conducted to test and evaluate the thermal performance of various charring, subliming, and melting ablators for use in the VLS. The results of these tests showed that subliming ablators of the carbon-carbon composite type experienced the least erosion when exposed to the test rocket exhaust plume. Both charring and melting ablative material suffered more erosion. However, the lower thermal conductivity of the charring ablator resulted in less heat penetration through the insulation material. The melting ablator did not offer any performance advantage. The erosion of the charring ablator, while greater than the erosion of the subliming ablator, was not unmanageable. The result of this testing was the design of replaceable charring ablative tiles, which could be replaced by ship's force personnel when warranted. These ablative tiles consisting of rubber modified glass phenolic would be located in the plenum of the launcher where the full rocket motor exhaust would be experienced. The rest of the missile launcher would be protected with a cast in place charring ablator.

The ablative system designers for the VLS were able to concentrate more on the thermal capabilities than the mechanical capabilities of the ablative materials. While the ablative materials would be exposed to the rocket exhaust of the missile, these materials would not be exposed to deck traffic, hull deflections, or the sea environment. Because the ablative material would not be repaired by ship's force personnel, trowelability was not a factor in the VLS design.

While it was decided that subliming ablative material was not best suited to the VLS design, researchers were very impressed by its performance. At present, research is being conducted to design subliming carbon-carbon tiles to be used with the intumescent coatings on conventional missile launchers. These carbon-carbon tiles would be small and placed only in the areas of greatest erosion of the intumescent coating. The object for the use of these tiles is to reduce the amount of coating maintenance required by ship's force personnel.

The result of the charring ablative system design for the VLS is a weapon system which can very capably handle the heat transfer load associated with a dense anti-aircraft scenario. Testing has shown that the VLS is capable of rapid missile launch, and long-range cruise missile launch. Designers estimate that the VLS can fire seven complete magazines of missiles before refurbishment becomes necessary. The VLS ablative system is also capable of allowing a complete restrained firing (missile does not leave launcher) of a missile. This restrained firing does necessitate refurbishment of the ablative material after the firing of the magazine. However, the missile launcher and the rest of the magazine is still available to an operational commander after the restrained firing. Because the charring ablative system effectively isolates the heat penetration from the rocket exhaust, the VLS can be easily integrated into a ship design. The installation of the VLS on cruisers and destroyers is scheduled to begin in the near future. The ships that will be outfitted with the VLS will also have advanced electronics and radars, which will make these ships the most capable anti-aircraft combatants in the world.

CHAPTER 9

USE OF INTUMESCENT ABLATIVE MATERIALS AS FIRE RETARDANT COATINGS FOR SHIPBOARD APPLICATION

"Fire at sea is one of the most feared hazards and one of the greatest dangers confronting shipboard personnel, both in wartime as well as during peacetime operations. Fire is often the cause of impaired mission capability, and a major hindrance to continued operation and combat efficiency in battle. Peacetime fires, whether caused by accident or arson, pose an equally serious problem. Some of the most tragic fires have resulted in casualties, considerable loss in property, costly repairs, and tedious and vexing clean-up operations." This quote from the article "Fire Safe Materials for Navy Ships" written by Dr. D.R. Vertriglio succinctly expresses the need for improved fire protection, and fire-retardant systems for shipboard use.

In the late 1960's, the Navy experienced the two largest shipboard fires since World War II, neither of which were the result of enemy or hostile action. In July 1967, the aircraft carrier, the U.S.S. Forrestal experienced an accidental onboard firing of a five-inch rocket. This simple pilot error resulted in a catastrophic aircraft carrier flight deck fire. The end result of this fire was over two hundred million dollars of damage, and the loss of life of 134 crew members. When most present Navy members hear the name of the U.S.S. Forrestal, they are reminded of the fire-fighting training movie they watched during their indoctrination training. This movie graphically shows the tragic death of members of the fire-fighting team as bombs on the flight deck exploded due to the heat of the fire. Less than two years after the U.S.S. Forrestal fire, another serious aircraft carrier flight deck fire occurred.

In January 1969, a rocket warhead onboard the U.S.S. Enterprise allegedly exploded due to heat impingement of the exhaust from a jet engine starter unit. The explosion and associated fire resulted in extensive damage to the ship and onboard aircraft, and serious injury or loss of life of 108 crew members. Safety board findings from both aircraft carrier fires concurred that shipboard fire-fighting teams simply had insufficient time to control and extinguish the fires before other munitions ignited and exploded.

