# ABLATION MATERIALS

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| Chairman | Mr. H. S. Schwartz |
| Speaker | Mr. D. L. Schmidt |
| Panel Members | Lt. L. Hjelm<br>Mr. R. Harned (BMD)<br>Lt. W. Jones<br>Mr. D. Hart (Edwards AFB) |

# ABLATIVE MATERIALS

Donald L. Schmidt

Directorate of Materials and Processes, ASD

## Introduction

Advances in aeronautics and astronautics have been closely associated with significant increases in operational temperatures. In chemical combustion systems, flame temperatures are approaching 5500°F and higher. Gas temperatures at least twice that high are being encountered in the boundary layer of hypersonic atmospheric entry vehicles. These extremely high temperature conditions may lead to thermal destruction of an exposed vehicle or a component, unless suitable protection is provided.

Protection of a structure in a very high temperature environment may be accomplished with ease through the use of a new class of engineering materials. These thermally protective materials are known as ''ablators'' or ''ablative materials''. They are applied to the exterior of a load bearing structure and thereby isolate it from the hyperthermal environment. The structure is thus maintained near its initial temperature, at which it exhibits optimum strength characteristics.

Ablative materials are unique in that they accommodate virtually any temperature or heat flux condition, automatically control the surface temperature, greatly restrict any internal flow of heat, and expend thousands of Btu's of energy for each pound of material. These capabilities are the result of a self-regulating, orderly and gradual removal of exposed surface material, which takes place during interaction of the high temperature environment with the material.

## Ablative Process

Materials ablation in high temperature environments is a subject of great complexity, and as a consequence is not too well understood. Certain chemical and physical aspects of the process have been identified, however, and they shall be given for the case of an ablating vitreous fiber reinforced plastic. Initially, heat incident to the surface is absorbed and then conducted into the material substrate. Heat penetration proceeds at a low rate, due to the very low thermal conductivity of the ablator. The surface temperature thus rises rapidly, and thermal degradation begins in some form. Organic components of the composite vaporize into numerous gaseous products of varying molecular weights, often leaving behind a residual char layer. Thermochemical and mechanical attack of this porous carbonaceous structure results in surface recession, thus exposing the reinforcing fibers to the hot gas stream. Fusion of the fibers occurs and the molten material covers the surface either as a film or as droplets. This melt is partially vaporized, and the remainder is convected along the surface under the influence of the external forces of gas pressure and shear.

Ablative degradation of the reinforced plastic is illustrated in figure 1. Damage to the material is noted in four distinct layers. First, surface material has been removed by the combined action of thermal, chemical and mechanical effects. On the ablated surface is a thin film and several droplets of melted glass, which have been formed from the reinforcing fibers. Under this surface layer, a porous carbonized material reinforced with residual glass fibers is evident. The volatile-loss layer is adjacent to the char layer, and has been designated as such because of the slight loss of organic resin. The virgin material lies beneath these damaged zones, and has experienced little or no rise in temperature.

## Thermal Parameters of Ablation

During high temperature exposure, an ablative material is generally able to absorb, dissipate and block between 500 to over 10,000 Btu's for each pound of material. This phenomenal capability is due to the various thermal accomodation parameters which function during material ablation. These parameters are shown in figure 2. Sensible temperature rise of the ablator and its pyrolytic products accounts for some heat absorption the magnitude of which is generally small. Additional heat is expended by chemical reactions of the thermally degrading material, such as cleavage of chemical bonds. Various endothermic phase changes take place. Some of these energy absorbing processes are depolymerization, melting, vaporization, sublimation, and others. A small amount of energy may be transported to another physical location by mechanical shearing of solid material from the ablating surface. Likewise, any surface melt on the ablator may be removed by imposing forces of the environment. Gases formed in the material substrate are heated to a higher temperature as they percolate to the surface. Due to their high heat capacity, they are able to absorb a large amount of heat by sensible temperature rise. The newly formed gases are ejected into the adjacent boundary layer greatly reducing the effective temperature level of the environment. Consequently, less heat is transferred to the ablating surface. Energy is dissipated by surface radiation, with the rate of heat transport depending upon the temperature and emittance of the ablator. Additional heat will be radiated into the material substrate, provided the material is radiation transparent or semi-transparent.

The amount of heat expended by each of the above processes depends critically upon the nature of the heating environment and the material being considered.

## History of Ablators

The first known ablative materials were meteorites. These thermally degraded bodies coming to us from space were indeed a subject of great curosity, since they had demonstrated in principle the utility of aerodynamic ablation for thermal protection of atmospheric entry objects. Perhaps in these bodies were hidden the secrets to successful reentry of man-made vehicles. Research was thus initiated to discover their composition and construction. Information obtained was interesting, but it provided few usable clues. Furthermore, it was apparent that the stony and iron meteoritic materials were not suitable for application to man-made thermal protection systems. Hence, the search for workable ablative materials was continued.

Man-made ablative materials were discovered only a decade ago. Various techniques were being explored to protect and insulate structural metals while exposed to a hot rocket exhaust. Certain reinforced plastics and ceramics were seen to exhibit remarkable durability during short time hyperthermal exposure. In addition, the high temperature of the environment was restricted to the surface region of the ablating material. These thermal barrier materials apparently had great potential for solving the high temperature problems associated with re-entry heating and rocket propulsion systems. In the next several years, thousands of different material compositions and constructions were characterized and evaluated on a trial-and-error basis. The high temperature facilities used were various combustion torches, small rocket motors, arc plasma jets, pebble bed heaters, arc imaging furnaces, and others. Environmental simulation was often impossible to obtain with these facilities, but their use permitted the generation of test conditions in which much useful materials information was obtained. Meanwhile, ablative theories were being formulated and experimentally verified. These theories helped to explain materials behavior at very high temperatures, and provided some guidance for their engineering application. Various types of materials were investigated, and plastics and ceramics in homogeneous and composite compositions were found most promising. Composite construction was the most versatile, since the unique properties of individual components were incorporated into a single material system. Furthermore, it was possible to adjust these material components to obtain the desired balance of properties and to tailor them to a specific environment. By these trial-and-error and systematic materials investigations, a wide variety of ablative materials have been identified. Many of these materials are shown in table 1.

TABLE 1

ABLATIVE MATERIALS COMPOSITIONS

| Homogeneous Ablators | Composite Ablators |
|---|---|
| Plastics<br>Polytetrafluoroethylene<br>Polyethylene<br>Polyamides<br>Phenolics<br>Modified epoxies<br>Expanded (foamed) resins<br>Carbonized resins | Reinforced Plastics<br>Organic resins reinforced with various fibrous materials, such as glass fiber reinforced phenolic<br><br>Reinforced Ceramics<br>Ceramic filled metal honeycomb<br>Metal fiber reinforced ceramic |
| Ceramics<br>Fused silica<br>Zirconia<br>Magnesia<br>Expanded (foamed) ceramics | Impregnated Systems<br>Organic resin filled porous ceramic<br>Inorganic particle filled refractory |

This list is not an all inclusive one, but it identifies materials which have exhibited relatively good performance in several different hyperthermal environments.

### Advantages and Limitations

Ablative materials have been widely used in heat protective systems of hypersonic atmospheric vehicles, rocket propulsion systems, various thermal barriers, and other high temperature applications. This extensive acceptance in aerospace systems is due to the unique combination of properties and characteristics offered by the materials. Figure 3 lists the major advantages of ablative materials, and their twofold limitations.

Ablative materials absorb and dissipate high heat loads with minimum surface erosion, and provide excellent thermal insulation of the substrate. They have no upper service temperature limit, and they can accommodate virtually any operational temperature by controlled material degradation. They are usually light and vary from about ten pounds per cubic foot for foamed plastics to over two hundred pounds per cubic foot for metal fiber reinforced ceramics. Organic ablators inherently possess good resistance to both thermal and mechanical shock, but ceramic ablators are shock sensitive. This material deficiency has been greatly reduced by the use of fiber or honeycomb reinforcements. Ablative materials are readily available and are non-strategic. Their relative costs are low. Designing with ablative materials is not any simple task, but it certainly involves less complexity than with other thermal protection schemes. Lastly, ablative materials degrade in a self-regulating and orderly manner, thus eliminating any requirement for an actively controlled cooling system.

The thermal efficiency and effectiveness of an ablator is reduced with increasingly higher mechanical forces. A second limitation of these materials is their service time dependency. Optimum performance is generally obtained for minutes of operation or less, with reduced performance with increasing exposure times.

## Ablative Performance

The performance of an ablative material is a complex function of both materials and environmental variables. Since the design spectrum of hyperthermal environments is very large, it is impossible for a single material to be optimum for all types of environments. Each material exhibits optimum performance characteristics for a specific environment, and may even become unusable in other high temperature environments. It thus becomes necessary to develop a wide variety of ablators, which have the collective capability to accommodate the entire design spectrum of hyperthermal environments.

A proper balance of materials properties and characteristics leads to optimum ablative performance. Important materials variables are shown in figure 4, together with the desired property trend. It is noted that the empirical heat of ablation value should be as high as possible to minimize the weight of material required to accommodate the incident flux. The strength of the intact ablator and its residual surface material should also be high, and adequate to withstand the imposing mechanical forces of the environment. Other materials properties which require high numerical values include: the enthalpy of phase changes, specific heat and thermal shock resistance. A low thermal conductivity is desirable for obvious reasons of insulation. Low density materials are generally optimum, provided they can accommodate the imposing forces of the environment. The dimensional erosion of the surface should be relatively low, uniform, and predictable. Gaseous species formed by material degradation should be of low molecular weight, a factor which leads to optimum transpiration cooling. Surface emittance should approach unity for maximum heat dissipation. Materials that gasify completely exhibit excellent heat blockage; therefore, all of the initial solid material should be converted to gaseous products. Certain other properties and characteristics of an ablator interact strongly with other materials, environmental and design parameters. Consequently, no general trend for optimum performance can be given. To illustrate, a high ablative temperature is generally desired for conditions involving a very high heating rate. The converse is true for a low heating rate environment.

Environmental variables and their magnitude greatly influence the behavior of an ablator. In figure 5, the important thermal, mechanical and chemical aspects are given for a high temperature environment. Their exact numerical value is dependent upon the specific application and body location being considered. To further complicate the problem, many of these environmental variables may change constantly in a given application (as a nose cone re-entering the earth's atmosphere).

When the mode of surface heating is primarily convective in nature, the ablative material should form a large volume of gas to block the incident flux. If radiation is the predominant mode of incident heat transfer, the ablating surface should exhibit good reflection characteristics or possess a high emittance for maximum re-radiation. The instantaneous flux and its variation with exposure time must also be considered, since it may be desirable to use a "graded layer" ablator instead of a homogeneous and uniform material. The total heating time dictates the amount of material required for ablative and insulative purposes, and often means lowered material performance with increasing exposure times. Mechanical forces of pressure, shear, vibration, acceleration and deceleration are detrimental. High pressures tend to crush the thermally weakened surface material, and gas shear may erode away solid and liquid materials. Vibration accelerates removal or detachment of the ablating material. Unpredictable problems may be introduced by forces of acceleration and deceleration. For example, molten material on a highly decelerating re-entry heat shield may move in the direction of the apex (opposite to the direction of the gas stream). Thus, first order changes of the heat shield geometry may occur with associated effects on the aerodynamics of the vehicle. Chemical reactivity of the environment is also extremely important, since it may affect the mechanism, thermodynamic and kinetics of the ablative process. To illustrate, oxygen present in the environment accelerates material ablation by oxidation of carbonized systems. It has little effect on molten oxide ablating surfaces.

To summarize, the ablative performance of a material may be altered by many different environmental variables. Careful consideration should therefore be given to each of these factors in determining a materials performance, and in selecting an ablator for a specific high temperature environment.

## Research Programs

Although great advances have been made in ablative materials technology, our understanding of these materials in very high temperature environments is inadequate. Numerous problems continue to plague us thereby restricting new developments. Some of these important problem areas are under research by the Air Force and its contractors. In figure 6, the categories of research activities are listed. Each is discussed in detail in this paper.

### Ablation Theories

Since materials ablation is a very complicated process, theories are necessary: to obtain additional insights and a better understanding of the process; to identify the materials physical and chemical properties of importance; to predict performance; and to guide future materials research.

Theoretical models have been formulated for the various classes of ablators, and mathematical formulas are available to express their performance. These ablative models have proven to be helpful in predicting material performance, but they require further refinement to extend their utility. At the present time, they contain temperature-dependent thermophysical properties of the ablator which likely are unavailable in the literature. Kinetic expressions may be used in the formulas, some of which are difficult to measure or compute. Lastly, they may contain ill-defined quantities, such as the heat of chemical reaction for an ablating polymeric material.

