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(54) Title: HIGH PRESSURE, HIGH PERFORMANCE SOLID ROCKET HYDROXY-TERMINATED POLYBUTADIENE PROPELLANT FORMULATIONS (57) Abstract A solid rocket propellant formulation with a burn rate slope of less than about 0.15 ips/psi over a substantial portion of a pressure range of about 1,000 psi to about 7,000 psi and a temperature sensitivity of less than about 0.15 %/°F is provided. The solid propellant formulation contains from 35 % to 55 % by weight ammonium perchlorate particles having an average size of 200 μm, from 25 % to 40 % by weight ammonium perchlorate particles having an average size in the range of from 2 μm to 50 μm, from 7 % to 10 % by weight hydroxy-terminated polybutadiene binder and at least one member selected from the group consisting of a co-oxidizer, a ballistic additive, and a polyisocyanate curative. A high performance solid propellant rocket motor including the solid rocket propellant formulation is also provided. The rocket motor is encased in a high strength low weight motor casing which is further equipped with a nozzle throat constructed of material that has an erosion rate of about 2 to about 3 mils per second during motor operation. The solid rocket propellant formulation can be cast in a grain pattern such that an all-boost thrust profile is achieved.		

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HIGH PRESSURE, HIGH PERFORMANCE SOLID ROCKET
HYDROXY-TERMINATED POLYBUTADIENE PROPELLANT
FORMULATIONS

5

ORIGIN OF THE INVENTION

10 Certain of the specific formulations
described herein were made under U.S. Navy
Contract #N00014-92-C-0134.

BACKGROUND OF THE INVENTION

1. Field of the Invention

15 This invention relates to high
performance tactical rocket motors and solid
propellant formulations operable at high pressures
with burn rates relatively insensitive to changes
in pressure and propellant temperature. More
20 particularly, this invention relates to propulsion
vehicles including the high performance propellant
formulations in a high strength, low inert weight
casing equipped with an erosion-resistant nozzle
throat.

2. Description of the Related Art

25 Conventional solid propellant rocket
motors operate by generating large amounts of hot
gases from the combustion of a solid propellant
formulation stored in the motor casing. The solid
propellant formulation generally comprises an
30 oxidizing agent, a fuel, and a binder. During
operation, the gases generated from the combustion
of the solid propellant accumulate within the
combustion chamber until enough pressure is

amassed within the casing to force the gases out of the casing and through an exhaust port. The expulsion of the gases from the rocket motor and into the environment produces thrust.

5 Thrust is measured as the product of the total mass flow rate of the combustion products exiting the rocket multiplied by the velocity of the exiting combustion products plus the product of the change in pressure at the exit plane
10 multiplied by the exit area.

Increasing the pressure at which the gases are expelled from the combustion chamber raises the thrust level, which in turn increases the propulsion rate of the vehicle containing the
15 rocket motor to thereby permit the vehicle to achieve higher speeds.

Since pressure is a measurement of force per unit exit area, it follows that the gas expulsion pressure can be increased by decreasing the
20 diameter of the rocket motor nozzle throat through which the combustion products are expelled.

Decreasing the diameter of the nozzle throat can also increase the expansion ratio of the throat. Expansion ratio is the ratio of the area
25 of the nozzle exit located aft of the nozzle throat to the area of the nozzle throat. Conventional tactical rocket motors have expansion ratios in the range of 6 to 9. Increased expansion ratios result in higher levels of rocket
30 performance.

With conventional solid rocket propellant formulations, as the operating pressure increases by decreasing the diameter of the nozzle throat, for example, the burn rate of the propellant also
35 increases, as shown in Fig. 1. The change in burn rate (R_b) as a function of the pressure change is defined as the burn rate slope, n :

$$\text{Burn rate slope} = \frac{\Delta \log \text{burn rate}}{\Delta \log \text{pressure}}$$

-3-

Data for determining burn rates at different pressures are typically gathered either by standard strand testing or by test motor analysis. The determination of burn rates by such testing procedures is well known in the art. Generally, conventional solid rocket propellant formulations have burn rate slopes of 0.15 ips/psi or greater.

Propellants which exhibit generally flat regions in their pressure versus burn rate curves are known as plateau propellants. Plateau propellants have generally flat regions over an operating range of at least 1,000 psi. Conventional propellants, including plateau propellants, usually exhibit a dramatic positive increase in burn rate slope at pressures above about 3,000 psi, as shown in Fig. 1.

One of the problems associated with conventional propellant formulations having an exponentially increasing propellant burn rate is that an increase consumption of propellant generally increases the operating pressure, which in turn increases the risk of catastrophic failure of the rocket motor casing.

The conventional solution to avoiding catastrophic failure of the rocket motor casing is to strengthen the rocket motor casing by constructing the casings with thick walls from strong, dense materials, such as steel. This approach, however, deleteriously imparts a severe weight penalty to the vehicle. Consequently, a greater amount of thrust and an increased propellant burn rate is required to propel the vehicle at a comparable rate.

