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ANTICIPATED INTERCEPTOR PROPULSION TECHNOLOGY ADVANCEMENTS BY THE LATE 1990's

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ABSTRACT

Advanced components and materials have exciting properties which make their utilization in solid-propelled propulsion subsystems particularly attractive. All of the factors that influence the substitution of a new material for a traditional one must be carefully examined to derive an accurate prediction of the potential of the new material. For example, in the rocket industry, where the consequences of a propulsion subsystem malfunction can be very disastrous, there is considerable reluctance to incorporate advanced materials without extensive testing and prototyping.

The supply of advanced composites, polymers, ceramics, metals provides a major competitive advantage in virtually every propulsion subsystem component. Unfortunately, too often, little attention is given to the exploitation of these materials, and even those materials which have demonstrated very attractive properties in the laboratory have failed to achieve commercial success. Unless this attitude changes, most of the investment in developing the new materials will be wasted.

The discussion format that will be followed will be first a discussion of the state-of-the-art of a particular component and will then be followed by a discussion of advanced materials that are applicable as replacements.

INTRODUCTION

Ground-based interceptors comprise a major element of the strategic defense against hostile (non)nuclear intercepts of reentry vehicles (RV) dispersed from ICBM, SLBM and tactical attack. The changing world's political environment, has done little towards reducing their importance in the overall US defense doctrine. A broad spectrum of materials of construction, etc., are used in the fabrication of these interceptors. These components must be of higher performance characteristics if they are to offer promise to be exploited in advanced interceptors. The demands to reduce the cost and increase the reliability of interceptor propulsion subsystems is the motivation for the defense community to investigate new materials and manufacturing techniques for every component in order to upgrade the future propulsion subsystem.

This paper presents a description of materials that have a recognized potential of providing improved performance and properties for propulsion subsystem components as well as overcoming some of the existing shortcomings. This discussion will provide a comparison of the state-of-the-art of the materials used in present US Army Strategic Defense Command propulsion subsystems, namely, external insulations, motor cases, internal insulation liners, propellants, etc. This will be followed by identifying their potential advanced materials which hold major promise for their replacements.

This paper will identify the innovative components and materials that should be considered for incorporation into solid-propelled propulsion subsystems during the 1990's and beyond. This will involve selecting those components and materials of construction which are currently in commercial production and in extensive use within the aerospace industry, and which can be realistically incorporated into propulsion subsystems and replace those which are in general use in state-of-the-art components. Illustrations of such components are: polybismaleimides, polyimides, liquid crystal polymers, such as: poly p-phenylenebenzobisoxazole (PBO), polybenzimidazole (PBI), etc., rigid-rod ordered polymers, polydimethylsiloxane, etc. These newer classes of organic/inorganic, high-performance ingredients will result in reduced weight, increased payload, increased maximum attainable velocity and improved reliability of kinetic energy weapons for the U.S. Army.

It will, also, include an extensive discussion of Liquid Crystalline Polymers; provide some information on similar resin developments which have occurred within the former Soviet Union and close with a discussion of the "Future Directions in Materials Development".

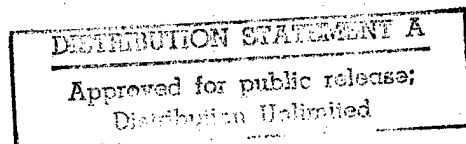
STATE-OF-THE-ART INTERCEPTOR COMPONENTS

There are three interceptor propulsion subsystems which have been under development, or nearing completion of development, by the U.S. Army Strategic Defense Command, that are used, in this paper, as an appropriate base of reference for establishing the state-of-the-art. Cross-sectional drawings of these developmental propulsion subsystems are presented in Figure 1. These are: 1) the Exoatmospheric Reentry Vehicle Interceptor Subsystem, whose acronym is ERIS, and whose mission is to destroy Reentry Vehicles before they return into the atmosphere, and is representative of 1986 technology; 2) the Solid Propellant Booster Development, whose acronym is SPBD, and is representative of 1991-92 technology, and; 3) the Missile Integrated Stage Technology, whose acronym is MIST, and is representative of 1993-94 technology.

Of particular significance, when these propulsion subsystems are compared, is the close similarity of the compositions of the various components although three different propulsion companies were responsible for their development. This is one of the topics that will be addressed in this paper.

CROSS-SECTION OF A TYPICAL MOTOR SEGMENT

By way of introduction to the subject, and orientation, an interceptor propulsion subsystem is fabricated in layers, usually from the motor case inwards in successive layers, as depicted in Figure 2. Each component is designed to serve a clearly-defined function. Breakdown of any of these components would result in a malfunction when the propellant is ignited.



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THERMOSTABLE EXTERNAL INSULATIONS

The state-of-the-art insulations thermostable external motor case insulation which are in general use are either cork-filled, or silica-filled phenolic resins, epoxy resins, teflon or Korotherm. Their limitations are: inadequate thermal characteristics, excessive weight, limited protection from aerodynamics and radiant heating, cost, limited damage control against nuclear blast effects.

The effectiveness of the conventional external motor case insulations as compared to polydimethylsiloxane is presented in Figure 3. Over the upper exposure temperature ranges (300-550 F), polydimethylsiloxane is almost universally more thermally stable.

ADVANCED THERMOSTABLE EXTERNAL INSULATIONS

A proposed replacement for these state-of-the-art insulations is polydimethylsiloxane (PDMS) which is depicted in Figure 4. It offers the following attributes: reduced weight, increased effectiveness, void free, reduced thermal degradation, reduced off-gassing, and cleaner combustion observables. The structural formula of PDMS and its similarity to rubber is presented in Figure 4. A comparison of tensile strength, elongation, and Shore A hardness of PDMS, when aged in air at 204 C (400 F), and Shore A hardness and modulus at low temperatures are also presented in Figure 5 and 6. These highlight the superiority of the mechanical properties of PDMS over rubber.