In the past fourteen years, two research efforts involving the use of intumescent coatings were begun to improve the fire safety of ships. One research effort was specifically designed to find an ablative coating which would reduce the danger of self-ignition (cook-off) of ammunition. The second research effort was an experimental evaluation of the response of various materials to shipboard fires. Unlike the case of ablative research for missile launchers, these two research efforts were done by different groups with no interaction. While the results of the ammunition self-ignition prevention research have been applied, the results of the second research effort have not received the attention they deserve.

After the second aircraft carrier fire, the Navy became interested in finding a coating which could be applied to munitions to decrease the munitions tendency to self-ignite. At the Naval Weapons Center located at China Lake, California, different munitions and missile warheads were exposed to burning JP-5 aviation fuel. These tests were designed to simulate an aircraft carrier deck fire. Under these experimental conditions, unprotected munitions and warheads exploded within three minutes of exposure to the fuel fire. With present active fire-fighting equipment and a normal degree of training, a shipboard fire-fighting team generally requires five minutes to control and extinguish a fire.

After establishing the need for a coating system, the Navy Weapons Center began testing various coating materials. These tests showed that an intumescent ablative coating when applied to the warhead of a rocket increased the average time for self-ignition to at least 8.5 minutes.

The selected intumescent coating for these tests was a commercial product manufactured by Pfizer Corporation named Firex. The Firex coating was applied as a paint with normal spray equipment. Due to the proven fire retardant capability of the intumescent coating and ease of application, standards were established for the use of the intumescent paint on selected munitions and rocket warheads. To ensure fire safety, the intumescent coating is also applied to the pipes and valves of the aviation fuel handling systems, and on selected bulkheads in areas where an aviation fuel fire might occur. Unfortunately, these standards for the use of intumescent paints apply only to aircraft carriers.

The next tragic shipboard fire occurred in November 1975, when the aircraft carrier, the U.S.S. Kennedy, and the guided missile cruiser, the U.S.S. Belknap, collided. This accident depicted at the same time the merit in the use of intumescent ablative coatings, and the need for further use of passive fire retardant coatings on Navy ships. On board the U.S.S. Kennedy, the collision ruptured aviation fuel lines causing a major fire. However, helped by the use of intumescent paint coatings, the aircraft carrier fire-fighting teams were able to quickly contain the fire, and with the loss of only one life, extinguish the fire. A short time after the collision, the U.S.S. Kennedy was able to continue its assigned mission with full combat capability. The true heroes in the containment of the aircraft carrier fire were the qualified fire-fighting teams, and the excellent fire-fighting equipment. Nevertheless, it should be pointed out that passive fire retardant intumescent paint allowed these active fire-fighting procedures to be carried out.

The effect of this collision on the U.S.S. Belknap was much different. Immediately after the collision, a major fire started on the superstructure of the cruiser. This fire was initially fueled by the aviation fuel dropped from the aircraft carrier flight deck. The fire spread quickly through the superstructure, and divided the ship in half longitudinally with a wall of fire. Fire boundaries could not be set, and therefore, the fire continued to spread rapidly. The heat from the fire caused some magazine munitions to self-ignite. An officer aboard the cruiser remarked that the fire spread so quickly that fire-fighting teams were unable to become organized. This remark is similar to the findings of the investigations of the 1960's aircraft carrier fires. If the other ships in the area had not provided quick and effective assistance, the damage to the cruiser would have been more extensive. The result of the collision and fire on the cruiser was the loss of six lives and millions of dollars in damage. The U.S.S. Belknap required over three years to repair.

In 1969, the Navy contracted the Center for Fire Research at the National Engineering Laboratory, National Bureau of Standards to research shipboard fire safety. The purpose of this research was twofold:

(1) To improve interpretation and application of present fire testing methods.

(2) To develop improved laboratory test methods which could provide meaningful correlation with observed fire buildup in actual fires.

This research project was structured into three phases. The first phase was a review of shipboard construction materials to determine fire performance. The second phase was the development and performance of laboratory fire tests which modeled actual shipboard fires. The third phase was the interpretation and application of the testing done in the second phase.