Theoretical research on ablative materials is presently concentrated on composite systems. Formulas are being developed to express the steady-state temperature distribution in the material substrate, instantaneous char layer thickness and charring rate, and heat of ablation as functions of both materials and environmental variables. Internally ablating composites are being intensely studied. This type of material system is represented by a porous refractory ceramic skeleton impregnated with a thermally unstable organic resin. The impregnant vaporizes during heating and flows out of the porous skeleton. In so doing, the vapors cool the surface and maintain its dimensional stability.

## Mechanisms of Ablation

Ablative materials programs to-date have been primarily of the engineering type, with little regard for the detailed mechanisms by which these ablators are thermally degraded. To fill this void and to provide a fundamental understanding of material ablation, various specialized studies have been initiated. They have generally been concerned with identifying the important physico-chemical aspects of ablation, thermodynamics and kinetics of material reactions, and the influence of both materials and environmental variables on the modes of ablation.

Ablative mechanisms are deduced from research information obtained on the individual reactions and processes of a thermally degrading material. The thermodynamics and kinetics of reactions taking place are analyzed from a theoretical standpoint. Chemical reactions of importance are thus identified, and later studied in detailed investigations. Some of these studies relate to the rate and mode of material decomposition, chemical and physical reactions of the newly formed gaseous products, interactions between the pyrolytic gases and the residual ablative surface, and reactions between the atmospheric constituents and the ablative products. Vacuum pyrolysis and thermogravimetric analysis have been helpful in obtaining the rate of material loss as a function of increasing temperature. Chemical reactions occurring within the material, on the surface and in the boundary layer are followed by such analytical techniques as mass spectrographic analysis, emission spectroscopy, elemental chemical analysis, X-ray diffraction, and others. Energy exchanges accompanying these reactions are being investigated with differential thermal analysis (DTA). Transient species and final gaseous products coming from the ablating surface are identified and quantitatively measured with a time-of-flight mass spectrometer. For carbonizing ablators, electro-thermal analysis is used to follow the conversion of organic material into residual carbon. Residual products contained on the material surface after exposure are analyzed for chemical composition, physical structure, crystallinity, porosity and pore spectra, density changes, strength properties and related material characteristics. The effects of the individual components of the atmosphere on ablative materials are being reviewed. Pure thermal effects on ablators are being investigated with thermal radiation from an arc imaging furnace. Gaseous plasmas similar to those of very high temperature boundary layers are produced with a radio frequency discharge tube. Their mechanism of free radical attack on material surfaces are being researched. For simultaneous simulation of thermal, chemical and mechanical effects, an electric arc plasma jet has proven to be very useful.

From these studies on the mechanisms of material ablation, it has been possible to categorize the ablative modes. These are: simple melting (like an inorganic ceramic), sublimation (such as polyethylene), melting-vaporization (like a resin reinforced plastic), and carbonization-vaporization (such as a phenolic resin). A voluminous amount of information has been obtained. For example, it has been determined that the rate controlling ablative mechanism of a carbonized plastic in high temperature air is primarily that of oxidation. For the case of ceramic oxides in high temperature air, material ablation is controlled predominantly by melting and vaporization processes. As new knowledge is generated on the mechanisms of material ablation, greater control over the ablation process may be exercised to increase heat absorption and insulation.

## Elimination of Material Deficiencies

Major emphasis in this area of materials research is devoted to improving the sturctural characteristics, dimensional stability and useful service life of ablative materials.

The thermally weakened surface layer on an ablating material can be made stronger by reinforcement with a suitable refractory fibrous material. Good results have already been achieved with fibers of silica, zirconia, carbon, graphite, tungsten and other compositions. Significant improvements in the ablative characteristics of ceramics have been obtained with the use of refractory metallic wires, meshes and honeycomb. A second promising concept for improving the structural properties of an ablator concerns the "in situ" synthesis of a refractory on the surface during hyperthermal exposure. This approach utilizes the heat and pressure of the environment to effect the desired reaction. For example, a composite of organic resin and quartz reinforcing fibers will form carbon and molten silica during intense heating. These two products of pyrolysis may react endothermically to form a surface refractory of silicon carbide. However, techniques have to be satisfactorily worked out for maintaining the newly formed carbide on the ablating surface.

Improvements in the dimensional stability of ablative materials is being pursued from three different technical approaches. The first concept under exploration concerns proper orientation of the reinforcing agent in an ablative composite. It has been shown that fibers perpendicular to the exposed surface invariably result in a minimum rate of linear ablation. Intumescent ablators (swell in response to heating) offer another interesting approach to the development of dimensionally stable materials. For example, thermal exposure of certain modified epoxies results in a plastic char which has a tendency to swell. Material loss at the surface is thus compensated dimensionally by internal swelling of the carbonizing plastic residue. Internally ablating composites offer a third solution to the problem of dimensionally stable ablators. Excellent results have been obtained with porous skeletons of refractory oxides impregnated with non-carbonizing resins. The original dimensions of the ablator are assured by continual surface cooling with internally generated gases.

Efforts are underway to extend the service life of ablative materials. An obvious approach is to maximize the heat of ablation value, the insulation index, or both. Material compositions with heats of ablation approaching those of graphite, but with better thermal insulation are being studied. Superior ablative insulators are required for long time exposures, such as satellite re-entry heating. Most ablators behave primarily as a heat sink in this type of environment, and have poor insulative qualities. In order to force the ablative process in low heating rate environments, materials are required to undergo extensive depolymerization and vaporization at temperatures of 1000°F or lower. New long chain, non-carbonizing plastics of this type have been synthesized, and used successfully for up to 10 minutes in simulated satellite heating conditions.

Several of the new ablative compositions have been found to be semi-transparent to radiation from the environment. Heat is thus transferred into the material substrate with an associated increase in its internal temperature. New thermal barrier concepts for these materials have recently been proposed, and they are being reduced to practice. Some of these approaches are: incorporation into the ablative material of embedded scattering particles, absorbing substances, foil reflectors, and multilayer dielectric reflectors.

## Synthesis and Formulation

Numerous research programs are devoted to the syntheses of new material compositions and constructions. Organic and inorganic polymers with high endothermic capacity are being created by: modification of conventional polymeric structures, copolymerization of available resins, and synthesis of new polymeric matrices. There is a primary interest in the high-carbon aromatics, metalloxanes, triazines, polyazaporphyrins, organometallic chelates, borazoles, and other polymeric systems. Flexible polymers with high carbonization potential are being synthesized for use as rocket case liner materials. Two notable achievements have been reported in this area. They are the synthesis of castor oil modified epoxies and the incorporation of elastomeric polymers into the phenolic resin structure.

Resinous materials which are inexpensive, castable, and cure at room temperature are the object of current materials research. Excellent results have been obtained with modified epoxies and those filled with various carbonizing particulate matter.

Considerable research effort is being devoted to the synthesis and development of refractory fibrous materials, which exhibit good thermostructural properties for reinforcement of ablative matrices. Primary interest is centered on compositions of refractory metals, graphites, carbides, oxides, nitrides and borides. Fine diameter fibers of tungsten, tantalum, molybdenum, titanium, and zirconium have been prepared for incorporation into ablative ceramic and plastic composites. Successful synthesis of the following materials have been reported: long fibers of quartz, zirconia and elemental boron, short length crystals of alumina, titania, and thoria, and very short length whiskers of silicon carbide, pyrolytic graphite and beryllia. Refractory carbon and graphite fibers have been made by conversion of synthetic organic fibers under conditions of high temperature and vacuum. These fibrous materials have exhibited extremely high sublimation temperatures and increasing strength with elevated temperatures. Their uses to date have been limited by a relatively low strength, oxidation at high temperatures, and a moderately high thermal conductivity. Successful synthesis of long metallic carbide fibers appears likely within the near future. When available, these non-melting fibers will be widely used in ablative composites.

Particle fillers of various chemical composition and sizes are being studied as possible additives in ablative composites. Their purpose is generally a highly specialized one, such as to increase the surface emittance and temperature, alter the viscosity and surface tension of the inorganic components, generate a large volume of low molecular weight gases, increase the endothermic absorption of heat, and other functions. Several problems have been encountered with their use, such as an undesirable influence of the filler on other ablative reactions, uncontrolled degradation of the particle, and loss of the particle from the surface before it performs its intended function.

Ceramics are receiving increasingly greater attention as potential ablative materials, since their tendency to spall and thermally fracture have been overcome by the use of suitable reinforcing agents. Pure and mixed oxides of zirconia, thoria, magnesia and hafnia are being formulated for use as bulk ablators or as coatings for other materials.

Formulation and fabrication of ablative composites have been progressing rapidly. Metallic, ceramic and plastic elements have been successfully incorporated into single material structures, and maintained as a unit during hyperthermal exposure. An example of this type of multilayer construction is shown in figure 7, which is a photograph of an entrance cone of a test rocket nozzle. The internal surface is an arc plasma sprayed tungsten coating, the purpose of which is to provide short-time thermal protection by delaying the internal heat transfer. This metallic coating is diffusion bonded to a substrate insulative layer, which is itself composed of a porous zirconia foam reinforced with stainless steel honeycomb. The external load bearing member of the composite is a silica fiber reinforced plastic, adhesively bonded to the reinforced ceramic layer. This type of construction has successfully withstood a solid propellant firing involving a flame temperature of 6800°F.

## Materials Characterization

Increased emphasis on materials synthesis and formulation has lead to the generation of many new ablative materials. Considerable burden has thus been placed on the evaluation engineer to determine their ablative characteristics and potential for specific types of high temperature environments. This activity may be costly, time consuming and complex, due to the large number of available materials, and, the environmental aspects which must be investigated. The most satisfactory solution obtained, involves a division of this research into two sequential steps. First, newly synthesized candidate materials are rapidly screened at several standardized test conditions. Obvious ablative characteristics and material limitations are observed, measured and computed. These generally involve: uniformity and rate of ablation, surface characteristics including spalling, internal heat penetration, surface temperature and radiation, heat of ablation, and possibly other performance indices.

Several high temperature facilities have been developed and are readily available for materials screening and characterization studies. These testing devices are given in table 2, along with their performance characteristics, advantages and limitations. The type of facility selected for a particular materials evaluation will depend upon the objectives of the work and the materials research information desired.

Materials intended for re-entry heating environments are rapidly screened in small 50 to 500 kilowatt electric arc-jets. They are generally prepared in the configuration of a flat faced cylindrical rod, and exposed to non-variant test conditions in the arc jet. Figure 8 shows three research specimens after exposure to high enthalpy air from an arc wind tunnel. The most promising materials identified in screening tests are then scaled up into larger models, and evaluated further in highly specialized are heaters and under carefully controlled conditions.

Materials intended for rocket exhaust environments are screened in a combustion gas device, such as a subsonic or supersonic oxy-acetylene torch. Either cylindrical rods or flat plates are used to obtain general ablative characteristics of the materials. Figure 9 illustrates this type of materials screening, and shows a ceramic ablator being exposed to supersonic combustion products from an oxy-acetylene torch. Promising materials obtained from these comparative materials studies are scaled up into nozzle or insulator sections, and further characterized with small rocket motors.

Nozzle ablative materials have been characterized in a variety of liquid propellant motors, one of which is the hydrogen-oxygen motor. This particular evaluation facility has been widely used, since it generates flame temperatures, mass-flow parameters and gas chemical effects of interest. Candidate materials are fabricated into small research nozzles, in preparation for motor firing. A nozzle specimen is fastened to the end of the motor, as shown in figure 10. Material exposure is accomplished by exhausting the combustion products through the nozzle section. A photograph of a material research nozzle before and after firing is shown in figure 11. Note the throat erosion and surface charring which has taken place in this molded plastic specimen.

Flexible ablators are fabricated into small blast tube specimens and characterized by exposure to a solid propellant flame. Up to eight different materials can be exposed simultaneously, as shown in figure 12. Each candidate material is arranged in a circle about the blast tube section which forms a part of the actual motor wall. In this manner, direct comparative results on various materials are obtained with economy of operation.

Some of the remaining problems to be solved in materials characterization and evaluation are: limited availability and high costs of materials screening devices, limitations in instrumentation for accurate measurement of both environmental parameters and materials response, development of more meaningful indices of material performance, difficulties in identifying the mechanisms and causes of material failure, and the inability to scale up from small research specimens to larger end item applications.

### Material-Environment Interactions

As new ablative materials are considered for use in specialized hyperthermal environments, it often becomes necessary to conduct material-environment interaction studies. The purpose of these studies is generally to: identify and quantitatively determine the reactive species present in the environment, elucidate their mechanism of interaction with the ablator, and develop new techniuqes for inhibiting undesirable reactions.