COMPOSITE MOTOR CASE MATERIALS

The three propulsion systems, namely ERIS, SPBD and MIST incorporate similar graphite fibers. IM7X, T1000 and T40 are somewhat different because they are made by different manufacturers. These are presented in Table 1. Graphite fibers are the primary reinforcing fibers in use today in the fabrication of composite motor cases.

Graphite fibers produced within the Western World are manufactured from either special polyacrylonitrile (PAN) fiber or from coal-based or oil-based pitch. Rayon fibers are also, used because of economic considerations. Surprisingly, these fibers are not unique to the Western World. The former Soviet Union has developed graphite fibers by thermal decomposition manufacturing the same raw materials as those used in the Western World but also by using an entirely novel starting material, known as Oxalon. Oxalon, in controlled thermal decomposition conditions, yields graphite fibers which are claimed to be of high tensile strengths and ultrahigh tensile modulus. An apparent advantage of using Oxalon as a graphite fiber precursor instead of the other precursors could be based on its ability of introducing trace quantities of reactive "moieties" into the polymer precursor. These groups could serve to modulate the elasticity of the graphite fiber for special purposes through the controlled introduction of certain functional groups.

Graphite fibers-reinforced composites have impressive strength and stiffness properties, and have seen use in many weapons applications. However, they fall short in some areas, such as, impact resistance, corrosion and chemical attack, ability to make thin low cost structures, delamination around fasteners, and fatigue due to thermal cycling.

ADVANCED MODIFIED GRAPHITE FIBERS

Graphite fibers can be readily modified to enhance certain characteristics such as: 1) twisted tows which contain protruding fibers producing a stronger bond between the fiber and the resins, 2) multi-component hybrid fibers to provide increased interlaminar shear and lower void content, 3) metals (such as nickel, copper) deposited on graphite fibers for increased electrical conductivity and reduced susceptibility to electromagnetic radiation and electrostatic buildup, and 4) bromine intercalation to produce increased (5X) electrical conductivity.

EXTENDED CHAIN POLYETHYLENE FIBERS

A replacement for graphite fiber is the extended-chain polyethylene fiber. It is the stiffest and strongest available fiber, and is described in Figure 7. Its pressure x volume/weight is 6.03×10 in. and has a higher than high tensile strength graphite fibers. It is marketed under the tradename of Spectra 900 and 1000. The difference between the conventional and extended-chain polyethylene fibers are: molecular weight, degree of orientation, and chain folding.

To understand how polyethylene, the soft plastic of squeeze bottles, can, without chemical alteration, be transformed into fibers with a tensile strength greater than an equivalent weight of steel, one must follow the underlying changes that occur in its microstructure. The microstructure of polyethylene, like that of most semicrystalline polymers, is dominated by spherulites: structures resembling sunbursts, made up of crystalline plates radiating from a common center. Within each of the plates, the polymer chains fold back and forth between two planes, filling the spaces between the plates are amorphous regions.

As the semicrystalline polymer is drawn into a fibril, the spherulites pull apart, and the plates break up into small blocks of folded chains. The chief structural elements of the fibril are microfibrils, in which crystalline blocks are lined up end to end. The blocks are separated by less ordered regions, but linked by the molecular extending from block to block.

Extrusion, or extensive slow drawing at a temperature near the melting point of the polymer is one way of achieving orientation. Another method consists of converting the polymer to a gel, by solvent action, from which the oriented fibers are drawn. In the gel, the network of micromolecules, making up the material, is expanded, reducing its resistance to drawing.

COMPOSITE MOTOR CASE RESINS

The resins which may have been used in the fabrication of these composite motor cases is probably a blend of epoxy compounds, as depicted in Figure 3. They could be a blend of 40% diglycidyl ether of Bisphenol A, plasticized with 40% of diglycidyl ether of 9,12-octadecadiendioic acid and 20% of a viscosity depressant of diglycidyl ether of 1,4-butanediol.

Epoxy resins have been the workhorse polymers of the composite industry because of their superior properties. Among these features are good bonding to a range of reinforcements and substrates, good chemical resistance, wide availability in variant forms with diverse curing agents tailored to processing user needs, high dimensional tolerance, and good electrical insulation properties.

ADVANCED COMPOSITE MOTOR CASE RESINS

A) EPOXY RESINS

The epoxy resin blend which is currently in use in the fabrication of composite motor cases is seriously out of date. There are improved epoxy resins which are commercially available which offer high temperature-resistance and toughened properties.

Possible modification of epoxy materials can be introduced to improve their characteristics. Some of these are listed in Table 2 which identifies some of their attributes and limitations are: 1) using diglycidyl ether of tetrabromobisphenol A which is available from Great Lakes Company. It is available commercially, and used to impart fire retardancy to apparel. 2) an expandable monomer, 3,9-bis(5'-norbornene-2-yl)-1,5,7,11-tetraoxa [5.5]undecane. This compound was developed by the U.S. Army Strategic Defense Command. When it is incorporated into an epoxy blend, it produces a void-free polymer which, during polymerization, undergoes expansion, rather than shrinkage (which is characteristic of resins). This material is available from Epolin, Inc.

Thermosetting bismaleimide resins and their copolymers, addition and condensation type polyimides, thermoplastic liquid crystal polymers, and thermoplastic polyalkylsiloxanes can all be considered as replacements for epoxy resins for a diversity of applications.

B) BISMALEIMIDE/POLYIMIDES

While the dominance of epoxy resins is challenged by new entries, the performance criteria of alternatives are benchmarked against this durable pioneer. Bismaleimides (BMI) are an advance over epoxy resins in high heat resistance, as are phenolics (with new cure systems and low smoke-generating ratings), and condensation polyimides are at the forefront with properties maintained even at exposures near to 700 F. But processing advances and property improvements are still being sought before these materials will be more widely used.

C) POLYIMIDE

The polyimides, of which bismaleimide, (since it is derived from maleimide) is the simplest member of the polyimides. The structural formulas of bismaleimide, PMR-15 and LARC-160 are depicted in Figure . PMR-15 and LARC-160 are prepared from the condensation product of bicyclopentadiene and maleic anhydride. The polyimides have thermal characteristics that place them in an intermediate position between the epoxy resins and the liquid crystal polymers NASA has been responsible for most of the efforts on polyimide development for the past several years, however, with the promise offered by the liquid crystal polymers they appear to be losing their attractiveness.