The Center for Fire Research conducted full-size and quarter-scale shipboard compartment fire tests. The results of these tests provided valuable insight concerning the behavior of various materials in actual fires. This research lead to the concept of flashover. Flashover is defined as the condition when thermal radiation levels become high enough to simultaneously ignite combustible materials within a compartment. The concept of flashover was then used to evaluate the performance of passive fire retardant coatings. The condition of flashover equates to a bulkhead temperature of approximately 1200 degrees Fahrenheit, and a radiant heat flux on the order of 6 Btu per square foot per second.

The Center for Fire Research tests demonstrated the value intumescent ablative paint coatings have as a passive fire retardant coating. As shown by Table 12, in compartments with the hot bulkhead coated with an intumescent paint, the flashover condition did not occur within ten minutes. The intumescent paint coating sets effective passive fire barriers which allow shipboard fire-fighting teams the needed time to extinguish a fire. The thermal performance of the intumescent paint reported by the Center for Fire Research appears reasonable based on the testing done by Lieutenant Marques and E-Systems Inc.

The Center for Fire Research showed another significant advantage to the use of intumescent ablative coatings. Experimental tests showed that intumescent coatings greatly reduced the overall generation of carbon monoxide, hydrogen cyanide, hydrogen chloride, and smoke in compartment fires. The intumescent paints were shown to be especially suited for use on submarines. The reduction in both the spread of heat and generation of smoke and potentially hazardous combustion gases by intumescent paint coatings allow the normal cooling and filtering systems of the submarine to maintain a safe atmosphere.

The experimental testing done by the Center for Fire Research demonstrated that an intumescent coating, to be fully effective, should be applied to a thickness of at least 0.025 cm. The normal decorative paint is applied to a thickness of approximately 0.010 cm. Since decorative paint and the intumescent paint have approximately the same density, there is a weight penalty of about 0.03 pounds per square foot of intumescent application. This appears to be a small weight penalty considering the fire retardant value of the intumescent coating. However, this does not mean that every bulkhead in a ship should be coated with intumescent paint.

Table 12. Results of Center for Fire Research thermal tests.

Material	Average Bulkhead Temperature (°F)	Average time to flashover (min)
Decorative paint	1425	0.5
Intumescent paint	680	>10

Note: Results based on full scale compartment testing with the same heat input from a gas burner.

Considering the fire tragedies the U.S. Navy has had in recent years, and the research findings of the Center for Fire Research, one would expect that the U.S. Navy aggressively utilizes intumescent coatings. However, while the Navy does employ intumescent coatings for isolated applications, there appears to be little interest by ship designers in fire retardant coatings. The author contacted the design teams of the current major Navy ship designs, and found very little design effort (except for submarines) is being applied to make ships less susceptible to the rapid fire spreading that occurred on the U.S.S. Belknap. The ship designers, when asked about fire retardant systems, would reply that the Navy active fire-fighting systems are sufficient to protect ships and crews. The ship designers base their opinions on preliminary findings of the British experience during the Falkland Island War. The findings indicate that if the British had employed U.S. design practices concerning compartment air- and watertight integrity, and active fire-fighting procedures, the fire damage to their ships would have been significantly less. The author does not dispute the value of active fire-fighting procedures, but the author does find that ship designers have not fully grasped the lessons of the U.S.S. Forrestal, U.S.S. Enterprise, and the U.S.S. Belknap experiences. Without a time margin to set fire boundaries and organize fire-fighting efforts, a shipboard fire-fighting team's effectiveness can be severely limited.

At present, the U.S. Navy has specifications for the application of intumescent paint on aircraft carriers, submarines, and the new mine countermeasures ship (MCM). The aircraft carrier application has been previously discussed, and the following is a discussion of other applications.

To prevent the detonation of magnetic mines, the new MCM ship has a wooden hull structure. Also to save weight in the design, nonmetallic materials have been used extensively throughout the ship. The designers were concerned about the effect a full fire in the engine room of the MCM would have on the strength of the hull girder system. To prevent hull damage, specifications were made for the use of intumescent paint in the entire engine room. While this is very effective use of the ablative fire retardant coating, it does not appear that the intumescent paint is fully utilized for this design. Considering the ship is heavily constructed of composite materials with reduced fire capability, fire retardant coatings should also be used extensively in design. While this is a weight critical design, the low weight penalty of the intumescent coating should not degrade the ship design.