Another problem associated with the use of conventional solid propellant formulations is that the burn rate of such formulations varies in response to changes in the temperature of the

-4-

propellant at ignition. Temperature sensitivity, π_k , is a measure of the sensitivity of the motor pressure to changes in propellant bulk temperature at ignition. π_k is defined as:

5
$$\pi_k = \frac{\Delta \log \text{ motor pressure}}{\Delta \log ^\circ \text{F}}$$

Motor and strand testing at various temperatures and pressures generate the data required to determine π_k . A typical nominal ignition
10 temperature is in the range of 70°F to 80°F; temperature sensitivity is usually measured over a range of -65°F to 160°F. The effect of temperature sensitivity on rocket performance is shown in Fig. 2. Conventional propellants have
15 temperature sensitivities in the range of 0.15%/°F or higher.

Typical rocket motors utilize nozzle throat materials that exhibit erosion during operation. These materials are selected primarily for their
20 low cost, rather than high performance characteristics. At lower nominal operating pressure, such as those in existing tactical missiles, the rate of erosion of the nozzle throat does not result in a large performance loss.
25 However, at operating pressures of 3000 psi and higher, use of existing nozzle throat materials results in substantially higher rates of erosion of the nozzle throat. Studies have shown that nozzle throat erosion is one of the most
30 significant sources of performance loss, and that, not surprisingly, the magnitude of this loss increases as motor operating pressure and temperature increases. Moreover, the continuous erosion of the nozzle adds an element of
35 unpredictability to the performance of the rocket motor.

-5-

An erosion-resistant nozzle throat material would allow high pressure motor operation at maximum performance efficiency without the expected performance limitations. Erosion-resistant materials should preferably have high melting points, and should be chemically inert to oxidizing gases or form an oxide that will reduce or inhibit further chemical erosion. Additionally, these materials must be capable of withstanding thermal shock and thermal stress and resisting extrusion. Although there have been motors developed that use non-eroding throat materials, such as tungsten, such non-eroding throats have generally been rejected in commercial use due to their relatively high expense and weight.

Most small diameter, for example, up to about 15 inches, tactical rocket motors comprise moderate to high strength steel cases. Air frame stiffness requirements of and the high operating pressures encountered during use of conventional solid propellants have driven the selection of high strength steel cases. In IM (insensitive munitions) testing, many of these steel case systems perform quite poorly, particularly when coupled with conventional HTPB/AP (hydroxy-terminated polybutadiene/ammonium perchlorate) propellants. Further, as described above, the overall weight of the solid propellant rocket motor propelled vehicle is a concern and increasing the weight of the motor case has an adverse impact on performance of the vehicle. Both lighter aluminum and titanium alloys have been investigated as possible materials for tactical motor casings above 5" diameter but have proven unsatisfactory for either effectiveness or cost reasons. There is a need for a rocket motor

-6-

case optimally designed and composed of materials suitable for use with high pressure rocket motors and which fulfill the requirements for air frame stiffness, maximum motor operating pressure and IM testing.

The design and geometry of propellant grain also effect the performance characteristics of solid propellant rocket motors. Many existing tactical missile rocket motors use a boost-sustain thrust profile which starts at a high thrust level for generating large amounts of thrust necessary for lift-off or deployment, and subsequently decreases to a lower thrust to allow for a lower in-flight motor operating pressure. Thus, propellant grain designs should be capable of being tailored to achieve a thrust profile that maintains high thrust and motor pressure conditions throughout the course of flight.

It would be a significant advancement in the art to provide a solid rocket propellant formulation operable at high pressures without a high positive burn rate slope or high temperature sensitivity. A low or negative burn rate slope and low temperature sensitivity would result in propellant burn rates that are insensitive to increases in operating pressure and changes in propellant temperature and thus the propellant would operate at high pressures within a narrower, more predictable pressure range without an associated increase in propellant burn rate. Such a propellant would result in a more predictable and reliable operation of the rocket motor and vehicle.

SUMMARY OF THE INVENTION

It is an object of the present invention to overcome the foregoing problems and achieve the

-7-

above advancement by providing a solid rocket propellant formulation having both a substantially insensitive burn rate over a substantial portion of a pressure range of from about 1,000 psi to about 7,000 psi, and a low temperature sensitivity.

Substantially insensitive burn rate means a burn rate slope of less than about 0.15 ips/psi. A substantial portion of the pressure range of from about 1,000 psi to about 7,000 psi is preferably a portion covering at least about 700 psi, and preferably 1000 psi. A low temperature sensitivity means a temperature sensitivity of less than about 0.15%/°F.