Among the thermoplastic replacements, in addition to the liquid crystal polymers are the ultrahigh thermally-resistant phthalocyanines.

COMPOSITE MOTOR CASE INTERNAL INSULATIONS

The predominant ingredients, used in internal motor case insulation, are Kevlar pulp filled ethylene-propylene-diene prepolymer crosslinked with sulfur or an organic peroxide. MIST differs from the compositions of ERIS and SPBD because it contains a diversity of chemical compounds as binder modifiers and as fillers. These compositions are listed in Table 2.

ADVANCED MOTOR CASE INTERNAL INSULATIONS

While most are of the opinion that crosslinking by the use of sulfur or an organic peroxide occurs at the alkenic bond in ethylene-propylene-diene (EPDM), it actually consists of reaction with the allylic hydrogen. This leaves the alkenic bond so that it can undergo cleavage, due to oxidative reactions, on aging as a consequence, EPDM needs to be replaced in advanced internal insulations. The promising replacement candidates are PDMS and LCPs, or modification of the EPDM to eliminate the alkenic bonds.

LINER-BARRIER COMPOSITIONS

The typical compositions of the liner-barriers, used in these motors are based on carbon-filled, polyisocyanate-crosslinked hydroxyl-terminated polybutadiene prepolymer, as presented in Table 4.

ADVANCED LINER-BARRIER COMPOSITIONS

Several approaches are available towards upgrading the qualities of liner-barrier compositions. These are listed in Table 5 and consist of: 1) replacement of the carbon powder with microballoons would result in liners of lower densities, 2) the incorporation of mercury thiocyanate or sodium silicate which would result in the formation of a thick char layer, lower thermal conductivity, thinner liner requirements, and significant further improvements can be achieved by 3) replacing the hydroxyl-terminated polybutadiene with polydimethylsiloxane or thermoplastic liquid crystal polymers.

SOLID PROPELLANT COMPOSITIONS

The ingredients which went into the propellants of ERIS, SPBD and MIST, are presented in Table 6. Crosslinked HTPB is the workhorse binder in SOTA solid propellants. MIST is the exception since it contains the binder, whose acronym is BNO-3. It is composed of Hycar 1300 x 13, end-capped with polyethylene glycol 600. Hycar 1300 x 13 is a copolymer of polybutadiene and acrylonitrile.

MIST also contains boron powder, as a replacement for aluminum, BDNPA/F which is a 50:50 mixture of bis (2,2-dinitropropyl) methanal (formal) and bis (2,2-dinitropropyl)ethanal (acetal) along with triethylene glycol dinitrate (TEGDN). The other propellants contain only the more common ingredients.

ADVANCED SOLID PROPELLANT BINDER RESINS

Several alternate binders to HTPB are under investigation and listed in Table 7. These are: 1) Polyethylene glycol (PEG) which is an oxygen-containing binder, and offers higher oxygen stoichiometry, 2) tetrahydrofuran-terminated polyethylene glycol (HTPE) and 3) Glycidyl azide polymer (GAP). Another possibility is the product of nitrogen pentoxide with HTPB, namely nitrate-nitro-HTPB. The latter has not been developed to the point to justify its inclusion in this listing.

A comparison of these binders insofar as oxygen content and the specific impulse value calculations, based on 20% polymer and 80% HMX, as compared with HTPB which contains almost 0% oxygen is contained in Table 8. Both PEG and GAP offer higher oxygen content and specific impulse values of 225 and 247-S, as compared to HTPB of 215-S. The considerably higher value of GAP is due to the fact that it contains the azide group.

A possible futuristic binder is included in Table 8 which offers higher oxygen content of 62% and a calculated specific impulse value (80% HMX/20% binder) of 257-S is polybis(3-oxapropyl)-bis(2,2-bisnitratomethyl)-1,3-propanedioate.

COMPOSITE PROPELLANT OXIDIZERS

There is little doubt that ammonium perchlorate is the standout oxidizer for use in solid propellants. It is also predictable that it will be the oxidizer of choice for the future since the facilities for its manufacture in millions of pounds annually exist.

ADVANCED COMPOSITE PROPELLANT OXIDIZERS

The most attractive novel oxidizer of the future that is under development is a polynitroaza-caged compound, code named CL-20, which is being produced in limited quantities. A comparison of its performance with HMX in an aluminized and a non-aluminized propellant formulation is presented in Figure 9. The high density of CL-20 is the basis for its attractiveness.

In comparable aluminized propellant formulations, the density-impulse of CL-20-containing propellant was calculated to be 17.83 lb-s/ft³ as compared to 17.70 lb-s/ft³ for HMX-containing propellant. Similarly, replacement of ammonium perchlorate in a non-aluminized propellant with CL-20 improved the density-impulse from by 0.14 lb-s/ft³.

ADVANCED MATERIALS - LIQUID CRYSTAL POLYMERS - A NEW CLASS OF HIGH-PERFORMANCE MATERIALS

While I have made several references to Liquid Crystal Polymers, it would be advisable to devote part of this discussion to them because of their newness and their potential for several different applications in advanced propulsion and materials subsystems.

Liquid crystal polymers derive their outstanding properties from their rigid-rod molecular structure which, at the macroscopic level, results in a self-reinforced material with the strength and stiffness of a composite, but without the matrix, and fiber-matrix interface problems.

Several thermoplastic liquid crystal polymers, whose acronyms are: Ultem, PBI, Ryton, PAEK, PEEK, Vitrex, PBO are either in or approaching commercial production. Their attractiveness for exploitation in propulsion subsystems is presented in Table 10. Their primary attributes are: high temperature resistance and thermoplastic characteristics, but they also enjoy a large number of additional attributes which make them very attractive for exploitation.