The ship type that most effectively uses intumescent fire retardant coatings is the submarine. Polyvinyl chloride nitrile (PVC) rubber foam material is used for both thermal and acoustic insulation on the interior of submarine hulls. However, the Center for Fire Research testing has shown this rubber foam poses a serious fire hazard due to flame spreading. This danger is accentuated due to the confined space, and very limited means of securing refuge from fire and combustion products on board a submarine. The Center for Fire Research conducted specific tests on the feasibility of coating the PVC foam material with intumescent paint. These tests demonstrated that the ablative coating effectively reduces the fire spread danger of the foam material. Also, the intumescent paint reduced the amount of harmful combustion products released to the atmosphere. As a result of the Center for Fire Research work, intumescent fire retardant coatings are used extensively on U.S. submarines.

In addition to the U.S. Navy, the offshore platform industry is interested in using fire retardant intumescent coatings as structure protection. During the Twentieth Annual Marine Coatings Conference, laboratory fire tests of structures were presented. These tests demonstrated that unprotected beams and columns under normal design loads collapse when the steel temperature reaches 1000 degrees Fahrenheit. When exposed to a fire, an unprotected column or beam can collapse after as little as ten minutes of exposure. These tests further showed that when red hot steel reacts with fire-fighting or other water, very explosive hydrogen gas results. The offshore industry has recognized that intumescent coatings provide the required fire retardant performance. Currently, the American Bureau of Shipping and the U.S. Coast Guard are involved in attempting to set standards for the use of fire retardant coatings. These coatings will be used to provide protected personnel escape routes and refuge areas where crews can await rescue. In addition, coatings will be used to protect essential services such as power cables, piping, and life support equipment.

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

The major conclusions and recommendations of this thesis concern intumescent ablative materials. While few articles are published on intumescent ablators, the field of application of this material is great. As a fire-retardant coating, intumescent paints provide a very effective passive fire barrier which allows time for active fire-fighting procedures to be carried out. The use of these paints is growing, but this growth is limited due to the scarcity of intumescent literature and advertisement. The weight and cost of intumescent ablative materials are not significant impediments to possible widespread use. As one thinks about the use of fire-retardant coatings, more applications come to mind. For instance, Professor Rohsenow, the advisor to this thesis, observed that intumescent paints would be an excellent way of "fire proofing" a safe.

The U.S. Navy has a mixed approach to the use of intumescent ablative material. The weapon-system designers use intumescent ablators as a trowelable missile blast protection for the ship hull. These designers are conducting extensive research to develop performance standards and analytical models for the intumescent materials in use. This research is centered on determining the thermal conductivity and decomposition behavior of the intumescent material. This work is in the forefront of intumescent ablative materials research. Unfortunately, this level of recognition of the value of intumescent materials is not shared bv the ship designers. While Navy-funded research demonstrated the effectiveness of intumescent paint as a fire-retardant coating, ship designers do not appear to fully appreciate the utility of this material. Intumescent paints are used effectively on aircraft carriers, submarines, and mine countermeasure ships; however, these ships account for less than 30 percent of the U.S. Navy inventory. The lack of published information is probably the reason for this lack of application. For instance, in a recent article in the Naval Engineers Journal titled "Fire Safe Materials for Navy Ships" (Reference 3), intumescent paint received only limited attention. Nevertheless, ship designers need to reevaluate their use of intumescent paints so as to help prevent shipboard fire tragedies that have occurred in the past.

The work of this thesis research team resulted in some findings concerning the thermal performance of intumescent ablative materials and areas for further research. The reader is encouraged to read the theses of Lieutenants Schwarting and Marques (References 16 and 17) to fully understand the work of the research group.

The major finding of this research effort was that the baseline intumescent material (I-1), for the application of concern, provided the most effective thermal insulation of the candidate materials. The performance ranking of the baseline material did not change with the change in heat load. Further, Lieutenant Schwarting proved that it was possible to accurately model the temperature response of this intumescent material. The mechanical properties of the baseline intumescent material compared very favorably with the other candidate materials.