During hypersonic atmospheric entry, an ablative material is exposed to a very high temperature boundary layer. Gaseous species present in the boundary layer are highly reactive, due to their ionized and dissociated states and their chemical composition. The effect of these gaseous species on ablative materials has been investigated with interesting results. Organic ablators were found to be more susceptible to plasma attack, when compared to inorganic ablative materials. Silicones and other thermosetting resins were more resistant to plasma attack than were the thermoplastic resins. Gaseous oxygen plasma produced a higher rate of chemical vaporization than did the less reactive nitrogen plasma. This effect was particularly evident with ablative materials that formed a carbonaceous surface during heating.

Combustion products from advanced propellants have introduced new chemical corrosion problems for ablative materials. Studies have been initiated on gas-solid, gas-liquid and liquid-liquid reactions, such as those occurring between high temperature water vapor and metallic carbides, fluoride vapors and inorganic oxide melts, liquid aluminum oxide and molten silica, and other suspected deleterious reactions. The chemical kinetics of these reactions are being investigated. Each system has its peculiar characteristics. For example, aluminum particles present in a solid propellant are oxidized to molten alumina in the combustion stream. These liquid droplets may then contact the ablating wall, transfer energy to it, and form a new low-viscosity eutectic which is rapidly swept away by the gas stream. The kinetics of this reaction are governed by such complex factors as: rate of impingement of the alumina droplets, wetting characteristics of the ablating wall, mobility of the alumina phase on the surface and internal diffusion rate, thermochemical state of the surface, and diffusion rate of reaction products away from the surface.

In the future, the chemistry of hyperthermal environments will likely continue to change as new propellants are developed and new planetary atmospheres are explored. It will then be necessary to ascertain the individual effects of the reactive atmospheric constituents on ablative surfaces.

## Applications Engineering

Effective and efficient design with ablative materials has seldom been achieved, due to the newness of the materials, lack of preceding similar designs, complexity of the design factors involved, and our incomplete knowledge concerning realistic design criteria. In designing with ablative materials, consideration must be given to the environmental variables and their time dependency, availability and uniformity of candidate materials compositions and constructions, materials properties and characteristics, materials formulation and fabrication, design requirements for thermal, mechanical and chemical properties, safety factors and other aspects peculiar to the design. Some degree of uncertainity exists for each of these factors, and designers have had a tendency to use an overall safety factor rather than one based on the uncertainty of each design criterion. Further research on optimum design techniques for ablative materials is required.

Another serious problem in the application of ablative materials is the frequent inability to use design data obtained on sub-scale models. Certain material components, such as a fiber diameter, are not proportionately scaled up in going to larger end items. Slight differences between the test environment of the sub-scale model and that of the actual end item may lead to significant differences in material performance.

The notable lack of standardized design criteria limits the effective use of ablative materials. Virtually all of the materials performance indices are in some way tied to the boundary conditions under which they were determined. For example, the heat of ablation of a material in an argon test environment may be vastly different from that obtained in an air environment.

Performance indices for ablative materials are not well defined, and this lack of standardization is leading to some confusion. To illustrate, there are many different definitions for the "heat of ablation". Some research is being conducted on refining this material performance parameter, and extending its utility to a greater number of design situations. Presently, only partial success has been obtained.

Properties of ablative materials, which are essential to optimum design, are rapidly being generated. The data are generally determined at equilibrium conditions and at temperatures up to the initial point of material phase change. For lack of available information, designers are often forced to use this data for transient ablative conditions involving considerably higher temperatures. Much of the materials property information given in the literature has limited utility due to the incomplete description of the important materials composition and construction, test environment, and experimental procedures used.

Many new problems are encountered in the fabrication of ablative materials. Few acceptance and rejection standards have been developed. Material and process specifications are virtually non-existent. Expensive and specialized equipment must often be used, such as tape winding machines for oriented woven fiber layups, high pressure presses for large exit cones of rocket nozzles, and vacuum furnaces for material syntheses. Ablative parts are generally made from several dissimilar components, thus requiring suitable techniques for joining them into an integral unit. Nondestructive inspection techniques of ablative parts are required for quality assurance and to improve fabrication techniques. Radiography and ultrasonics have been used with moderate success. Further work is required to identify and classify permissible defects (voids, cracks, matrix-starved areas) in ablative parts, and ascertain their influence on the ablative characteristics. These problems are representative of those faced by materials fabricators and suppliers.

Ablative parts are often subjected to various degrading conditions in the time interval between their fabrication and use in a hyperthermal environment. Some of these possible material degradation factors are: exposure to the elements of the weather, long time storage, handling shock and vibration, contact with chemicals, and similar items. The influence of these items on ablative performance has yet to be determined for many of the ablators presently in use. Further knowledge is required on these potential problem areas to increase the reliability of ablators.

## Several Typical Uses

The utility of ablative materials for thermal protection of structural elements has been demonstrated experimentally in a wide variety of laboratory generated hyperthermal environments. Ultimately, it becomes necessary to verify their performance in actual applications: (a) to prove their effectiveness and reliability (b) to confirm theoretical predictions of material performance, and (c) to provide a sound basis for the selection of optimum materials compositions and constructions. Two of the most heralded applications of ablative materials are discussed in detail. These are: re-entry heat shielding and protection from hot rocket exhaust environments.

### Hypersonic Atmospheric Entry

One of the most difficult and challenging problems of aerospace flight is the thermal protection of a vehicle as it enters hypersonically into a planetary atmosphere. Unless isolated from this very high temperature environment, the vehicle will likely be thermally destroyed in a manner similar to that of a meteor entering the earth's atmosphere. Research on this critical problem of re-entry heating has led to various workable solutions, such as transpiration and film cooling, radiant cooling, magnetohydrodynamic cooling, solid and liquid heat sinks, and ablative cooling. Of these thermal accommodation techniques, the last two have already been applied successfully to various man-made re-entry bodies. Ablative cooling has achieved the highest degree of success and it has been the most widely used. To-date, ablative materials have thermally protected nose cones of ballistic missiles, orbital entry bodies, and recoverable research vehicles. For the future, ablative materials appear highly promising for use on lifting aerospacecraft and planetary research probes.

Representative uses of ablative materials on atmospheric entry vehicles are shown in figures 13 through 15. Figure 13 is a photograph of an ablative materials research vehicle during launch by an intercontinental ballistic missile. In figure 14, a Discover orbital entry vehicle is shown with its ablative covering. Ablative materials have also been used successfully on manned orbital entry vehicles. Pictured in figure 15 is the Mercury capsule, with its broad, shallow ablative heat shield attached to the extreme forward part of the capsule. The specific ablative materials composition and construction used on these vehicles cannot be reported at this time, since the information is still classified. Nevertheless, it can be stated that each of these re-entry vehicles require different ablative materials because of its respective flight environments. To illustrate, orbital entry heating involving a high enthalpy, laminar flow condition is usually best accommodated with a low temperature, subliming plastic. Turbulent flow conditions and those environments involving high imposed dynamic forces dictate the use of a reinforced plastic or ceramic. The exact ablative material used on a given re-entry vehicle will depend largely on its body location and associated environmental conditions.

## Rocket Propulsion Exhausts

The containment and control of hot combustive gases in rocket propulsion systems is necessary for thrust purposes. These propellant gases constitute a severe engineering environment, since they are generally characterized by high temperatures, high mechanical forces, chemical corrosion, and occasionally particle erosion.

Ablative material have been used successfully in the propulsion systems of both solid- and liquid-fueled rockets. The most notable achievements have been in solid propellant motors, wherein the nozzle, sliver, insulation, liner and potting compound are composed of ablative-insulative materials. These ablative components comprise between 20 to 40 percent of the inert weight of the missile.

Rocket motors are constructed of composite materials, with each component material performing a specific function depending on its location. This type of construction is optimum, since the environmental conditions and hence the required materials properties vary greatly with motor position. Figure 16 illustrates this point by presenting the relative magnitude of gas temperature, velocity, pressure and their associated effect on surface heating and shear in various sections of an advanced solid propellant motor. In the aft end of the motor, an internal insulative material is used to protect the external structural case. It serves to transmit the chamber pressure forces into the wall, and insulate the external structural element from the high temperatures and reactive products of the combustion gases. The insulator should be flexible to permit it to follow (without cracking) the case expansion during motor ignition. A low modulus material is required to prevent high stresses in the liner-case bonded areas.

In general, motor insulators are composed of modified phenolic or epoxy impregnated asbestos materials. Recently, very promising results have been obtained with silica filled elastomers and epoxy modified polyurethanes. Environmental conditions become more severe in the entrance cone of the nozzle, and associated materials requirements change significantly. Increased material rigidity, structural strength, and thermal insulation are required. Some degree of dimensional surface change is permitted, since its influence on thrust is small. Refractories (metals, ceramics and graphites) are generally unsuitable for the entrance section of an uncooled nozzle, because of the size and configuration involved, and associated materials properties. Instead, fiber reinforced plastics which form a surface char, and possibly a viscous melt during heating, appear to be optimum.They consist usually of a phenolic-asbestos, phenolic-graphite fiber, or oriented silica fiber reinforced phenolic composition. The most critical part of the nozzle is the throat section, which experiences the highest level of heat flux (up to about 2,000 Btu/ft$^2$-sec), gas shear, and particle erosion. The original configuration and dimensions of the throat must remain constant throughout motor firing to insure non-variant chamber pressure and thrust conditions.

Ablative materials are seldom used in the nozzle throat, except for low chamber pressure motors or very short duration firings. Better performance is generally obtained with a refractory insert of tungsten, metallic carbide, high density graphite or pyrolytic graphite. These materials suffer from thermal shock failure, low elongation, and high thermal conductivity. This latter property requires the use of an insulative backup in the throat region. Material requirements for this insulator section are: high thermal stability, little or no gasification at temperature, high strength, moderate to high modulus, high heat capacity and moderate thermal conductivity. High temperature resins (phenolics, phenyl silanes and silicones) containing vitreous or asbestos fibers are often used in this region.

As the exhaust gases pass into the exit cone, the temperature and pressure levels decrease and the velocity increases. Added problems of high gas turbulence, shock wave effects, and acoustic vibrations impose structural stresses and possibly asymmetric ablation. Exit cone materials should be very light because of the large size involved, and they should ablate uniformly at a minimum rate for optimum nozzle efficiency and thrust vector control. The materials of construction are generally oriented (shingle- or end-grain) silica or carbon fabric reinforced plastic. In some cases, a random oriented quartz, or silica fiber plastic molding are used. The external structural elements of the rocket supports the mechanical and thermally induced stress, which are due to internal gas pressure, vibration, acceleration, thrust vector control and differential thermal expansion of component materials. To accommodate these factors, the structural material should have high strength, adequate modulus, and resistance to buckling. Either a high temperature metal (steel, titanium, aluminum) or a glass filament wound plastic are generally suitable for the nozzle exterior.

The use of ablative nonmetallic materials in liquid-fueled motors has been equally impressive, but certainly not as extensive. The factors which tend to limit the use of ablators in liquid-fueled rockets are: frequent lack of need for uncooled parts since the fuel may serve as its own coolant, burning times are relatively long, and engines are often proof tested by static firing.

One of the most impressive developments in the application of ablative materials to liquid propulsion systems is the ablative skirt for the second stage engine of the Titan ICBM. This hybrid nozzle is shown in figure 17. It is composed of a small regenerative cooled nozzle and a larger, uncooled extension. The purpose of the ablative skirt is to achieve optimum thrust at high altitudes, allow for a "dry jacket" altitude start thus minimizing pre-launch preparations, and preclude the possibility of engine compartment contamination by fuel leakage during first stage missile operation. The uncooled ablative skirt is constructed of an asbestos reinforced phenolic liner stiffened with a glass fabric reinforced phenolic honeycomb.

Ablative materials have been used successfully for uncooled, low thrust chambers of space control rockets. In these liquid propellant motors, the fuel flow is too low to provide regenerative cooling; some other form of cooling is required. Surprisingly, certain ablative reinforced plastics have exhibited remarkable durability during firing exposures on the order of 22 minutes. Furthermore, they have performed successfully with several thousand successive restarts of the engine. An exploded view of this type of rocket motor is shown in figure 18. The forward combustion chamber is composed of a phenolic resin reinforced with an oriented leached glass fabric, followed by a silicon carbide throat, and then an exit cone of a phenolic resin containing randomly oriented leached glass fibers. After assembly of the motor parts, the structure is filament wound with glass filaments and epoxy resin.