Polyetheretherketone (PEEK) was introduced in 1982, and immediately attracted attention for the benefit by forming by heat and low pressure. Additionally, the maintenance necessary for thermoset preregs binder refrigeration and shipment in dry ice, would be eliminated. Cure, and production times, can be accelerated with the more automated thermoplastic production technologies, and processing is much cleaner in several respects. In the decade of the 1990s, toughness and repairability are the driving forces to identify and adapt high-temperatures thermoplastics for use in composites. Other thermoplastic resins in use, though low in volume, are: polyphenylene sulfide (PPS), thermoplastic polyimides, polyarylates, polyetherimide (PEI) and liquid-crystal polymers.

The commercialization of LCPs, in which molecular chains line up as self-reinforcing within the resin itself is a significant advance. These exceptionally strong materials can be processed at high temperatures. They yield a thermally stable and solvent resistant finished product. Extruded LCP tapes, with and without fiber reinforcement, are expected to be a lower density competitors to epoxy preregs.

Liquid crystal polymers are molecular design in which the backbone of the polymer is inherently more rigid and straight. This occurs when aromatic (aryl) functional groups are incorporated into the chain, because they are stiffening elements. These aromatic groups are stabilized through resonance and impart double-bond character to adjacent single bonds in the backbone. When enough aromatic groups are incorporated into the polymer chain, the molecule resembles rigid rod.

An aromatic-polymer-chain design offers, a) rigidity of the individual moieties when stiffens the bulk polymer and, b) thin rod-like character causes them to become aligned under certain conditions. Certain rigid-rod polymers are liquid-crystalline which means that, in solution or in the melt, the macromolecules can spontaneously line up, like logs in a logjam, and form regions in which most of the molecules are oriented in one, or, perhaps two directions. The extent of the ordered, crystal-like regions can be increased under certain conditions of flow, such as, passage through a spinneret. Hence, it is easy to open a liquid crystal into fibers in which many of the

polymer chains are tensed, the links that are stressed are not weak intermolecular attractions, but covalent carbon-carbon bonds, the same links that account for the hardness of diamond.

Similarly, Aramid fibers, commercial fibers, spun from a liquid-crystalline phase, have a tensile strength comparable to that of steel. In their solid phase, liquid-crystalline polymers, also, benefit from chain alignment. The oriented regions that formed in the liquid phase, then act as reinforcing elements, greatly increasing the stiffness of the material. Such polymers enjoy high softening points and great resistance to most solvents.

GLASS TRANSITION TEMPERATURES

A key factor in determining the attractiveness of a particular resin for use in propellants is glass transition temperature which is the temperature range at which the properties of a polymer change from a brittle glass to a rubbery elastomer. It provides an indication of the macromolecular strands which may be intertwined by chain entanglement, thus creating a polymer with enhanced mechanical properties. Weak, secondary bonding for as can also result in the association of these individual strands, for example, hydrogen bonding in polyamides generally increase the glass transition temperature values considerably.

The improvements which are affected in the glass transition temperatures of the various resins, used in solid-propelled propulsion subsystems is depicted in Table 11.

SOVIET VS WESTERN WORLD RESINS

Based on the limited data which were accessed on the former Soviet developments in organic resins, the complacency as to the observation that the Western World is well in the forefront in advanced resin development is not warranted.

A comparison of Soviet developments in composite precursors with the Western equivalent is presented in Table 12.

Many of the Soviet organic resins, available for use in its military systems are identical to Western-produced resins in terms of chemical configuration and mechanical characteristics, e.g., epoxy, nylon, polyester, polyimides and polyolifins. Nevertheless, there are several differences because the Soviet tends to produce resinous materials based-on either acrylic or heterocyclic chemistry.

The Soviet produces Aramid fibers (under the tradename Terlon) that is chemically identical to Kevlar. It also produces another Aramid fiber whose mechanical characteristics are similar but not in chemical configuration. It is named Uniivlon and SVM (super high modulus). The chemical structures of SVM fiber appears to be a cross between PBI and Kevlar. The Soviet also produces a chemically identical polymer under the brand name of Fenilon, to Nomex. Soviet materials literature consistently claims that SVM/epoxy structural composites exhibit interlaminar shear that is, at least, 25% greater than Kevlar/epoxy when processed under conventional conditions.

With the pending completion of a large Bisphenol A production facility, Soviet products such as epoxy, polycarbonate, polyester and polysulfane resins will enjoy growing use.

Polybenzoxazole, another resin being produced in the Soviet offer thermal capabilities of 50C higher than epoxy resins (225 C) with comparable mechanical characteristics to epoxy resins.

Advances within the Soviet have been to the production of improved polyolifin materials with coefficients of friction reportedly better than those of fluoropolymers, such as, Teflon for low-friction seals.

Another Soviet product is polynitrooxadiazole. The nitro group offers the potential of being converted to an amino group which could then be reacted with epoxy or bismaleimide resins.

It is clear that Soviet resins development differs from the West in terms of basic chemistry but also appears to be based on variations of equivalent Western technologies. The West needs to continually study their different approaches which could easily lead to better solutions to our own problems.

FUTURE DIRECTIONS IN MATERIALS DEVELOPMENT

Developments in materials science and engineering over the past few decades have been dramatic, and progress is expected to continue. However, much of the focus on future R&D must change from what it has been in the past. During this decade, it will be necessary to learn to exploit what already has been invented in an economical, reliable and environmentally acceptable manner, rather than inventing additional new materials.

The following are a few thoughts as to how additional improvements can be affected to LCPs. A) If LCPs are extruded into biaxial film/tape form, the result could be a tensile strength value as high as 240 ksi and modulus value of 25 MSI. With appropriate heat treating, polymer's level of crystallinity and molecular alignment would be enhanced, the LCPs physical properties can be projected to be further increased. If LCP film were consolidated with thermoplastic adhesives, such as PEEK or advanced polyimides, it can then be used to fabricate highly efficient composite structures. The film form has advantages over fiber because it can be more readily processed into sheets, beams, stiffeners, tubes and other structural shapes. B) The LCPs may be metallated to increase its adhesion properties by reaction with n-butyllithium and N,N,N',N'-tetramethylethylenediamine in an argon atmosphere, and then quenched with CO₂ gas. The butyllithium reacts with the stabilized or the hydrogen on the benzene ring to form a carboxylic acid. By introducing carboxylic acid sites in the LCP microfibrillar structure a strong adhesive bond can be formed with interpenetrating epoxy and polyimide resins in the formation of laminar structures.