An interesting result was observed when the baseline intumescent material with a vinyloid coating was tested. The specimens with the coating experienced a larger thickness growth (see Figure 5), and a smaller temperature rise than the uncoated specimens. The vinyloid coating which is applied only to prevent handling damage results in improved thermal performance of the intumescent material. This coating effect should be evaluated further to verify the improved thermal performance. If verified, the computer model should be adjusted to account for the coating effect.

The research team was unable to develop a performance index with which to rank the thermal performance of the candidate materials. The finding that the thermal performance was heat-load dependent was anticipated before beginning the testing program. Thus, it appears that the only way of determining the relative performance of different types of ablative materials is through specific testing. Obviously, the more the test environment approximates the actual environment, the more validity there will be in the test results.

While the thermal performance of all the candidate materials could not be ranked according to a distinct parameter, the thermal performance of the intumescent materials could be ranked according to virgin thermal diffusivity values. Table 8 demonstrates that the lower thermal diffusivity values of the intumescent material correspond to a lower material temperature rise. This result was consistent for both pulse durations. With a sample size of only three materials, it is difficult to make a definitive conclusion. However, the results do suggest that there is a possibility of using the thermal diffusivity parameter to rank intumescent thermal performance. Further testing would be required to verify this performance index. Appendix B, a list of intumescent material manufacturers, is provided to aid in further intumescent testing.

The continued thermal testing of the candidate materials at higher heat loads would be of interest. Ablative literature indicates that at some level the heat load will be high enough that the charring ablators will provide more effective insulation than intumescent ablators. The higher heat loads should result in the parameter, effective heat of ablation, becoming more significant in the insulation process. It would be interesting to verify the existence and value of the performance crossover heat load.

APPENDIX A

CROSS REFERENCE OF ABLATIVE

MATERIAL INDICES TO PRODUCT NAME

AND MANUFACTURER

SUBLIMING ABLATORS

Index	Product Name	Manufacturer
S-1	LI-900	Lockheed Corp.
S-2	LI-1500	Lockheed Corp.
S-3	Fibrous Silicon	Generic
S-4	MOD 1A REI	General Electric Co.

CHARRING ABLATORS

Index	Product Name	Manufacturer
C-1	893-5	Avco Systems Division
C-2	DE-370	Flamemaster Corp.
C-3	DE-350	Flamemaster Corp.
C-4	Fiberfrax LDS	Carborundum Corp.
C-5	S-886	Flamemaster Corp.
C-6	S-885	Flamemaster Corp.
C-7	NYLON PHENOLIC	Generic
C-8	325	Dow Corning Corp.
C-9	REFRASIL PHENOLIC	Hughes Aircraft Co.

INTUMESCENT ABLATORS

Index	Product Name	Manufacturer
I-1	FIREX RX-2373	Pzifer Inc.
I-2	CHARTEK 59	Avco Systems Division
I-3	FLEXFRAM 605	Fiber Materials Inc.
I-4	FIREX RX-2376	Pzifer Inc.
I-5	EX-IC-82	NASA-Ames
I-6	2370 NS	Rockwell International Corp.
I-7	477	Ocean Chemical Co.

APPENDIX B

LIST OF MANUFACTURERS OF INTUMESCENT ABLATIVE MATERIALS

	Manufacturer	Product Name
1.	Pzifer, Inc.	Firex RX-2370
	640 North 13th Street	Firex RX-2373
	P.O. Box 548	Firex RX-2376
	Easton, Pennsylvania 18042	
2.	AVCO Systems Division	Flamarest 1600B
	Lowell Industrial Park	Chartek 59
	Lowell, Massachusetts 01851	
3.	Fiber Materials, Inc.	Flexfram 605
	Biddeford Industrial Park	
	Biddeford, Maine 04005	
4.	Ocean Chemical Co.	987
	440 Magazine Avenue	47-135
	Savannah, Georgia 31402	478
		477
5.	Albi Manufacturing	107A
	98 East Main Street	
	Rockville, Connecticut 06066	
6.	Atomic Weapons Research	Mk1
	Aldermaston	Mk2
	Reading, England	