## Future Challenges

The combined efforts of the materials researcher, fabricator, evaluation engineer and designer have resulted in the creation of a variety of ablative materials and their successful application to hyper-environments. Because of the unique aspects of future environments and the ever constant design trend towards increasing materials requirements, these materials may exhibit poor performance or be entirely unusable. Serious consideration must therefore be given to the forthcoming hyperthermal environments in an effort to:

a. Determine the potential of existing ablative materials for more severe heating conditions.

b. Identify critical and unusual aspects of future environments, and determine the balance of materials properties and characteristics required to accommodate these conditions.

c. Provide basic guidelines for future research on ablative materials.

d. Assure the availability of new and improved ablative materials for advanced designs as they are conceived.

### Atmospheric Entry Environments

The trend toward longer ranges and higher entry speeds of ballistic missile nose cones is resulting in significantly higher aerodynamic heating rates and applied mechanical forces. The higher peak heating rates do not present unsoluble problems because the thermal efficiency of most ablators increases with the severity of the thermal environment. However, high dynamic pressures may cause crushing and premature failure of a mechanically weak ablating surface. Higher gas shear stresses accelerate the mechanical erosion of a solid or molten ablating surface. For example, melting ablators may experience greater sloughing than vaporizing of the surface molten material. These environmental factors could mean catastrophic failure or at least greatly reduced thermal efficiency of many ablative materials. New techniques for structural reinforcement of ablative materials are obviously needed.

Ballistic entry satellites and other related vehicles encounter a relatively long period of heating at moderate incident fluxes during hypersonic atmospheric entry. Aerodynamic forces acting on the vehicle are comparatively low, and for this reason, the structural aspects of the ablative material may be de-emphasized to achieve maximum insulative capability. Low temperature ablators ( < 1000°F) are required, and they may possibly be synthesized by building "thermally weak chemical bonds" into the molecular structure. Low density ablators are required for this heating environment which have a thermal conductivity of 0.025 Btu-ft/hr-°F or lower.

The radiative flux encountered by present vehicles during entry into the earth's atmosphere constitutes only a small fraction of the total heating rate. However, higher velocities at lower flight altitudes will present an increasingly serious problem of radiative heating. Energy predominantly in the ultraviolet to near infrared spectra will be radiated from the hot air boundary layer to the vehicle surface. Similarly, hypersonic flight into other planetary atmospheres such as Venus and Mars will likely involve high radiative heating. This combination of radiative-convective heating presents new thermal protective problems, since the gaseous species leaving the ablating surface are largely radiation transparent. The most promising technique for accommodating combined radiative-convective heating is high surface re-radiation, coupled with a small amount of mass transfer from the ablating material. The formation of an emissive, refractory surface material during ablation is very desirable, since optimum surface radiation occurs at maximum values of temperature and emittance.

Ablative materials will likely be used for thermal protection of future aerospace vehicles as they enter hypersonically into other planetary atmospheres. In the time interval between vehicle launch and planetary entry, an ablative material will be exposed to the elements of the space environment. It will be necessary, therefore, to determine the resistance of candidate ablative materials to wide temperature variations, high vacuum, meteoric impact, and solar, cosmic, and Van Allen radiations. Individual and synergistic influences of the space environment have yet to be determined. Entry into planetary atmospheres of different chemical and physical compositions will introduce new problems, and both theoretical and experimental investigations will have to be made on the behavior of ablative materials behavior in simulated planetary atmospheres.

A superorbital vehicle when entering a planetary atmosphere at escape velocities will produce a very high energy shock wave ahead of itself. Theoretical studies have indicated that high enthalpy environments are best accommodated by material vaporization and subsequent mass transfer in the boundary layer. New light-weight ablative materials which gasify completely into very low molecular weight products should exhibit considerable promise.

Superorbital vehicles may encounter multiple heating phases during atmospheric entry, thus requiring a re-start capability for the ablative material. For example, some initial ablative heat protection may be required for a vehicle decelerating in the upper edges of a planet's atmosphere. The vehicle may then be maintained in a predetermined park orbit in preparation to planetary landing. Meanwhile, the external ablative material must aid in thermal control of the vehicle. Subsequently, the remainder of the ablative material is expended as the vehicle is commanded to land. Synthesis of new ablators and the tailoring of these for this complex environment will indeed present formidable challenges.

Entry vehicles of the future will probably be provided with some degree of lift for vehicle stability and control. The aerodynamic fins may be subjected to extremely high environmental temperatures, which will require some form of thermal protection. Present ablative materials may not be satisfactory in this type of application since high dimensional changes may occur in the region where the gas stream is redirected. New ablators with very high dimensional stability will be necessary.

### Rocket Propulsion Environments

Remarkable advances in rocket propulsion technology have been achieved. For the future, we can expect to see many new design concepts and continued improvements in the performance, reliability, and versatility of rocket propulsion systems. These developments will create a host of new material problems, since currently available materials will likely be unable to accommodate the new environmental parameters. Trends in design and associated environments are listed in figure 19, and the material requirements generated by them are discussed below.

Higher Temperatures—The continued development of higher performance propellants will, in certain cases, lead to appreciably higher combustion flame temperatures. At present, the temperature level is about 5400°F for a typical aluminized polyurethane propellant. Recent solid-fuel developments have extended this value to about 6300°F, with indications of continued increases up to 7000°F and higher. This trend in combustion temperatures is causing greater thermal shock, thermal stresses, and surface heating of ablative propulsion materials. At the highest flame temperatures, refractory throat materials will no longer be usable due to melting or excessive sublimation. It may be necessary to increase material vaporization upstream to the throat to provide some degree of film cooling to this critical area of a rocket nozzle.

Reactive Combustive Species—Improvements in rocket propellants and oxidizers is resulting in combustion products with greater chemical reactivity, corrosiveness and oxidation potential. Interaction of these combustion products with the ablating wall materials will likely result in greater material vaporization, because of deleterious exothermic reactions. Ablative materials will be needed which form a chemically inert surface during exposure to rocket exhaust products.

Surface Abrasion—Energetic particles of aluminum, lithium, beryllium, and boron may be used in future propellants to increase combustion stability and specific impulse. Impact of these particles on the ablating wall will lead to mechanical attribution of varying magnitudes. New ablative materials and novel techniques for handling the severe impact and shear of entrained liquid and solid particles are thus required.

Greater Thermal Shock—Future airborne operations at high altitudes and tactical missions may involve environmental temperatures down to about -75°F. Protection of the missile with special heating equipment is not desired, based on considerations of added weight, increased complexity, and lowered reliability. The ablative propulsion materials will therefore be conditioned at very low temperatures prior to motor firing. This will lead to two new problems, namely, increased thermal shock of the wall materials during initial motor firing, and possible cracking of the case insulation due to its inability to yield with motor pressurization. Ablative materials are required with better thermal shock resistance and low temperature properties.

Longer Burning Times—Two current developments in solid propellant technology will likely result in a considerable increase in firing duration from the present values of 30 to 70 seconds. These are the advent of the segmented motor, and the trend toward very large solid propellant motors. Ablative materials with useful service lives on the order of 100 seconds and longer will be required.

Higher Chamber Pressures—The chamber pressures of current solid propellant motors range from 100 to 2,000 psia, with the majority of values between 400 and 700 psia. The mean chamber pressure of solid-fueled rockets will tend to increase slowly in the future, and possible plateau at a value of about 1,000 psia. Increasing problems of material surface are expected, as well as increased structural requirements for the ablative materials.

Non-Uniform Erosion—The flow of combustion gases may be diverted in certain areas of a propulsion system to achieve proper motor design or thrust vector control. For these cases, non-uniform elliptical erosion may occur in the areas where the gas stream is diverted in direction. Materials and design techniques are required for maintaining better dimensional stability in these critical areas.

Ablators for New Designs—Many new designs in rocket propulsion systems are presently being evolved, and consideration should be given to the possible application of ablative materials to these systems.

Solid propellant motors of very high thrust are being designed either as a large unsegmented engine or as smaller segmented (building-block) motors. Multi-million pound thrust motors having diameters up to 14 feet, lengths up to about 63 feet, and burning times on the order of 85 seconds are being studied. The segmented motor approach involves multiple staging of conical propellant charges, which may be fired sequentially for optimum thrust. Each motor segment or group of segments are fitted with an uncooled ablative nozzle. The large number of possible motor thrust ratings and engine designs requires a far greater understanding of ablative materials for use in this wide spectrum of rocket exhaust environments.

As flame temperatures and corrosivity increase from their present level, attention is being focused on new nozzle configurations. One of the most promising developments is the application of plug-type nozzles to uncooled solid engines. This nozzle is of a mushroom shape design, and provides maximum exhaust expansion for minimum nozzle length and weight. It is competitive with the clustering of four DeLaval nozzles typically used on large solid propellant motors. A major limitation of the plug nozzle is the large mass of material which must be contained in the region of highest heat flux. Consequently, the amount of coolant required could be large to prevent excessive wall temperatures. The applicability of ablative materials to plug nozzle design is as yet relatively unexplored, and further work is required to define the materials problems involved.

Another interesting approach towards reducing the nozzle length and weight is the "internal" nozzle. This design concept is simply a conventional nozzle which has been recessed into a conventional or spherical motor case. Since both sides of the nozzle walls are exposed to the hot combustion gases, requirements for cooling are increased considerably.

Consumable rocket motor cases for solid propellants is another appealing concept for weight saving. In this application, the propellant charge is surrounded by an ablative material which is consumed as the fuel is advanced through the nozzle section. The selection of ablative materials and associated problems are currently on the study stage.

Some attention too is being focused on hybrid rocket motors which offer promise for volume-limited missile systems, thrust modulation, and on-off control of upper stage rockets. Work has been conducted with various hypergolic propellant combinations and liquid oxidizer systems. Ablative material problem areas are largely undefined, and thus some consideration should be given to this motor design.

To achieve variations in thrust and burning rates, new propellant grain designs are being investigated. The internal burning chamber designs of new motors (such as the spherical rocket engine) utilizes a propellant web to protect the fore and aft closure during burning. Less insulative material is thus required for thermal protection of the motor wall. On the contrary, the slotted tube configuration permits the combustive gases to erode the exposed motor wall sections, since the flame contacts these areas throughout firing. The requirement for an effective insulating liner for these new grain designs is apparent.

The use of composite materials in rocket propulsion systems is increasing rapidly. Problems encountered in fabrication and joining are more difficult, due to the dissimilar materials properties. Each basic material component reacts in a characteristic way to the hot propulsion environment, which leads to difficulties in maintaining them as a single functional element. New knowledge and techniques are required for fabricating advanced rocket engine components of various materials having greatly dissimilar thermophysical properties.

Finally, each new rocket design has a multitude of miscellaneous heating problems which may involve the use of ablative thermal barriers. Some of these problems are: skin heating of solid fueled rockets as they exit from the earth's atmosphere, combustion gases seeping back into the booster compartment of the missile, radiant heating due to the clustering of rocket engines, silo and ground equipment heating, and similar considerations.

## Summary

The significance of ablative materials to aerospace technology is now apparent. Our successes in solving the re-entry heating problem and in providing light-weight, high performance propulsion materials are history. The current state of the art represents only first generation developments, and only a small portion of the hyper-environmental spectrum has been investigated. Current material deficiencies must be overcome, and new ablative materials with unique properties and characteristics are necessary. Each new success in this work will permit a wider range of aerospace systems and new capabilities in aerospace technology.