SUMMARY

To summarize this discussion has addressed the state-of-the-art of ground-based interceptors production subsystems components and described avenues for advancing materials technology in order to affect increases in performance with cost and weight reduction. A matter of concern is the close similarity of the materials used by the propulsion community and the degree of conservatism that they have shown.

The advanced materials which have major potential of upgrading propulsion subsystem performance already exists within the aerospace industry and stand ready to be exploited.

Some of the more exciting materials that were discussed are: extended-chain (stretched) polyethylene fibers, polydimethylsiloxane, liquid crystal polymers, bismaleimides, polyimides, CL-20, etc.

And finally, based on the limited data which were accessed on the Soviet Unions' developments in organic resins, it can be concluded that the US materials technology is not advanced over that of the Soviet Unions.

Table 1. Composite Motor Case Compositions

COMPONENT	MISSILE INTEGRATED STAGE TECHNOLOGY (MIST)	SOLID PROPELLANT BOOSTER DEVELOPMENT (SPBD)	ERIS LOW COST BOOSTER
GRAPHITE FIBER TYPE	T-40	T1000	IM7X
RESIN TYPE	1908 EPOXY (AMOCO)	LRP-205 EPOXY (THIOL)	HBRF309 (HERCULES)
CURING AGENT	AMINE	.	AMINE

* NOT AVAILABLE

Table 2. Advanced Composite Motor Case Compositions

TECHNOLOGY ADVANCEMENTS	ATTRIBUTES
• THERMOSETTING TETRABROMODIGLYCIDYL ETHER OF BISPHENOL A 	• HIGHER TEMPERATURE TOLERANCE • GREATER FLAME RESISTANCE • INCREASED INSULATIVE CHARACTERISTICS • REDUCED WEIGHT • COMMERCIALY AVAILABLE
• EXPANDABLE MONOMER - EPOXY MODIFICATION 3,9-BIS (5'-NORBORNENE-2'-YL)-1,5,7,11-TETRA-OXOSPIRO [5.5] UNDECANE	• VOID-FREE • COMMERCIALY AVAILABLE - (EPOLIN, INC) - (WESTINGHOUSE) - (HITACHI)
• BISMALEIMIDE COPOLYMERS (BMI) 	• HIGHER TEMPERATURE TOLERANCE THAN EPOXY - (450 F VS 350 F) • REACTION CURED - (NO CURING AGENT) (800 F) • HOT MELT WIND
• POLYIMIDES (ADDITION & CONDENSATION TYPES)	• COMMERCIALY AVAILABLE - LARC-160 (MITSUBISHI) - LARC-171 (MITSUBISHI) - PMR-15 (HYDRO) - POLYIMIDE 790 (LENZING) - POLYIMIDE MATRAMID 9725 (CIBA GEIGY) - NEW TYPE POLYIMIDE (MITSUBI-TDATSU)
• THERMOPLASTIC - LIQUID CRYSTAL POLYMERS • POLYDIMETHYLSILOXANE	
• PHTHALOCYANINES	
SOTA: EPOXY (POLYOXIRANYLMETHYL) BLENDS	

Table 3. Internal Insulations

COMPONENT	MISSILE INTEGRATED STAGE TECHNOLOGY (MIST)	SOLID PROPELLANT BOOSTER DEVELOPMENT (SPBD)	ERIS LOW COST BOOSTER
METHOD OF MANUFACTURE	TAPE WOUND	FILAMENT WOUND	WOUND ONTO MANDREL
BINDER	EPDM	EPDM	EPDM
BINDER MODIFIERS	TRILENE 67, AGERITE RESIN D, ZINC OXIDE, STEARIC ACID		
FILLERS	DECHLORANE PLUS, KEVLAR, SILICA, ANTIMONY OXIDE, FERRIC OXIDE	KEVLAR	KEVLAR
CURING AGENT	SULFUR	ORGANIC PEROXIDE	SULFUR

Table 4. Liner-Barrier Compositions

COMPONENT	MISSILE INTEGRATED STAGE TECHNOLOGY (MIST)	SOLID PROPELLANT BOOSTER DEVELOPMENT (SPBD)	ERIS LOW COST BOOSTER
BINDER	HTPB	HTPB	HTPB
CROSSLINKING AGENT	IPDI-TDI DIMER	.	.
FILLER	CARBON BLACK	.	.
CURE ACCELERATORS	DIBUTYL TIN DILAURATE		
BURNING RATE ACCEL		CATOCENE	

Table 5. Advanced Liner-Barrier Compositions

• MICROBALLOONS	• LOWER DENSITIES
• POLYBENZIMIDAZOLE (PBI)	• HIGHER THERMAL RESISTANCE
• MERCURY THIOCYANATE	• THICK CHAR LAYER FORMATION
• SODIUM SILICATE	• LOWER THERMAL CONDUCTIVITY
	• THINNER LINER THICKNESS
	• HIGHER MOTOR LOADING
• POLYDIMETHYLSILOXANE	• LOWER THERMAL CONDUCTIVITY
• THERMOPLASTIC POLYMERS	• THINNER LINER THICKNESS
	• HIGHER MOTOR LOADING
HTPB	45.0
CARBON	40.0
BOND PROMOTER	4.0
REACTION ACCELERATOR	0.1
CATALYST	0.1