In accordance with one embodiment of this invention, these and other objects are achieved by providing a solid propellant formulation comprising at least one oxidizer, at least one polymeric binder, and at least one member selected from the group consisting of a co-oxidizer, a ballistic additive, and a polyisocyanate curative. The solid propellant formulation is designed to exhibit a burn rate slope of less than 0.15 ips/psi extending over at least a substantial portion of a pressure range between 1,000 psi and 7,000 psi, the burn rate slope being equal to:

$$\frac{\Delta \log \text{ burn rate }}{\Delta \log \text{ pressure }} .$$

The combination of the solid propellant formulation, non-eroding nozzle throat material, high strength low weight rocket motor casing, and all-boost thrust profile has been shown to provide as much as a 300% increase in missile trajectory over conventional technologies. The combination results in rocket motors with expansion ratios of up to 17, a significant improvement over conventional technologies using an eroding nozzle throat material, heavy rocket motor casing, and

-8-

boost-sustain thrust profile. It is through the synergistic effect of the technologies that the above-noted 300% increase is achieved.

5 These and other objects, features and advantages of the present invention will become apparent from the following detailed description of the invention when taken in conjunction with the accompanying figures which illustrate, by way of example, the principles of the present
10 invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a pressure versus burn rate plot for a conventional solid rocket propellant formulation.

15 Fig. 2 is a time versus pressure plot illustrating the effect of temperature sensitivity on propellant performance.

Fig. 3 is a plot of the effect of burn rate slope on nominal maximum pressure.

20 Fig. 4 is a plot of the combined effects of π_k and burn rate slope on the ratio MEOP:Pmax.

Fig. 5 is a sectional schematic view of a portion of a nozzle throat assembly utilizing non-eroding nozzle throat material.

25 Figs. 6 through 9 are pressure versus burn rate plots for solid rocket propellant formulations according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

30 The maximum pressure under nominal operating conditions produced by the solid propellant, Pmax, is one parameter that effects numerous design aspects of rocket propelled vehicles. Another important design parameter is the maximum expected operating pressure (MEOP). Off-nominal operating

-9-

conditions such as higher operating temperatures, manufacturing variations in propellant geometry, flaws in motor construction, variation in nozzle erosion rate, and variation in propellant burn rate with temperature influence the MEOP causing it to be greater than P_{max} .

It is highly desirable, from a vehicle design viewpoint, to have the margin between MEOP and P_{max} as small as possible. Nonetheless the vehicle, particularly the rocket motor casing, preferably is designed to function safely at MEOP, not merely P_{max} . Therefore, a large margin between MEOP and the P_{max} can result in, for example, a vehicle and rocket motor casing being significantly over-designed in order to meet MEOP levels. This over-design can result in increased inert weight from the use of, for example, a rocket motor casing designed to MEOP levels which are greatly above P_{max} levels. The propellant formulations of the present invention have relatively small burn rate slopes and low temperature sensitivities, thereby permitting a lower margin between MEOP and P_{max} to be achieved. Preferably, the burn rate slopes are less than about 0.15 ips/psi, more preferably, in a range of less than about 0.15 to about zero ips/psi, and most preferably, about zero to less than zero ips/psi.

The effect of the burn rate slope of the propellant on the MEOP can be determined in the following fashion. The pressure generated by the propellant is roughly a function of propellant burning surface area (A_s), nozzle throat area (A_t), and the propellant burn rate slope (n) so that under nominal operation the following relationship exists:

-10-

$$P_{\max}/P_{\text{avg}} = \frac{(A_{\max} A_{\text{avg}})}{(A_{\text{tmax}} A_{\text{avg}})} * (P_{\max}/P_{\text{avg}})^n \quad (1)$$

wherein,

P = chamber pressure

5 $A_{\max}$ = propellant burning surface area at $P_{\max}$

A_{avg} = propellant burning surface area at P_{avg}

n = propellant burn rate slope

A_{tmax} = nozzle throat area at $P_{\max}$

A_{avg} = nozzle throat area at P_{avg} .

10 Under nominal conditions, the maximum and average pressures will be effected directly by changes in the propellant surface area and changes in the nozzle throat area and exponentially by the propellant burn rate slope.

15 Further simplifying equation (1), by combining the pressure change drivers, A_s and A_t into Z , wherein Z_x equals A_{s_x}/A_{t_x} , yields:

$$P_{\max}/P_{\text{avg}} = Z_{\max}/Z_{\text{avg}} (P_{\max}/P_{\text{avg}})^n \quad (2)$$

20 Equation 2 is plotted in Fig. 3 for a range of $Z_{\max}/Z_{\text{avg}}$ values over several burn rate slope values.

25 If $Z_{\max}/Z_{\text{avg}}$ is equal to 1.0 (that is, either the burning surface area and the nozzle throat area do not change, or the changes compensate for each other), then the burn rate slope does not influence the $P_{\max}/P_{\text{avg}}$. However, in most practical situations, $Z_{\max}/Z_{\text{avg}}$ will have a value greater than 1.0, and the burn rate slope will have a significant effect on $P_{\max}/P_{\text{avg}}$, as shown in Fig. 3.

30 Conventional solid propellant formulations have positive burn rate slopes and thus $P_{\max}/P_{\text{avg}}$ will be greater than $Z_{\max}/Z_{\text{avg}}$. Propellants according to the present invention have small or

-11-

negative burn rate slopes and thus P_{max}/P_{avg} is only slightly greater than Z_{max}/Z_{avg} , or even smaller than Z_{max}/Z_{avg} , if the burn rate slope is negative.