	Manufacturer	Product Name
7.	Glidden-Durkee Division SCM Corporation 900 Union Commerce Bldg. Cleveland, Ohio 44115	Insul-Blaze 5027
8.	Iowa Paint Manufacturing Co. 17th and Grand Avenue Des Moines, Iowa 50309	Fire-Plug 5550
9.	M.A. Bruder and Sons, Inc. 52nd and Grays Avenue Philadelphia, Pennsylvania 19143	Flame-Shield 76-100
10.	NASA-Ames Research Center Moffett Field, California 94035	169 313 EX-IC-82
11.	Naval Air Development Center Warminster, Pennsylvania 18974	P-124
12.	Naval Surface Weapons Center White Oak Silver Spring, Maryland 20910	INSUNOL NX-1871
13.	Randolph Products Co. 92 North 12th Street Carlstadt, New Jersey 07072	37886
14.	Rockwell International Corp. Space Division 12214 Lakewood Blvd. Downey, California 90241	2370 AH 2370 NS
15.	VIMASCO Corp. Nitro, West Virginia 25143	FRP 62-10 IA WC-1

REFERENCES

1. Schmidt, D.L., Thermal Parameters of Reentry Ablative Plastics, Wright Air Development Division Technical Report, WADD TR60-101 1960.

2. Schmidt, D.L., Ablation of Plastics, Directorate of Materials and Processes Aeronautical Systems Division, Air Force Systems Command, ASD TR61-650, 1962.

3. Ventriglio, D.R., "Fire Safe Materials for Navy Ships," Naval Engineers Journal, Vol. 94, No. 5, October 1982.

4. Rohsenow, W.M., and J.P. Hartnett, Handbook of Heat Transfer, McGraw-Hill Book Co., New York, 1973.

5. Rohsenow, W.M., and H.Y. Choi, Heat, Mass, and Momentum Transfer, Prentice-Hall Inc., New Jersey, 1961.

6. Bowman, W.H., and R.M. Lawrence, "Ablative Materials for High-Temperature Thermal Protection of Space Vehicles," Space Resources for Teachers, New York, 1971.

7. Schwinghamer, R.J., "Cork Ablator for Thermal Protection is B-Staged for Easy Application," Material Engineering, Vol. 93, No. 4, April 1981.

8. Schneider, P.J., "Correlation of Low Density Thermal Protection Materials in Mild Heating Environments," AIAA 12th Aerospace Sciences Meeting, February, 1974.

9. Sawko, P.M., and S.R. Riccitiello, "Improved Intumescent Coating," NASA Technical Brief, NTN-78/0178, Spring 1977.

10. Hauser, R.L., "Ablative Coatings," Progress in High Temperature Coatings, November 1961.

11. Sawko, P.M., and S.R. Riccitiello, Intumescent Ablators as Improved Thermal Protection Materials, NASA Ames Research Center, Moffett Field, California, 1977.

12. Sauers, D.G., "Water-Based Intumescent Paint," NASA Technical Brief, Vol. 5, No. 2, Summer 1979.

13. Laganelhi, A.L., T.P. Harper, and R.P. Fogaroli, "Integral Solution for Thermal Performance of a Charring Ablator," AIAA/ASME Thermophysics and Heat Transfer Conference, Boston, Massachusetts, July 1974.

14. Curry, D.M., Analysis of Charring Ablation Thermal Protection Systems, NASA TND-3150, 1965.

15. Clark, K.J., A.B. Shimizo, K.E. Suchsland, and C.B. Moyer, Analytical Modeling of Intumescent Coating Thermal Protection System in a JPS Fuel Fire Environment, Aerotherm Corporation, Mountain View, California, 1974.

16. Marques, J.P., Thermal Evaluation of Ablative Materials in Transient Low Heat Flux Environments, Ocean Engineering Thesis, Massachusetts Institute of Technology, 1983.

17. Schwarting, R.A., One-Dimensional Model of an Intumescent Ablator, Ocean Engineering Thesis, Massachusetts Institute of Technology, 1983.

REFERENCES (Cont.)

18. Shea, J.W. Flexfram 605 and Dynatherm E-340N Ablatives On Board USS Kidd (DDG-993) MK 94 BTV Flyaway Firing Results, Naval Surface Weapons Center, NSWC TR81-498, 1982.

19. Sharpe, R.A., Development of Thermal Protective Systems for Aircraft Applications, E-Systems Inc., Dallas, Texas, 1978.