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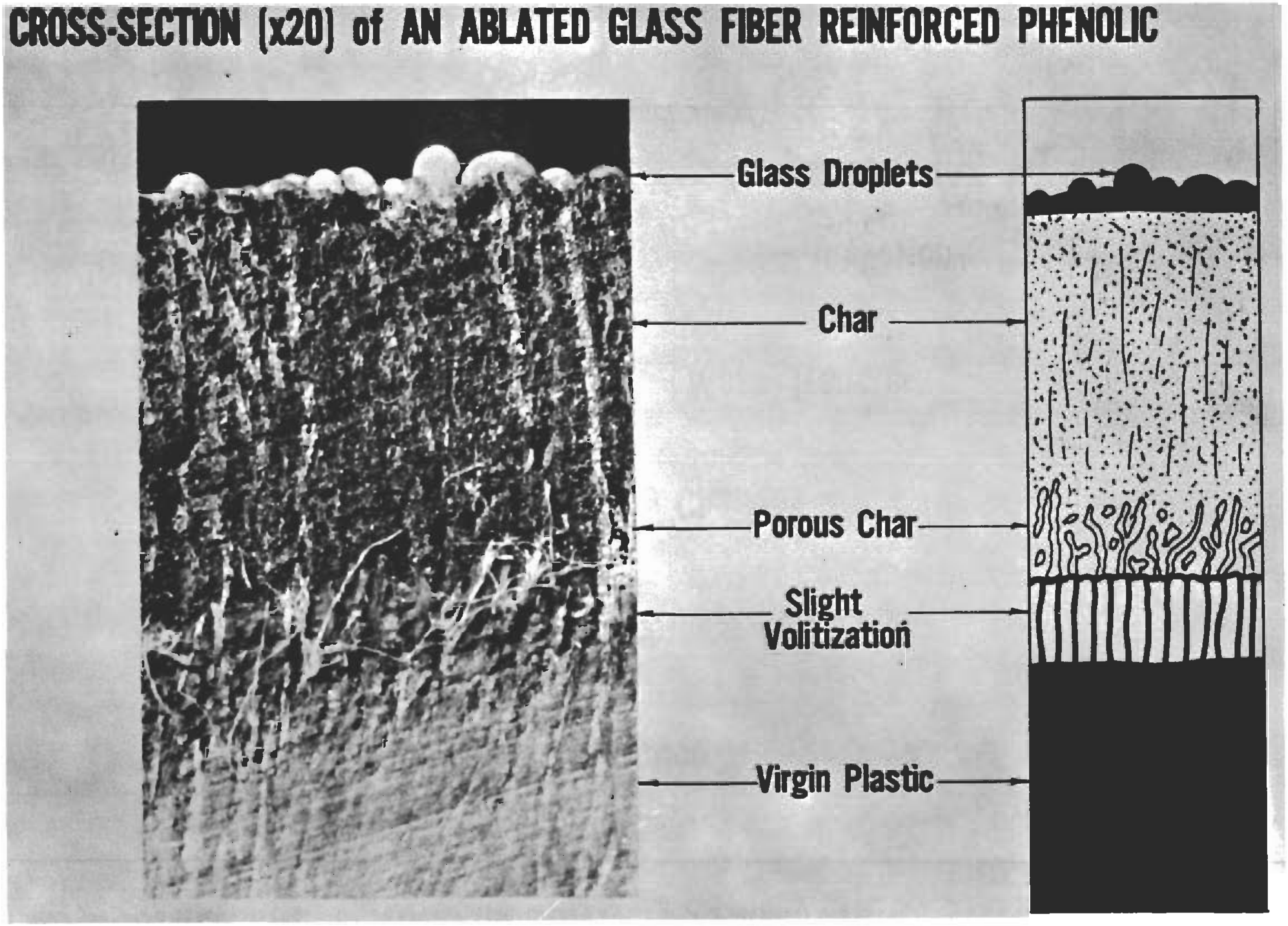
| Figure 12 | Atlantic Research Corporation |
| Figure 13 | The Martin Company |
| Figure 14 | The B. F. Goodrich Company |
| Figure 15 | McDonnell Aircraft Corporation |
| Figure 18 | North American Aviation - Rocketdyne |

| Type of Facility | Gas Enthalpy (Btu/lb) | Gas Velocity (fps) | Gas Mass Flow (lb/sec) | Stagnation Point Conditions Pressure (psf) | Stagnation Point Conditions Initial Heat Flux (Btu/ft$^2$-sec) | Test Fluid Composition | Available Testing Time (min) | Test Area Diameter (ft) | Principal Advantages | Principal Disadvantages |
|---|---|---|---|---|---|---|---|---|---|---|
| Chemical Torch (oxy-acetylene) | 1,000 | 100 to 750 | 0.002 to 0.021 | 50 to 1,000 | 100 to 650 | Combustion products | Near continuous | 0.04 to 0.14 | Inexpensive.<br>Simple and rapid materials screening device. | Low enthalpy.<br>Small exposure area.<br>Chemical reactivity of gases. |
| Rocket Motor (oxy-gasoline) | 1,500 to 3,500 | 7,000 to 8,000 | 0.5 | 10,000 to 80,000 | 300 to 3,000 | Combustion products | 0.5 to 10 | 0.08 to 0.70 | Simulates actual rocket exhaust environment.<br>Accommodates large model sizes.<br>High stagnation pressures and supersonic flow. | Inability to change heat flux without greatly affecting stagnation pressure. |
| Electric Arc Heater (500 kw) | 1,000 to 20,000 | 1,500 to 2,500 | 0.005 to 0.040 | 2,000 to 4,000 | 100 to 1,500 | Air, argon, nitrogen or helium in molecular, dissociated, and ionized states. | Near continuous | 0.03 to 0.10 | Means for continuously heating variety of gases to very high temperatures | Low mass flow.<br>Small exposure area.<br>0.1 to 5% electrode contamination of gas.<br>High power requirement. |
| Electric Air Arc Tunnel (500 kw) | 2,500 to 12,500 | 2,000 to 15,000 | 0.005 to 0.040 | 200 to 2,000 | 100 to 1,500 | Air in molecular, dissociated and ionized states. | Near continuous | 0.03 to 0.15 | Re-entry simulation. | Low mass flow.<br>Small exposure area.<br>0.1 to 5% electrode contamination of gas.<br>High power requirement. |
| Graphite-Resistor Furnace | 1,300 | 3,000 | 0.03 | 6,000 | 200 to 800 | Inert gases or air | 0.1 to 3.0 | 0.04 to 0.10 | Inexpensive.<br>Versatile. | Erosion of furnace walls.<br>Small exposure area. |
| Pebble Bed Heater | 1,200 | 3,600 to 5,500 | 0.1 to 10 | 70 to 15,000 | 50 to 400 | Air | 0.1 to 2 5 | 0.04 to .08 | High stagnation pressure. | Small exposure area.<br>Air temperature declines (10°F/sec) with exposure time.<br>0.5 to 1.0% ceramic dust contamination of gas. |
| Arc Image Furnace | -- | 0 | 0 | 0 to 2,000 | 50 to 2,500 | Vacuum, or any gas | 15 to 30 | 0.02 to 0.08 | Non-contaminated heat source.<br>Control of environmental conditions.<br>Variety of available chemical environments. | No imposing aerodynamic flow.<br>Highly absorbent surface required.<br>Small exposure area.<br>Surface volatiles interfere with radiant transmission. |

Table 2



CROSS-SECTION (x20) of AN ABLATED GLASS FIBER REINFORCED PHENOLIC

Figure 1.

# THERMAL ACCOMMODATION PARAMETERS of ABLATION

**Sensible Heat Absorption**

**Chemical Reactions**

**Phase Changes**

**Mass Transfer**

**Radiation**

Figure 2.

# ABLATIVE MATERIAL SYSTEMS

## Advantages

- High Heat Absorption And Dissipation
- Exceptional Thermal Insulation
- No Maximum Service Temperature
- Weight Savings
- Resistance To Thermal And Mechanical Shock
- Availability
- Design Simplicity And Flexibility
- Non-Strategic Materials
- Low Cost
- Passive In Operation

## Limitations

- Susceptible To High Mechanical Forces
- Service Life Is Time Dependent

Figure 3.

## THE IDEAL ABLATIVE MATERIAL

| Desired Trends | | | |
|---|---|---|---|
| --------→ ∞ | --------→ 0 | --------→ 1 | Variable |
| Heat Of Ablation | Thermal Conductivity | Surface Emittance | Ablative Temperature |
| Strength | Density | Fraction Vaporized | Melt Viscosity |
| Enthalpy Of Phase Changes | Dimensional Erosion | | Melt Surface Tension |
| Specific Heat | Molecular Weight Of Volatiles | | |
| Thermal Shock Resistance | | | |

Figure 4.

## ENVIRONMENT INFLUENCES ABLATIVE PERFORMANCE

| Thermal | Mechanical | Chemical |
|---|---|---|
| Mode Of Heat Transfer | Pressure | |
| Total Heat Load | Shear | Reactivity |
| Shape Of Heat Pulse | Vibration | Oxidation |
| Peak Heating Rate | Acceleration | Reduction |
| Heating Time | Deceleration | |

Figure 5.

## RESEARCH ON ABLATIVE MATERIALS

- Ablation Theories
- Mechanisms Of Ablation
- Elimination Of Material Deficiences
- Synthesis And Fabrication Of New Ablators
- Materials Characterization
- Material-Environment Interactions
- Applications Engineering

Figure 6.