Table 6. Solid Propellant Compositions

COMPONENT	MISSILE INTEGRATED STAGE TECHNOLOGY (MIST)	SOLID PROPELLANT BOOSTER DEVELOPMENT (SPBD)	ERIS LOW COST BOOSTER
BINDER	BNO-3	HTPB	HTPB
OXIDIZER	AMMONIUM PERCHLORATE	AMMONIUM PERCHLORATE	AMMONIUM PERCHLORATE
	RDX		RDX
FUEL	BORON	ALUMINUM	ALUMINUM
BURNING RATE ACCELERATOR	NONE	CATOCENE	
MODIFIERS	PLASTICIZER-BDMPA-F, TEGDN		
CROSSLINKING AGENT	DESMODUR N-100 TRISOCYANATE*		HEXANE DIISOCYANATE

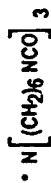


Table 7. Advanced Solid Propellant Binders

• HYDROXYL-TERMINATED POLYBUTADIENE $\text{HO}-\left[\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2 \right]_n-\text{OH}$	• SOTA
• POLYOXIRANE, POLYETHYLENE GLYCOL (PEG) $\text{HO}-\text{CH}_2-\text{CH}_2-\left[\text{O}-\text{CH}_2-\text{CH}_2 \right]_n-\text{OH}$	• HIGHER PERFORMANCE • OXYGEN-CONTAINING BINDER • HIGHER OXIDATION STOICHIOMETRY • COMMERCIALY AVAILABLE (ANTI-FREEZE) • LOW COST
• TETRAHYDROFURANE-TERMINATED POLYOXIRANE (HYDROXYL-TERMINATED POLYETHER (HTPE)) $\text{HO}-\left[\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O} \right]_n-\left[\text{CH}_2-\text{CH}_2-\text{O} \right]_y-\text{H}$	
• POLYOXIRANYLMETHYL AZIDE (POLYGLYCIDYL AZIDE POLYMER) (GAP) $\left[\text{H}_2\text{C}-\text{CH}(\text{CN}_3) \right]_n \rightarrow \text{HO}-\left[\text{CH}-\text{CH}_2-\text{O} \right]_n-\text{H}$	• LOW COST • EASILY MANUFACTURED • LIMITED PRODUCTION • INSENSITIVE • MANUFACTURED FROM GLYCIDYL CHLORIDE (EPOXY RESINS) + SODIUM AZIDE (AUTOMOBILE GAS BAGS)

Table 8. Comparison of Solid Propellant Binders

BINDER TYPE	OXYGEN CONTENT (%)	SPECIFIC IMPULSE (lb-s/lbm) (1000 → 14.7 psf) (80% HMX/20% POLYMER)
• HYDROXYL-TERMINATED POLYBUTADIENE (HTPB) $\text{HO}-\left[\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \right]_n-\text{OH}$	0	215
• POLYETHYLENE GLYCOL $\left[\text{O}-\text{CH}_2-\text{CH}_2 \right]_n$	36	225
• POLYGLYCIDYL AZIDE $\left[\text{CH}-\text{CH}_2-\text{O} \right]_n$ $\left[\text{CH}_2-\text{N}_3 \right]_n$	16	247
• POLYBIS (3-OXAPROPYL)-BIS (2, 2-BISNITRATOMETHYL)-1, 3-PROPANEDIOATE $\left[\text{O}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O} \right]_n$	62	257

Table 9. Comparison of Performance of HMX and CL-20 (Non) Aluminized Propellants

Aluminized Propellants	Isp, sec	Density, lb/in.3	Isp, sec * ρ
10 HTPB/20 Al/58 AP/12 HMX	265.8	0.0666	17.70
10 HTPB/20 Al/58 AP/12 CL-20	265.7	0.0671	17.83
Nonaluminized Propellants			
HTPB/HMX (87%)	235	0.0628	14.75
HTPB/AP (87%)	251	0.0647	16.04
HTPB/CL-20 (87%)	249	0.0650	16.18

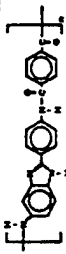
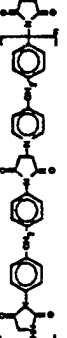
Table 11. Improvement of Glass Transition Temperatures of Resins

RESIN	GLASS TRANSITION TEMP (F)
BIS A EPOXY	300-250
NOVOLAC	400-450
BISMALEIMIDES	400-490
POLYIMIDES	640
POLYBENZIMIDAZOLE	815

Table 10. Thermoplastic Liquid Crystal Polymers

PRODUCT	PROPERTIES
POLYETHERETHERIMIDE (ULTEM) (GE)	• HIGH TEMPERATURE RESISTANCE
POLYBENZIMIDAZOLE (CELAZOLE) (CELANESE)	• GOOD DAMAGE TOLERANCE
	• LOW VOID CONTENT (<1%)
P-PHENYLENESULFIDE (RYTON) (PHILLIPS PETROLEUM)	• COMMERCIALY AVAILABLE
	• REDUCED FABRICATION COSTS
POLYARYLETHETHERKETONE (PAEK) (UNION CARBIDE)	• REDUCED MOISTURE PICKUP
	• REDUCED MOISTURE DEGRADATION
POLYETHERETHERKETONE (PEEK) (duPONT) (IMPERIAL CHEM)	• HIGH HEAT DISTORTION/GLASS TRANSITION TEMPERATURE
	• RESISTANT TO SOLVENTS
POLYETHERSULFONE (VITREX) (IMPERIAL CHEMICAL)	• LOW MOISTURE SENSITIVITY
	• NO CURE CHEMISTRY INVOLVED
POLYPHENYLENEBENZOBENZOXAZOLE (PBO) (DOW CHEM)	• FABRICATED INTO COMPONENTS BY THERMOFORMING
	• JOINTS READILY WELDED

Table 12. Comparison of Former Soviet and Western World Resins

SOVIET RESIN/FIBER	USA EQUIVALENT
FENILON	HOMEX
TERLON	KEVLAR
NYLON (DIFFERENT CHEMICAL CONFIGURATION)	KEVLAR
GRAPHITE PRECURSORS POLYACRYLONITRILE (PAN) PITCH RAYON	GRAPHITE PRECURSORS POLYACRYLONITRILE PITCH RAYON OXALON (PHENYLOXADIAZOLE)
	