5 The measurement of burn rates at various pressures for a given propellant formulation is accomplished by well known test methods, such as, for example, strand and/or test motor evaluations.

10 The propellants, according to the present invention, which exhibit small or negative burn rate slopes, provide increased options in the design of rocket motors and vehicles. These options include 1) operating at higher P_{avg} for the same P_{max} , 2) lowering P_{max} for the same P_{avg} ,
15 3) increasing Z_{max}/Z_{avg} for the same P_{max}/P_{avg} , and 4) combinations of the above. All of the options can lead to higher performance rocket motors and vehicles.

20 The effect of propellant temperature sensitivity on MEOP is utilized in the design of rocket motors and rocket propelled vehicles and can be calculated by the following equation:

$$P_T = e^{\pi k (T_{hot} - T_{nom})}$$

wherein,

25 P_T = Increase in MEOP due to temperature change

T_{hot} = Maximum expected initial propellant temperature

30 T_{nom} = Nominal initial propellant temperature.

Assuming a nominal initial propellant temperature of 70°F, a maximum expected initial propellant temperature of 165°F, and a conventional propellant temperature sensitivity of
35 0.15%/°F would result in a P_T of 1.10, or a 10%

-12-

increase in MEOP. Utilizing an exemplary propellant according to the present invention, with a π_k value of 0.038%/°F, the same temperature change would result in a P_r of 1.037, or for this example, a 6.3% smaller increase in MEOP from the temperature change as compared to the conventional propellant.

The combined effect of changes in burn rate slope and temperature sensitivity of a propellant formulation on the resulting ratio between MEOP and P_{max} for a conventional propellant and a propellant according to the present invention are illustrated in Fig. 4. The ratio MEOP/ P_{max} represents the pressure margin required for off nominal high temperature performance at the worst expected condition (MEOP). Fig. 4 was generated for a 75°F temperature increase and non-temperature pressure variabilities of 5%. At a given burn rate slope, the conventional propellant has a higher MEOP/ P_{max} ratio than the propellant according to the present invention.

A solid rocket propellant formulation, according to the present invention, is based on the use of a hydroxy-terminated polybutadiene (HTPB) binder. Suitable HTPB binders can be typical commercially available HTPB binders with an average molecular weights in the range of about 2,000 to 5,000 g/mol, such as R45M and R45HT manufactured by ARCO Chemical Company.

A solid rocket propellant formulation, according to an embodiment of the present invention, can be formulated from the following ingredients:

-13-

	<u>Ingredient</u>	<u>Weight % (Approximate)</u>
	AP Oxidizer - Total	60 - 90
	- Large Particle Size	35 - 55
5	- Small Particle Size	25 - 40
	HTPB Binder	7 - 10
	Al Fuel	0 - 20
	Ballistic Modifier	1 - 4
	Plasticizer	1 - 3
10	Stability Additive	0 - 3
	Bonding Agent	0.5 - 1
	Isocyanate Curative	0.5 - 2.5
	Processing Aid	0.02 to 0.06
15	Cure Catalyst	0 - 0.005
	Ballistic Additive	0 - 3
	Co-oxidizer	0 - 4

Ammonium perchlorate (AP) is generally incorporated into the formulation in the manner known in the art and AP may be used in multiple particle sizes. In particular, the large particle size AP can have a particle size in the range of about 185-215 μm , preferably about 200 μm , or alternatively, in a range of about 385-415 μm , preferably, about 400 μm , while small particle size AP in the range of from 2 μm to less than about 50 μm is preferable.

"Reduced smoke" formulations can also include a stability additive, preferably zirconium carbide, preferably at about 1 wt.%, instead of Al fuel. Other suitable reduced smoke stability additives include carbon, aluminum, and aluminum oxide.

"Metallized" formulations include Al fuel, instead of the stability additive, preferably contain the fuel in a range of about 18-22 wt.%.

-14-

The fuel can be comprised of aluminum metal with a particle size in the range of 100 to 130 μm , preferably about 117 μm . Other possible fuels include magnesium and boron.

5 A nitramine oxidizer, such as HMX, tetramethylene tetranitramine, an exemplary co-oxidizer, can be incorporated at about 2 to 4 wt.% to obtain the desired high pressure, low burn rate slope performance. Other suitable co-oxidizers
10 include AN (ammonium nitrate), TEX (4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane), RDX (trimethylene trinitramine), and CL20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-
15 hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}] dodecane).

 A ballistic additive, such as, for example, copper phthalocyanine, can be added at about 1 wt.% to obtain the desired high pressure, low burn rate slope performance. Other suitable ballistic
20 additives include HMX, RDX, CL-20, AN, and DCDA (dicyandiamide).