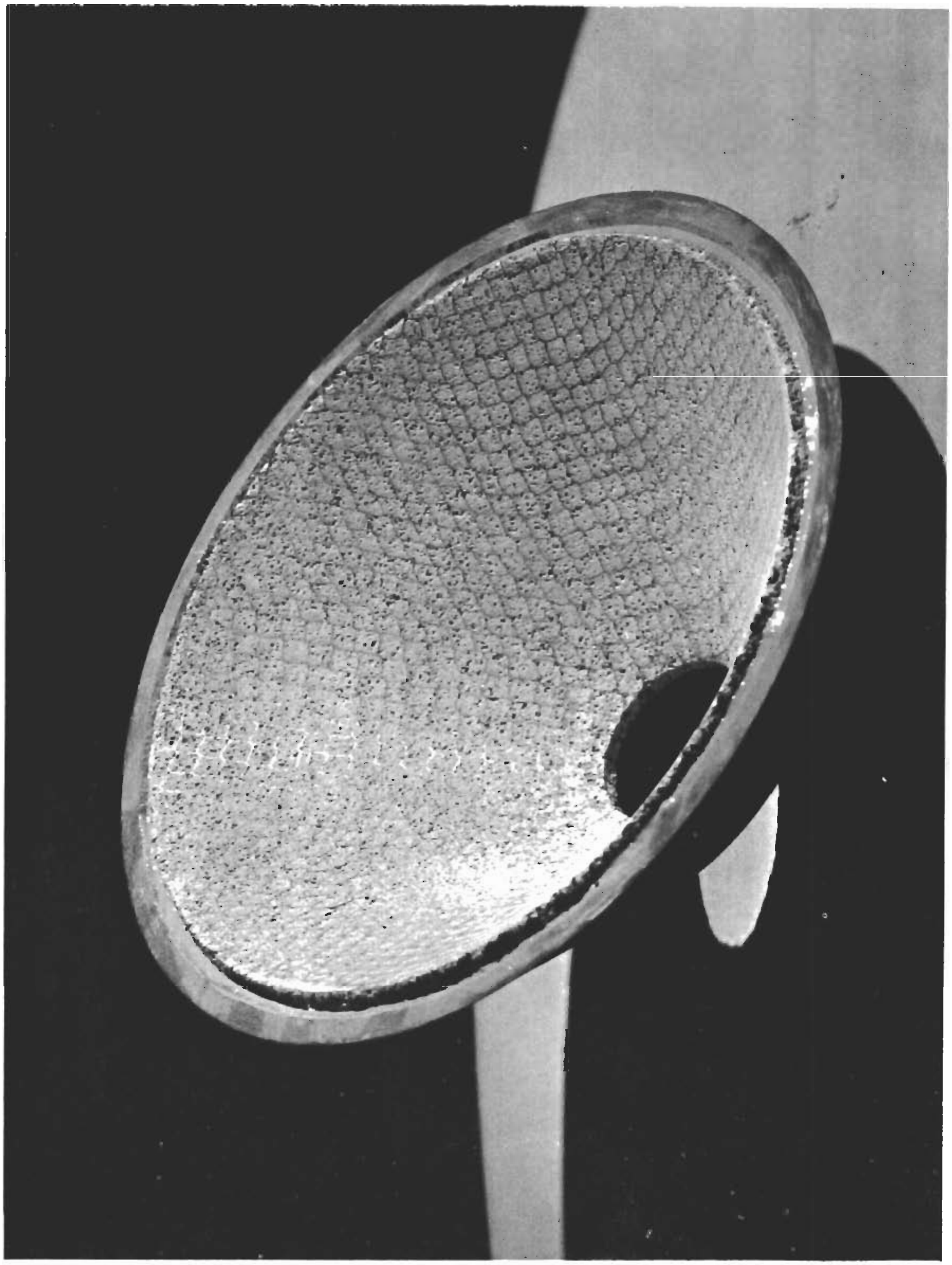


Figure 7. Composite Entrance Cone For Uncooled Rocket Nozzle

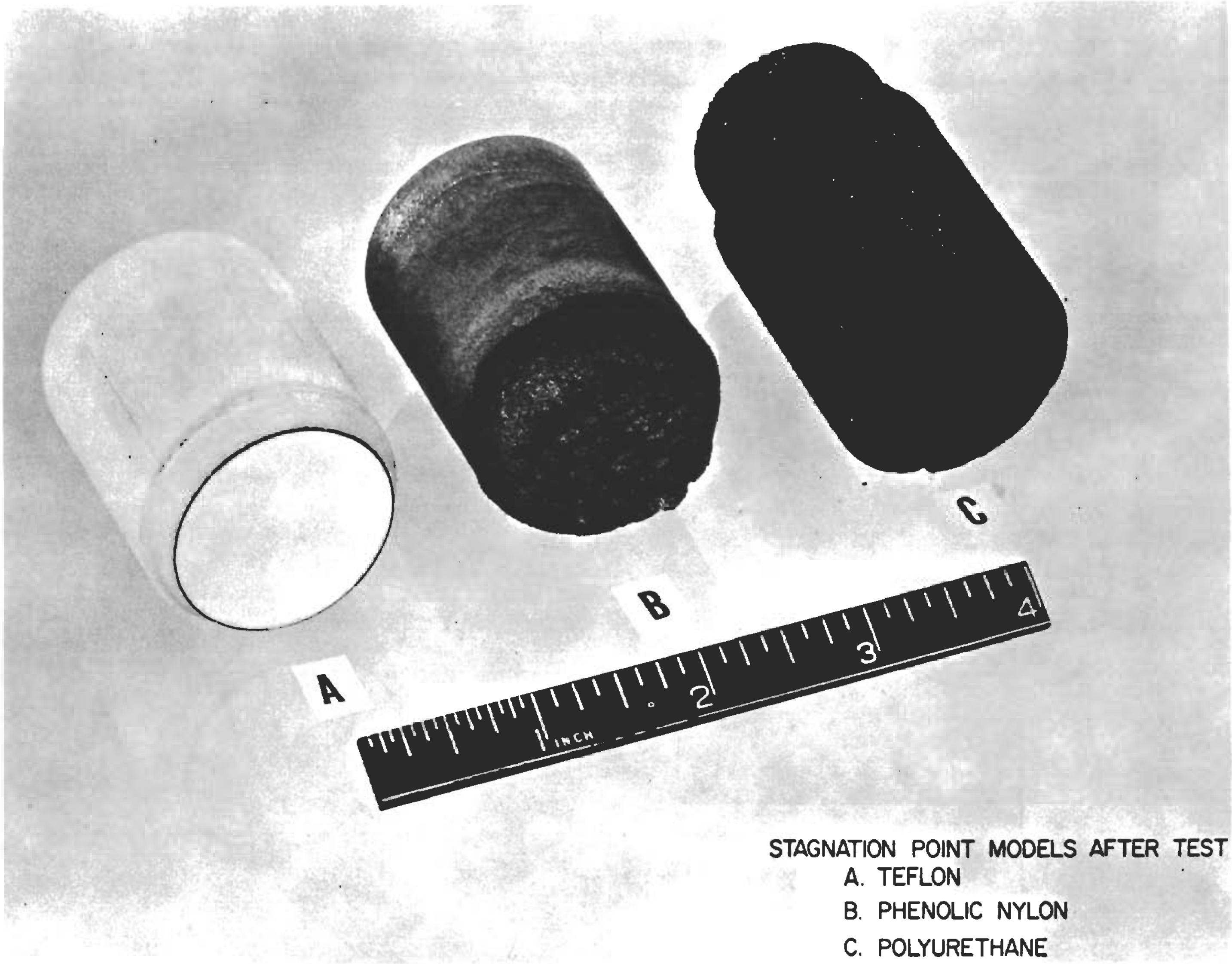


Figure 8. Several Ablative Materials after Simulated Satellite Heating

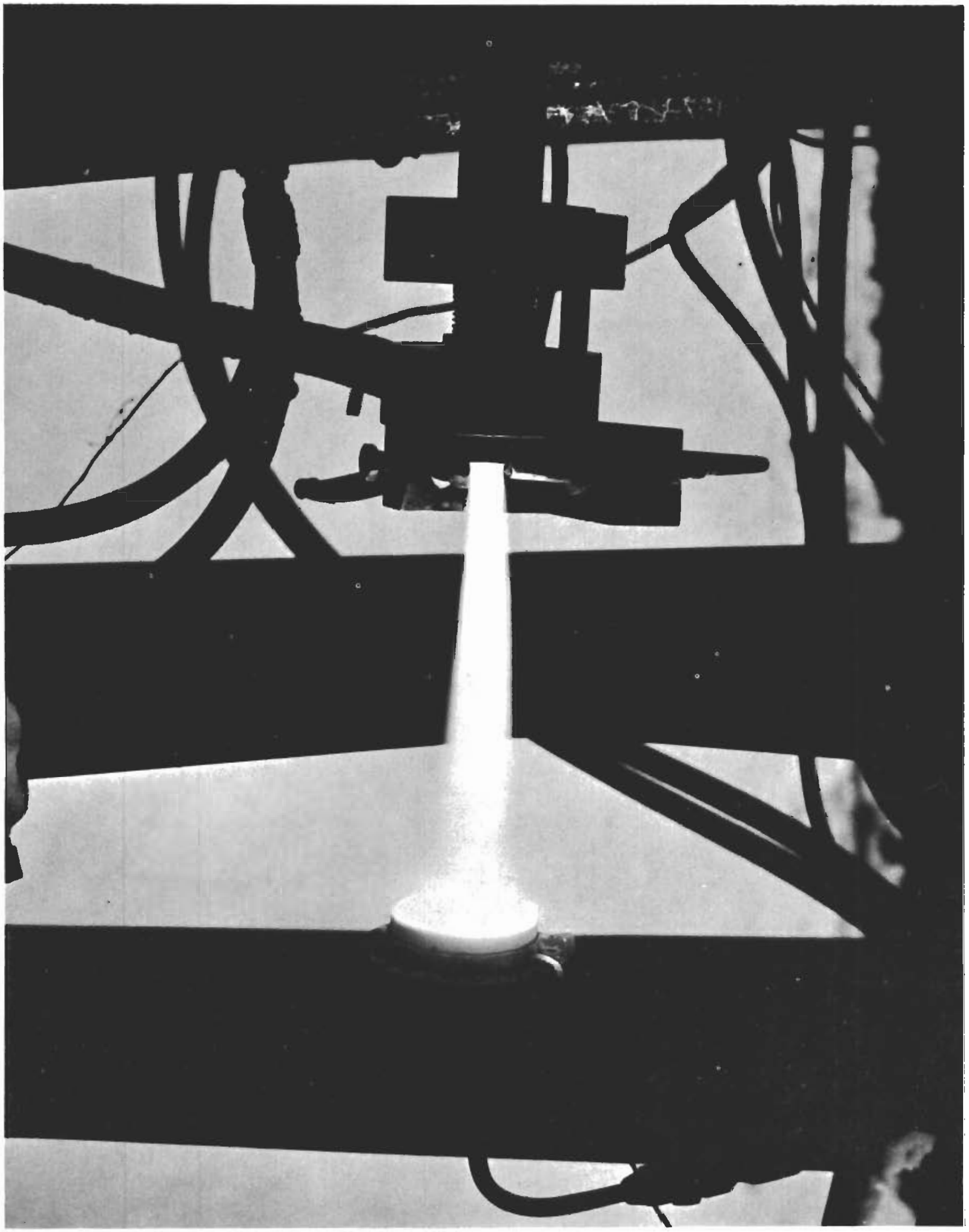


Figure 9. Supersonic Oxy-Acetylene Torch Facility

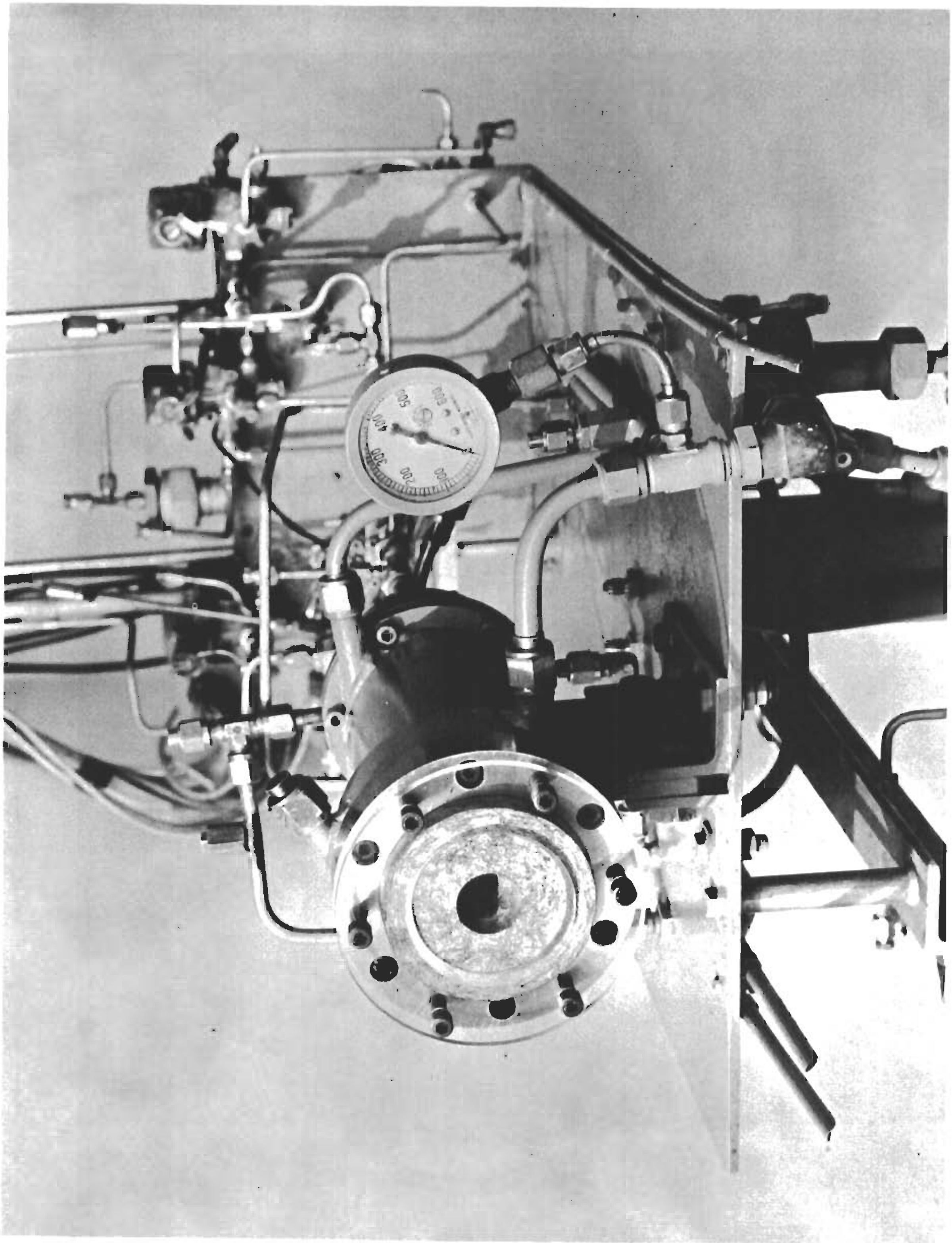


Figure 10. Gaseous Hydrogen-Oxygen Motor For Materials Characterization

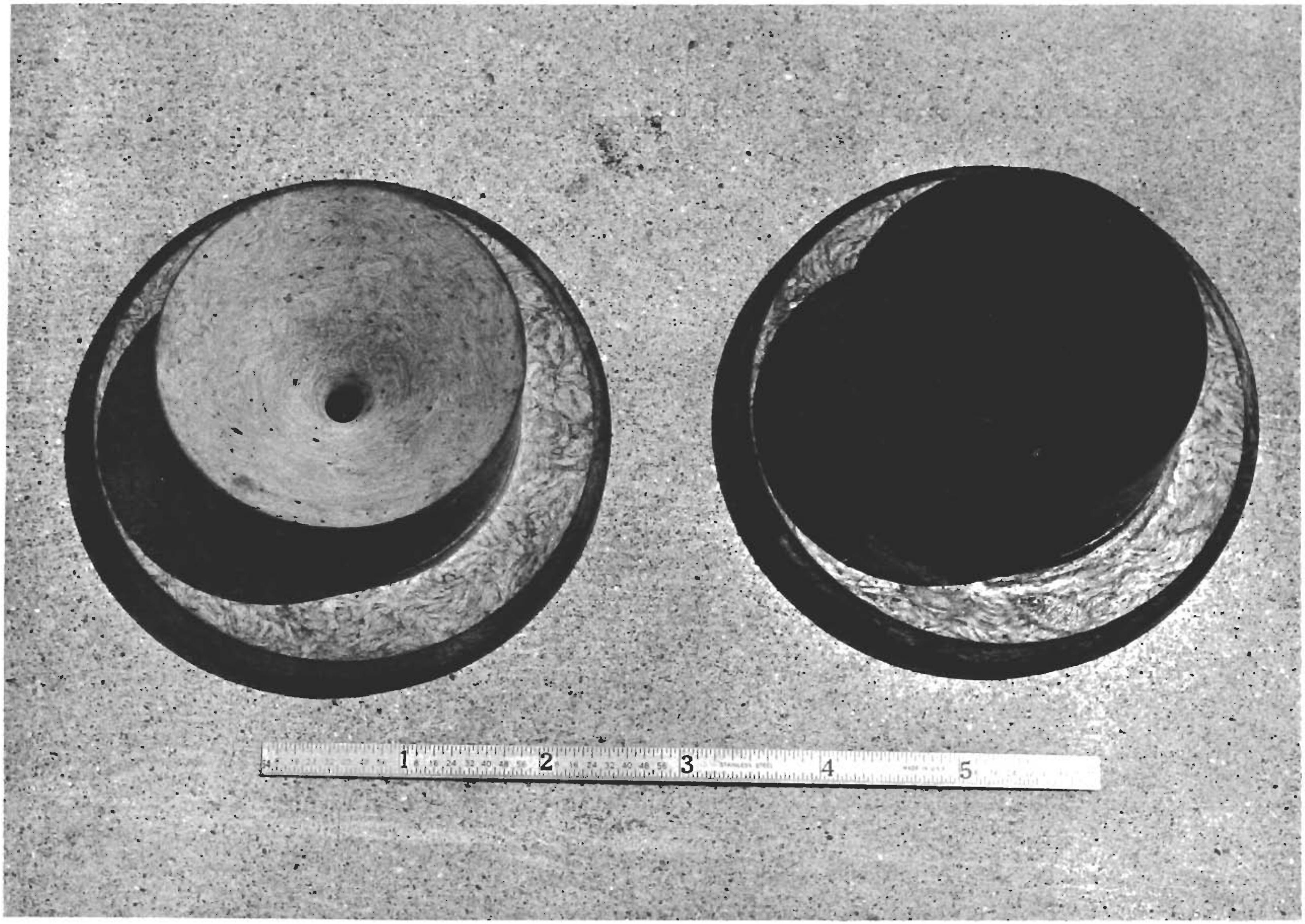


Figure 11. Research Nozzle Specimen Before and After Motor Firing

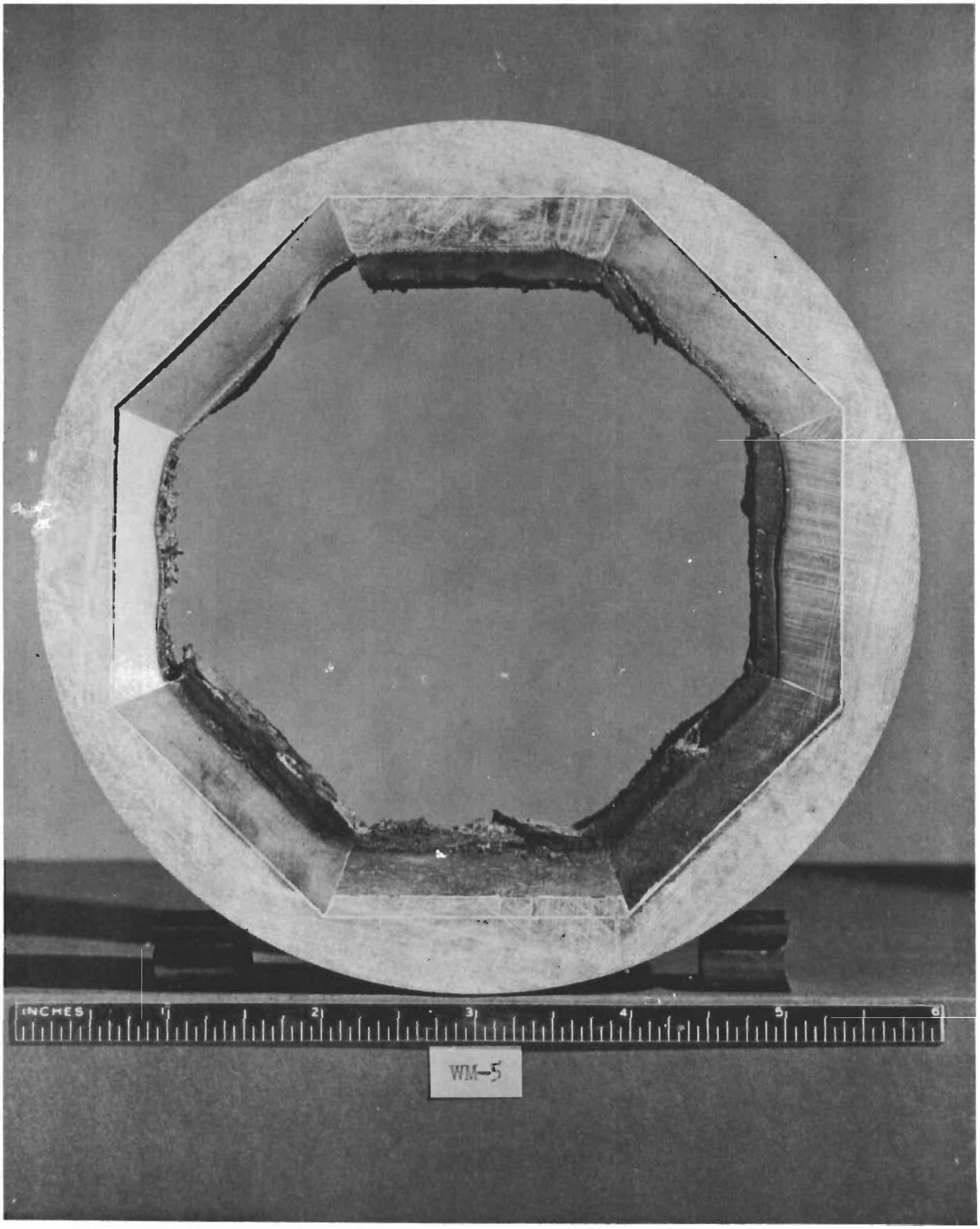


Figure 12. Ablative Insulators After Exposure to Solid Propellant Exhaust

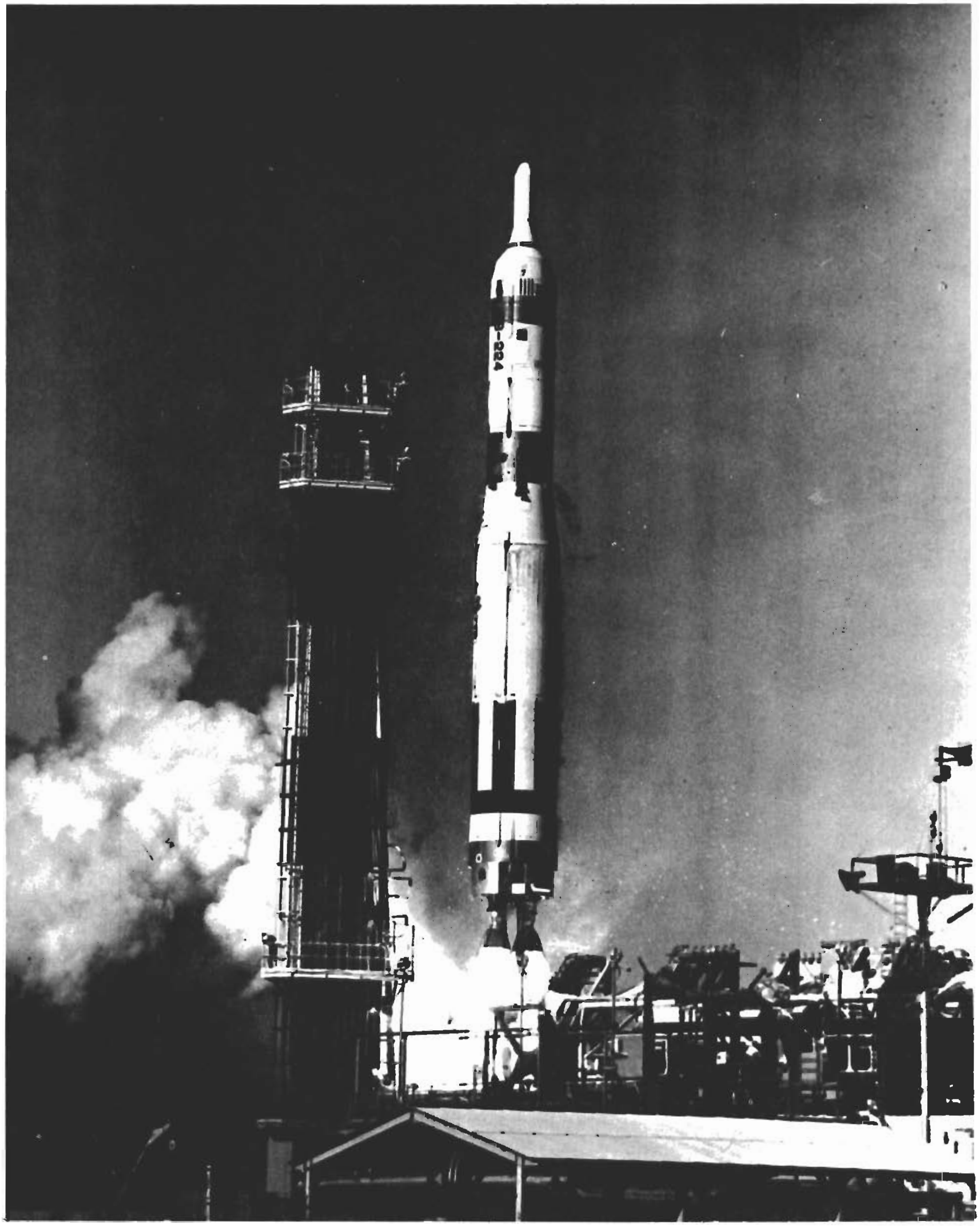


Figure 13. Ablative Materials Research Vehicle Being Launched by a Titan ICBM