	POLYBENZIMIDAZOLE (PBI)/KEVLAR HYBRID
	EPOXY
	NONE
PYRIDINE-REACTED POLYBISMALEIMIDE	POLYBISMALEIMIDE

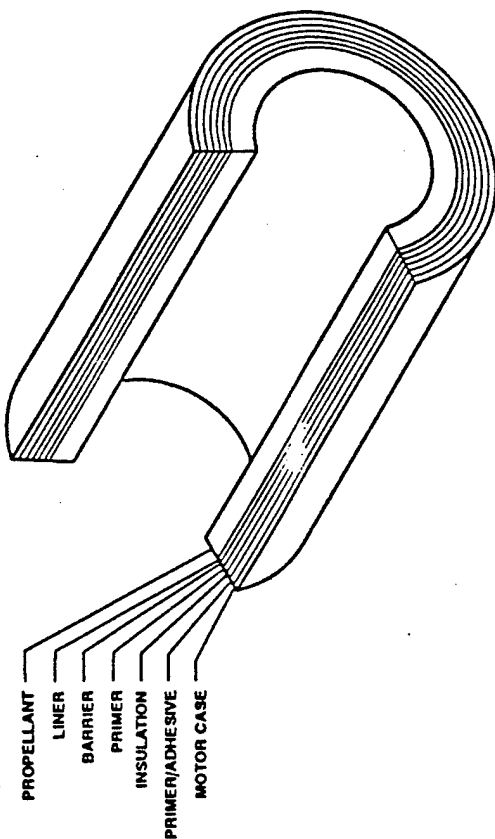


Figure 2. Cross-Section of a Typical Motor Segment

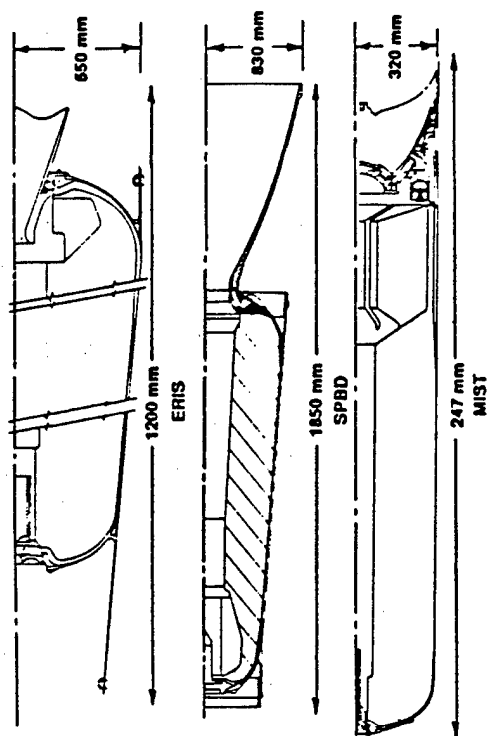


Figure 1. Cross-Sectional Drawings of Near (SOTA) Propulsion Subsystems

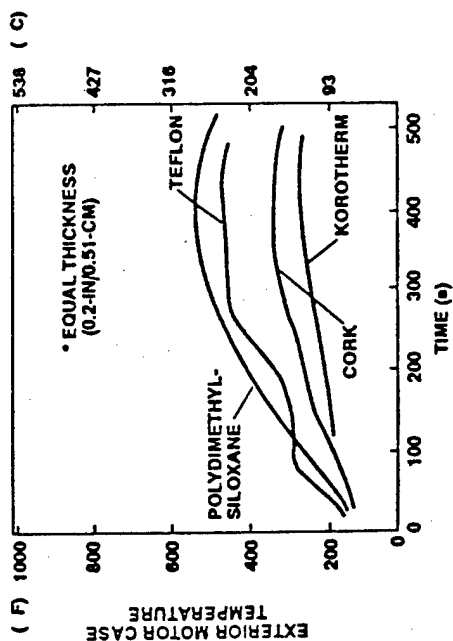


Figure 3. Effectiveness of External Motor Insulations

POLYDIMETHYL-SILOXANE		RUBBER	
CH ₃	CH ₃	H	H
-Si-O-Si-O-Si-O-Si-O	-Si-O-Si-O-Si-O-Si-O	-C-C-C-C-C-C-C	-C-C-C-C-C-C-C
CH ₃	CH ₃	H	H
		CH ₃	CH ₃

Figure 4. Similarity Between PDMS and Rubber

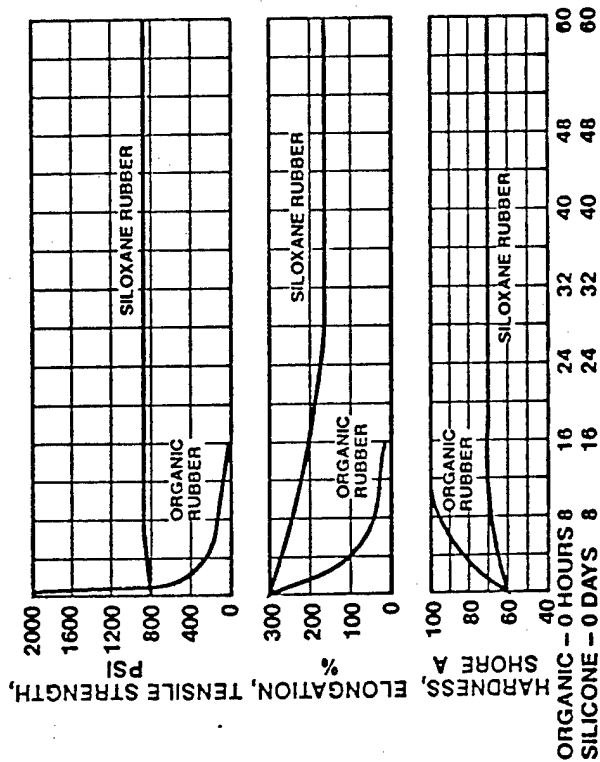


Figure 5. Changes in Mechanical Properties of PDMS and Rubber on Aging at 400 F in Air