 Suitable ballistic modifiers are refractory oxides, such as TiO_2 , ZrO_2 , Al_2O_3 , and SiO_2 and similar materials. Excellent results have been
25 achieved with both coarse (average size 0.5 μm) and fine (average size 0.02 μm) particle size refractory oxides and mixtures thereof. Suitable particle sizes range from about 0.01 to 2 μm . Preferably these refractory oxides are
30 incorporated into the formulations in a range of about 1 to 3 wt.%, most preferably at about 2 wt.%. Of these materials, TiO_2 is preferred, and is commercially available from Degussa Chemical as P-25 and T-805, for example. These commercially
35 available forms are generally coated with siloxanes to improve processability.

-15-

An example of a bonding agent suitable for these formulations is Tepanol HX878 commercially available from 3M Corporation. Other suitable bonding agents include Tepan, Tepanol HX-752 and related aziridines, and Thiokol BASH bonding agents.

ODI, octadecylisocyanate, is an example of a processing aid, and can be utilized either alone or in conjunction with Tepanol bonding agent.

Diethyladipate, DOA, is an example of a suitable plasticizer. Other suitable plasticizers include TEGDN (triethyleneglycol dinitrate), DEGDN, (diethyleneglycol dinitrate), TMETN (trimethylolethane trinitrate), and BTTN (butanetriol trinitrate). and BuNENA (n-butyl-2-nitratoethyl-nitramine).

The desired performance characteristics can also be achieved by utilizing a suitable curative preferably TMXDI (m-tetramethylxylene diisocyanate), instead of other isocyanates such as DDI (dimeryl diisocyanate) or IPDI (isophorone diisocyanate). The use of TMXDI in solid rocket propellants is the subject of U.S. Patent No. 4,913,753 to Ducote, the complete disclosure of which is incorporated herein by reference.

Suitable cure catalysts include TPB (triphenyl bismuth). Other suitable cure catalysts include triphenyltin chloride, dibutyltin diacetate, and dibutyltin dilaurate. These compounds and others may be used as needed to prepare a propellant formulation with the specific desired characteristics.

The various components of the propellant can be formulated and combined to form the solid propellant according to standard procedures as set forth, for example, in Principles of Solid Propellant Development, Adolf E. Oberth, CPIA

-16-

Publication 469, September 1987, the complete disclosure of which is incorporated herein by reference.

5 The formulated solid propellant is housed within a rocket motor case housing, which housing comprises a rocket nozzle located at its aft end. The throat of the rocket nozzle preferably is constructed such that an erosion rate is no more than about 2 mils per second during motor
10 operation.

Nozzle throat materials which exhibit acceptable non-erosive behavior may include metals and alloys of metals such as tungsten and rhenium; ceramic materials, such as hafnium carbide; or a
15 deposition or coating of metals such as rhenium, tungsten, hafnium, for example, onto structural substrates.

Preferably, the non-eroding throat materials are extended some distance downstream of the
20 nozzle throat into the exit cone thereby further preventing additional performance loss. Preferably, the application of these non-eroding materials is extended downstream into the exit cone of the nozzle to a point on the exit cone
25 where the expansion ratio is between about 2 and 4. Preferably, the non-eroding materials erode, under high pressure, that is greater than 3000 psi, at a rate of no greater than about 2 to 3 mils per second.

30 Chemical vapor deposition (CVD) of refractory metals on graphite and thicker shells of refractory metals with PAN (polyacrylic nitrile) phenolic overwrap can also be utilized. Preferred refractory metals include rhenium and tungsten.
35 Alloys of rhenium and tungsten can also be used, a preferred alloy is tungsten with 10% rhenium.

-17-

The present invention also encompasses high temperature monolithic and composite ceramics as non-eroding nozzle throat materials. Examples of such ceramic materials include HfO_2W , HfB_2 , ZrB_2 , HfC , TaC , and ZrC , particularly preferred are HfC , TaC , and ZrB_2 .

An example of a rocket nozzle utilizing the nozzle throat materials according to the present invention is illustrated in Fig. 5. The rocket nozzle has an inlet 1 preferably composed of a molded silica phenolic material located above a closure 13 covered by insulation 15. The rocket nozzle throat features an insert 3 of CVD coated rhenium/carbon graphite supported by a carbon phenolic tape wrapped throat support 5. Silica phenolic tape is utilized for both throat insulation 7 and exit cone insulation 9. The nozzle shell 11 is composed of steel, preferably 4130 grade steel.

The solid propellant according to the present invention achieves improved performance by operating at higher than normal pressures with a low or negative burn rate slope. In order to maximize and take advantage of the performance increases resulting from the higher operating pressures, minimizing the motor case weight is highly desired. Although conventional motor case materials, such as steel, can be employed, in order to reduce inert weight, preferably low weight, high strength materials are utilized. Examples of such suitable low weight, high strength materials include graphite materials and composite materials. Suitable composite materials include carbon and graphite fibers and filaments which can be laminated with high temperature polymer resins such as bismaleimides, polyimides,

-18-

epoxies, and PEEK (polyetheretherketone) thermoplastics.