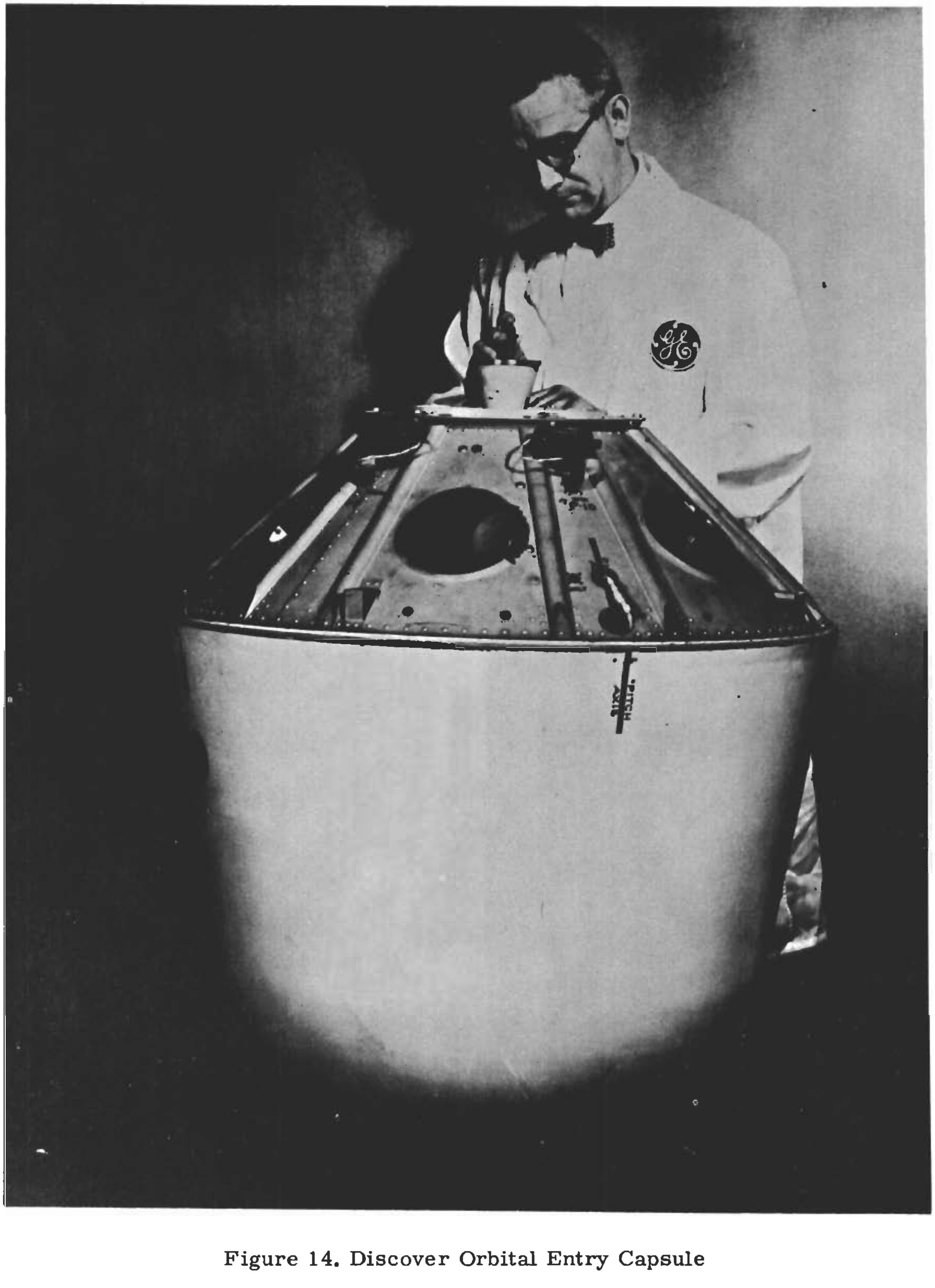
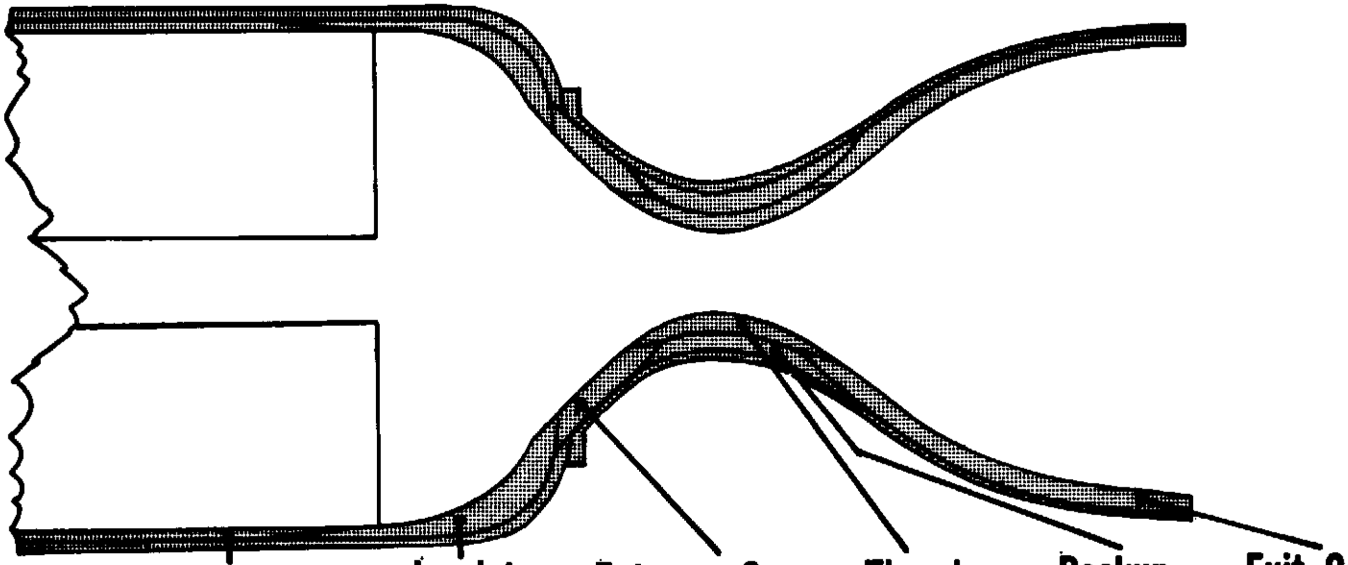


Figure 14. Discover Orbital Entry Capsule

Figure 15. Ablative Heat Shield on Manned Mercury Capsule

## SCHEMATIC of AN ADVANCED SOLID PROPELLANT MOTOR



| Environment | Liner | Insulator | Entrance Cone | Throat | Backup | Exit Cone |
|---|---|---|---|---|---|---|
| GAS TEMPERATURE | 6,300 °F | 6,300°F | 6,200°F | 6,100°F | — | 2,100°F |
| GAS PRESSURE | 800 psia | 800 psia | 760-570 psia | 450 psia | — | 230-15 psia |
| GAS VELOCITY | Low | Low | Subsonic | Sonic | — | Supersonic |
| SURFACE HEATING | Moderate | Moderate | High | Very High | High | Moderate |
| SURFACE SHEAR | Low | High | High | Very High | — | Moderate |

Figure 16. Schematic of an Advanced Solid Propellant Motor