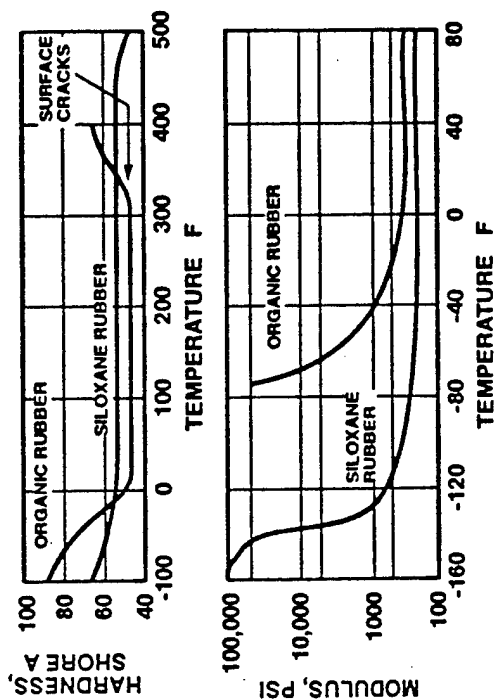
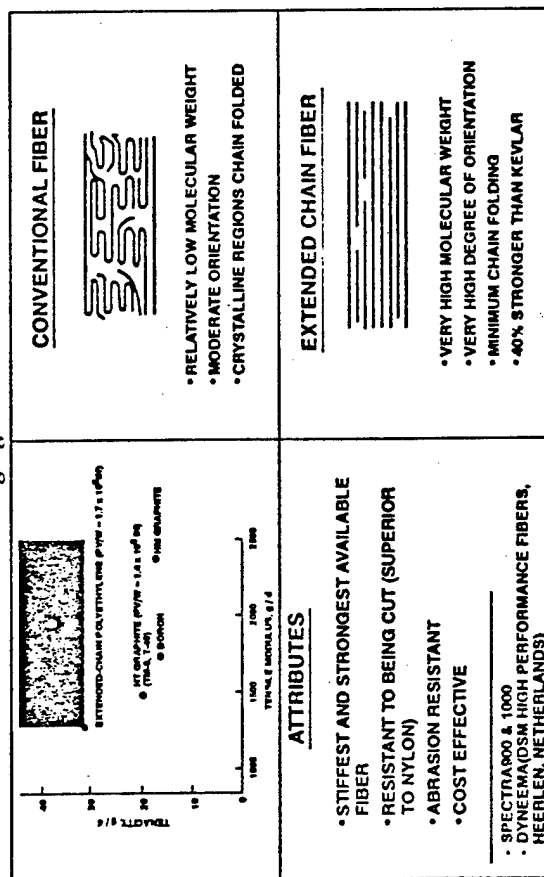


Figure 6. Low Temperature Effects on Mechanical Properties of PDMS and Rubber

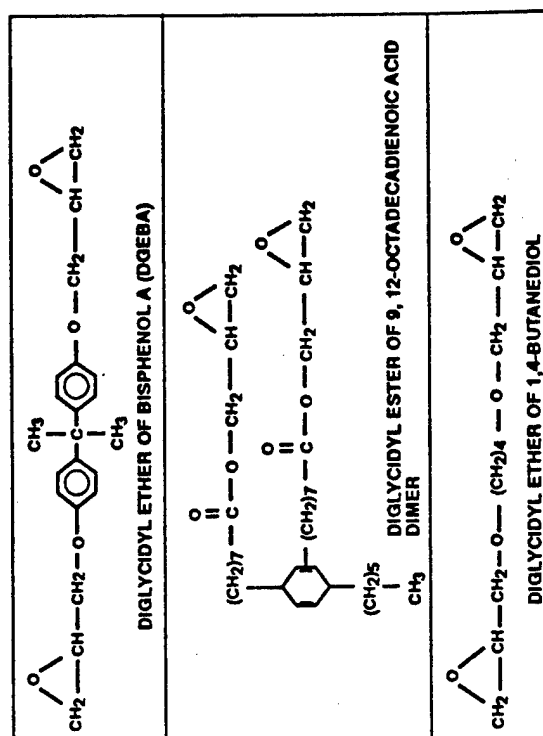


Figure 8. Composite Motor Case Epoxy Resin Blend

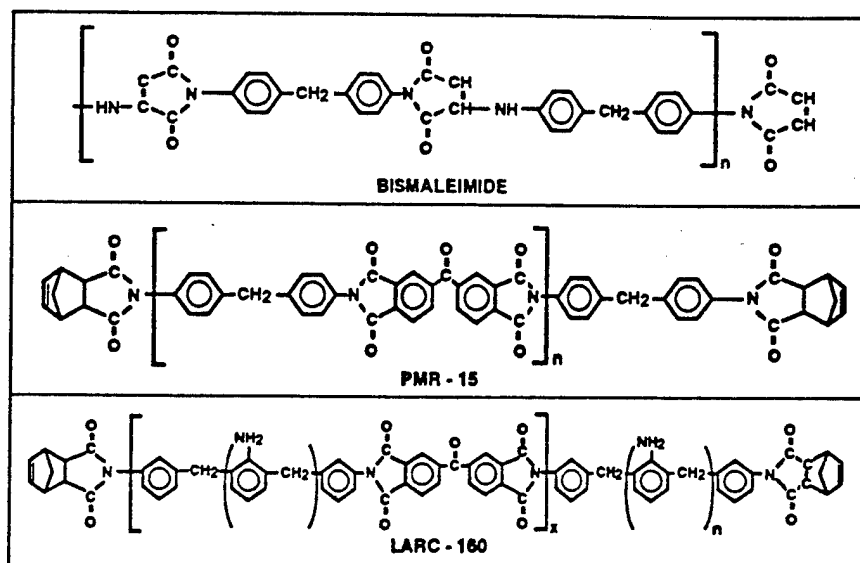


Figure 9. Polyimide Binders