20. DiGiorgio, J.D., Lockheed Corporation Interdepartment Communication, March 1982.

21. Carslaw, H.S., and J.C. Jaegar, Conduction of Heat, Oxford Press, Oxford, 1959.

22. Froberg, R.W., "Thermal Coating Slows Fire Progress," Modern Paint and Coatings," November 1980.

23. Schmidt, D.L., Interdisciplinary Research on Ablative Materials, Air Force Materials Laboratory Air Force Systems Command, 1965.

24. Lee, B.T., and W.J. Packer, Fire Buildup in Shipboard Compartments - Characterization of Some Vulnerable Spaces and the Status of Perdiction Analysis, Center for Fire Research National Engineering Laboratory National Bureau of Standards, May 1979.

25. Lee, B.T., and J.N. Breese, Submarine Compartment Fire Study - Fire Performance Evaluation of Hull Insulation, Center for Fire Research National Engineering Laboratory National Bureau of Standards, May 1979.

26. Lee, B.T., and W.J. Parker, Fire Performance Guidelines for Shipboard Interior Finish, Center for Fire Research National Engineering Laboratory National Bureau of Standards, June 1979.

27. Shea, J.W., Relative Performance Evaluation of Selected Ablative Materials to Replace Dynatherm 340-N on MK 11 GMLS, Naval Surface Weapons Center, Dahlgren, Virginia, April 1981.

28. Alexander, J.G., Thermal Flash Resistant Polymeric Coatings, Avco Systems Division, Wilmington, Massachusetts, September 1979.

29. Hoffman, J.P., and H. Hop, Chaparral Weapon System Blast Protective Coating Investigation, Philco-Ford Corporation, Newport Beach, California, October 1966.

30. Parker, J.A., and D.A. Konitides, Fireworthiness of Transport Aircraft Interior Systems, Ames Research Center, Moffett Field, California, May 1982.

31. Boyer, C.T., Proposal for Doctoral Dissertation, "Characterization of Expanding Ablators," Naval Surface Weapons Center, Dahlgren, Virginia, October 1982.

32. Henderson, J.B., L.P. Anderson, and G.R. Moore, Comparison of Ablative Materials in a Solid Rocket Motor Flow Field, Naval Surface Weapons Center, Dahlgren, Virginia, August 1979.

33. Biermann, E.E., and A.B. Coates, Rocket Motor Blast Effects and Proposed Ablative Protection for RAM Launching System EX43, Naval Surface Weapons Center, Dahlgren, Virginia, October 1979.

34. Henderson, J.B., M.E. Tant, and G.R. Moore, Determination of Kinetic Parameters for the Thermal Decomposition of Phenobic Ablative Materials by a Multiple Heating Method, Naval Surface Weapons Center, Dahlgren, Virginia, July 1980.

35. Barber, P.M., "Fire Endurance Coatings," Twentieth Annual Marine Coatings Conference, New Orleans, Louisiana, March 1980.

36. Seiferth, R.W., Ablative Heat Shield Design for Space Shuttle, Martin Marietta Corporation, Denver, Colorado, October 1975.

REFERENCES (Cont.)

37. Goldstein, H.E., D.B. Leiser, M. Smith, and D. Stewart, Opacified Silica Reusable Surface Insulation (RSI) for Thermal Protection of the Space Shuttle Orbiter, NASA Ames Research Center, Moffett Field, California, August 1977.

38. Scoville, C.L., and P.D. Gorsuch, "Thermal Protection Systems for the Space Shuttle," Proceedings of the Twenty-First International Astronautical Congress, Konstanz, West Germany, October 1970.

39. Dicus, D.L., R.N. Hopko, and R.D. Brown, Ablative Performance of Uncoated Silicone - Modified and Shuttle Baseline Reinforced Carbon Compositesa, Langley Research Center, Hampton, Virginia, December 1976.

40. Wilson, M.L., Environmental Tests of Coatings Designed to Provide a Minimum Five-Minute Bomb Cook-Off Delay, Naval Air Development Center, Johnsville, Pennsylvania, March 1970.

41. Pulley, D.F., Weapons Cook-Off Improvement Program Materials Digest, Naval Air Development Center, Johnsville, Pennsylvania, May 1978.

42. Pulley, D.F., Laboratory Evaluation of Candidate Exterior Coatings for the Thermal Protection of Munitions, Naval Air Development Center, Johnsville, Pennsylvania, January 1974.

43. Fiber Materials, Inc., advertisement literature concerning the product Flexfram 605, November 1981.


F