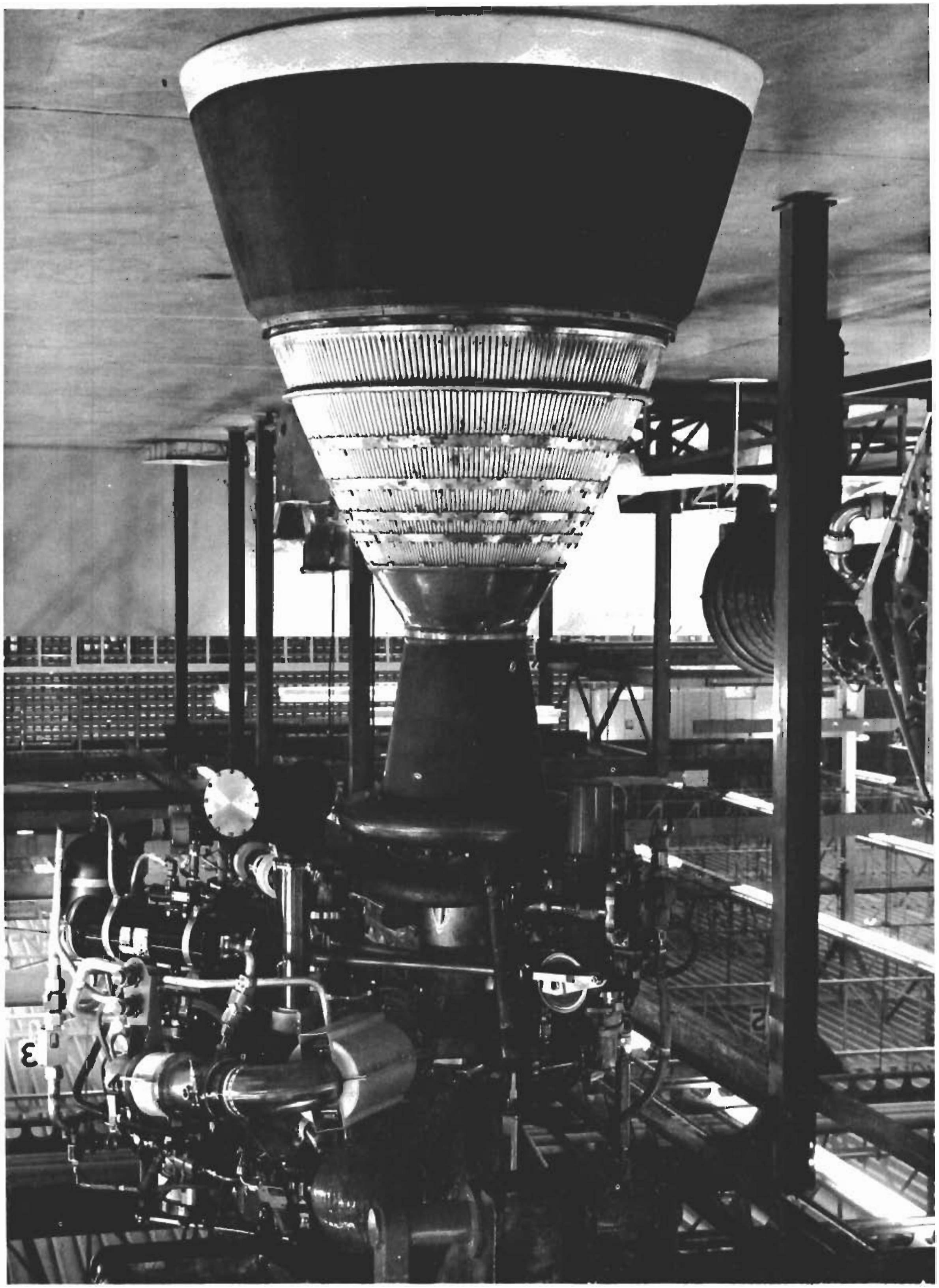


Figure 17. Ablative Skirt on Second Stage Titan Rocket Motor

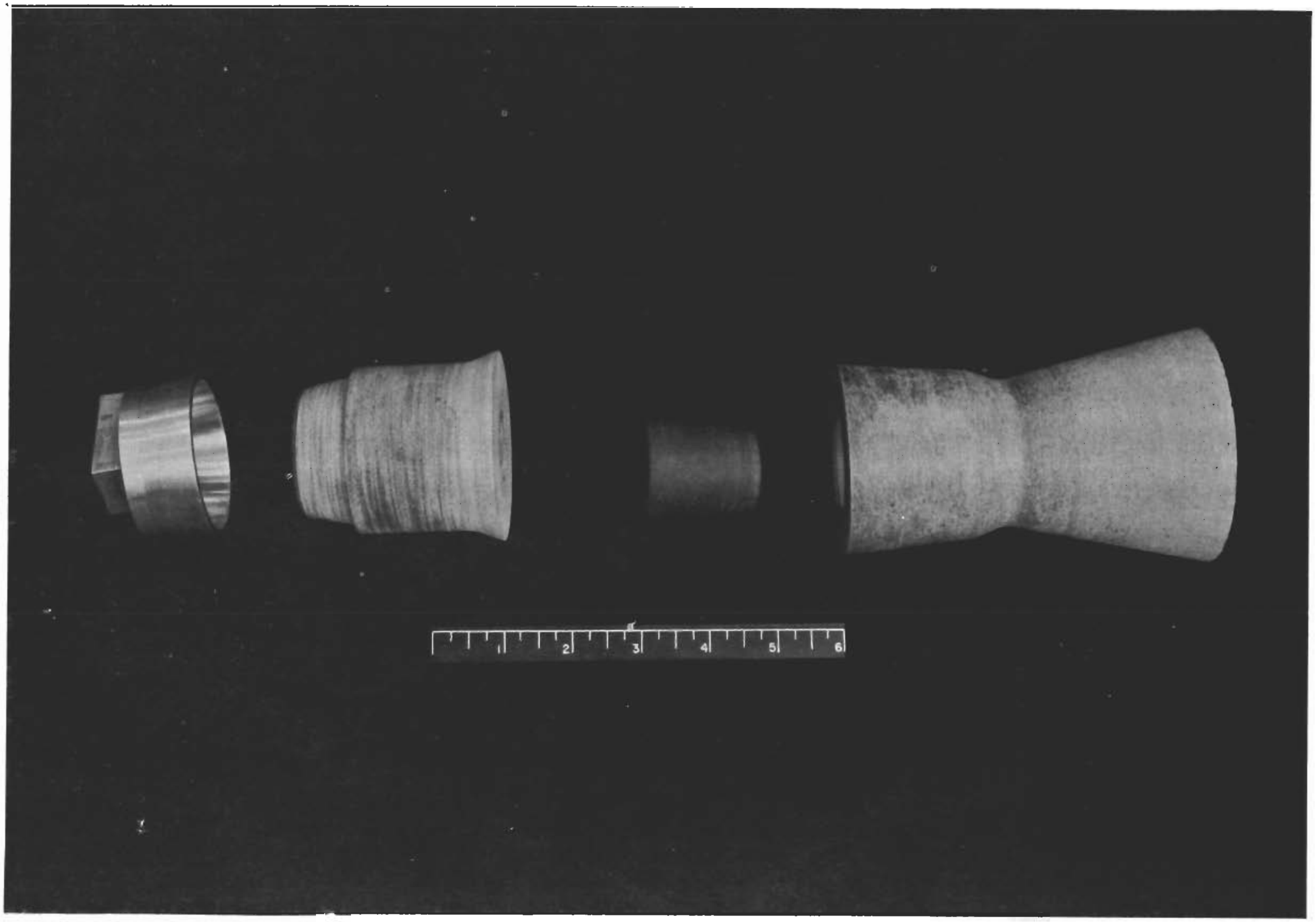


Figure 18. Exploded View of Uncooled Rocket Motor for Space Altitude Control

# NEW TRENDS IN ROCKET PROPULSION SYSTEMS

| Designs | Environments |
|---|---|
| High Thrust Boosters | Higher Temperatures |
| Hybrid Engines | Increased Chemical Corrosion |
| Re-Start Motors | Severe Particle Abrasion |
| Segmented Motors | Greater Thermal Shock |
| Thrust Vector Controls | Longer Burning Times |
| Nozzle Configurations | Higher Chamber Pressures |
| Unconventional Cases | Non-Uniform Gas Flow |
| Composite Construction | |
| Grain Configurations | |

Figure 19. New Trends In Rocket Propulsion Systems