High temperature performance of the composite materials is a key consideration in the selection of materials for use in rocket motor cases. The glass transition (Tg) temperature of the polymer resin largely determines the high temperature characteristics of the composite material. The temperature of the operational environment of a composite material should be at least 100°F below Tg for long duration service and at least 50°F below Tg for short duration service. Examples of suitable resin systems include epoxy (Fiberite 934 available from Fiberite), toughened epoxy (ERL 1908 available from Fiberite), amine toughened epoxy (Fiberite 974 available from Fiberite), bismaleimide (V388 available from Hitco), modified bismaleimide (Narmco 5245c and 5250 available from Cytek), and polyimide (PMR-15 available from US Poly).

Construction techniques which take advantage of the strength of the material and result in a finished case with improved strength also can be utilized. Of special concern, in utilization of the high strength graphite materials, is meeting case bending stiffness requirements while also providing for external missile attachments, such as launch lugs, fins and so forth. An exemplary case design according to the present invention utilizes high tensile strength graphite fibers for hoops and windings and high modulus graphite fibers for axial windings in a cross-ply arrangement to meet the above requirements. This design meets the bending stiffness requirements and still allows for higher pressure motor operation without excessive weight penalties.

-19-

The composite case according to the present invention must perform at higher stresses and at higher temperatures than past systems. These materials must have both high hoop strength and high axial stiffness throughout the operating temperature of the system.

A composite rocket motor case and methods for manufacturing are disclosed in U.S. Patents Nos. 5,280,706 and 5,348,603, the complete disclosures of which are incorporated herein by reference.

Depending on the desired application, the performance of the solid propellant according to the present invention may be further maximized by the use of an all-boost propellant grain design. An all-boost propellant grain design features a grain geometry that results in a high thrust level throughout the entire burn period. This is in contrast to conventional tactical missile rocket motors which utilize a boost-sustain thrust profile which starts at a high thrust level but over time falls to a lower thrust level. The boost-sustain thrust profile limits the performance advantages achieved with the present invention.

An all-boost grain design can result in vehicle velocities exceeding the current state-of-the-art design parameters due to the resulting increased thermal stress. The increases in thermal stress can be reduced by using, for example, a pulse motor design wherein the thrust is divided into two or more pulses and the propellant grains are separated by a pressure bulkhead. When necessary to reduce the maximum mach number to within design parameters, the rocket motor can have a delay between the pulses to allow the missile velocity to decrease before firing the next impulse. Grain patterns that are

-20-

known to those of skill in the art can be utilized to obtain the all-boost thrust profile.

It is possible by selection of varied formulation parameters to control the ballistic behavior of the propellant. The plateau regions and burn rates can be tailored via formula modification. Additionally, changes in selection of the curative and particle size of the ballistic modifier can produce plateaus at different burn rates and pressure regions.

The following examples are presented to provide a more complete understanding of the invention. The specific techniques, conditions, materials, proportions and reported data set forth to illustrate the principles of the invention are exemplary and should not be construed as limiting the scope of the invention.

EXAMPLES

Example 1

A reduced smoke HTPB propellant was prepared from the following formulation:

<u>Ingredient</u>	<u>Weight %</u>
AP Oxidizer - 200 μ m	52.7
- 2 μ m	32.3
HTPB	9.396
TiO ₂ , fine size	1.5
ZrC	1
DOA	2
Teponal	0.075
TMXDI	0.834
ODI	0.04
TPB	0.005

-21-

Performance testing was performed using strands of the formulation and the results are tabulated below:

	Plateau region	4250 - 5000 psi
5	<u>In plateau region</u>	
	Burn rate	2.88 - 2.91 ips
	Burn rate slope	0.07

Example 2

10 A reduced smoke HTPB propellant was prepared from the following formulation:

	<u>Ingredient</u>	<u>Weight %</u>
	AP Oxidizer - 200 μ m	52.08
	- 2 μ m	31.92
	HTPB	8.163
15	TiO ₂ , coarse size	2
	ZrC	1
	DOA	2
	Teponal	0.075
	DDI	1.722
20	ODI	0.04
	Cu phthalocyanine	1

Performance testing was performed using strands of the formulation and the results are tabulated below:

25	Plateau region	2020 - 3765 psi
	<u>In plateau region</u>	
	Burn rate	1.69 - 1.01 ips
	Burn rate slope	-0.84

Example 3

30 A reduced smoke HTPB propellant was prepared from the following formulation:

-22-

	<u>Ingredient</u>	<u>Weight %</u>
	AP Oxidizer - 200 μ m	51.46
	- 2 μ m	31.54
	HTPB	8.136
5	TiO ₂ , coarse size	2
	ZrC	1
	DOA	2
	Teponal	0.075
	DDI	1.722
10	ODI	0.04
	HMX	2

Performance testing was performed using strands of the formulation and the results are tabulated below:

15	Plateau region	2025 - 3270 psi
	<u>In plateau region</u>	
	Burn rate	1.20 - 0.76 ips
	Burn rate slope	-0.96

Example 4

20 A metallized HTPB propellant was prepared by from the following formulation:

	<u>Ingredient</u>	<u>Weight %</u>
	AP Oxidizer - 200 μ m	39.76
	- 2 μ m	31.24
25	Al fuel	15
	HTPB	9.101
	TiO ₂ , fine size	2
	DOA	2
	Teponal	0.075
30	TMXDI	0.764
	ODI	0.04
	TPB	0.02

-23-

Performance testing was performed using strands of the formulation and the results are tabulated below:

Plateau region	4000 - 5000 psi
<u>In plateau region</u>	
Burn rate	2.85 - 2.81 ips
Burn rate slope	-0.07

Temperature Sensitivity Testing

The temperature sensitivity testing of Examples 1 through 4 would be expected to show all four examples with π_k values of 0.15%/°F and lower.

The foregoing detailed description of the preferred embodiments of the invention has been provided for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise embodiments disclosed. Many modifications and variations will be apparent to practitioners skilled in this art. The embodiments were chosen and described in order to best explain the principles of the invention and its practical application, thereby enabling others skilled in the art to understand the invention for various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the following claims and their equivalents.

-24-

WHAT IS CLAIMED IS:

1. A solid propellant formulation consisting of:

from about 35% to about 55% by weight ammonium perchlorate particles having an average size of about 200 μm ;

from about 25% to about 40% by weight ammonium perchlorate particles having an average size in a range of from about 2 μm to about 50 μm ;

from about 7% to about 10% by weight hydroxy-terminated polybutadiene binder; and

at least one member selected from the group consisting of a co-oxidizer, a ballistic additive, and a polyisocyanate curative;

wherein said propellant formulation has a burn rate slope of less than about 0.15 ips/psi over a substantial portion of a pressure range of from about 1,000 psi to about 7,000 psi and a temperature sensitivity of less than about 0.15%/°F,

wherein said burn rate slope is equal to

$$\frac{\Delta \log \text{ burn rate}}{\Delta \log \text{ pressure}}$$

2. A solid propellant formulation according to claim 1, further consisting of at least one member selected from a bonding agent, a processing aid, a plasticizer, and a ballistic modifier.

3. A solid propellant formulation according to claim 1, further consisting of at least one member selected from the group consisting of Al fuel and a stability additive.

-25-

4. A solid propellant formulation according to claim 1, further consisting of a cure catalyst.

5. A solid propellant formulation according to claim 1, wherein said co-oxidizer is tetramethylene tetranitramine.

6. A solid propellant formulation according to claim 1, wherein said ballistic additive is copper phthalocyanine.

7. A solid propellant formulation according to claim 1, wherein said polyisocyanate curative is m-tetramethylxylene diisocyanate.

8. A solid propellant formulation according to claim 1, wherein said burn rate slope is between about 0 and about 0.15 ips/psi.

9. A solid propellant formulation according to claim 1, wherein said burn rate slope is less than about zero.

-26-

10. A solid propellant rocket motor consisting of:

a solid propellant formulation according to claim 1 having an all-boost thrust grain profile;

said solid propellant formulation housed within a rocket motor case housing;

said rocket motor case housing comprising a rocket nozzle located at the aft end of said housing;

said rocket nozzle further comprising a nozzle throat; and

said nozzle throat constructed such that an erosion rate is no more than about 2 mils per second during motor operation.

11. A solid propellant formulation consisting of at least one oxidizer, hydroxy-terminated polybutadiene polymeric binder, and at least one member selected from the group consisting of a co-oxidizer, a ballistic additive, and a polyisocyanate curative, said solid propellant formulation exhibits a burn rate slope of less than 0.15 ips/psi extending over a substantial portion of a pressure range between 1000 psi and 7000 psi, the burn rate slope being equal to

$$\frac{\Delta \log \text{burn rate}}{\Delta \log \text{pressure}}.$$

12. A solid propellant formulation according to claim 11, wherein the burn rate slope is less than zero.

-27-

13. A solid propellant formulation according to claim 11, wherein said solid propellant formulation has a temperature sensitivity of less than about 0.15%/°F over a temperature range of about -65°F to 160°F, and wherein said temperature sensitivity is a percentage change in burn rate of said solid propellant formulation per degree Fahrenheit change in propellant temperature at ignition.

14. A solid propellant formulation according to claim 11, wherein said oxidizer comprises:

from about 35% to about 55% by weight, based on the total weight of said solid propellant formulation, of ammonium perchlorate particles having a particle size of about 200 μm ; and

from about 25% to about 40% by weight, based on the total weight of said solid propellant formulation, of ammonium perchlorate having a particle size in a range of from about 2 μm to about 50 μm .

1 / 8

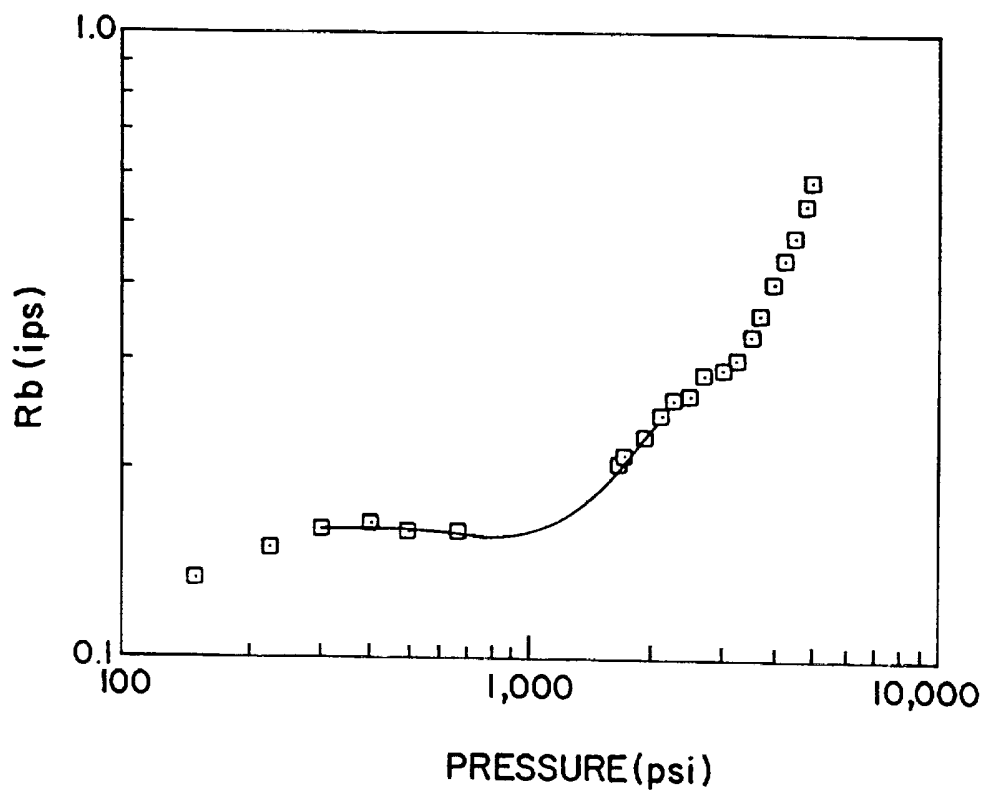


FIG. 1 (PRIOR ART)

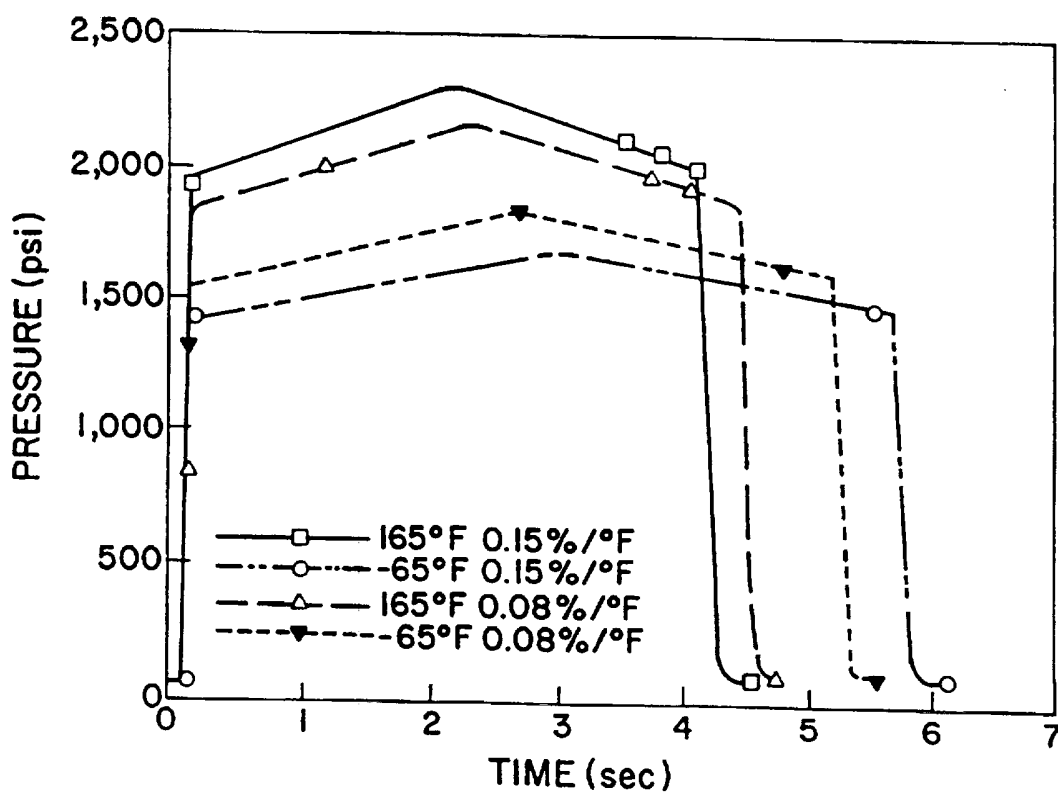
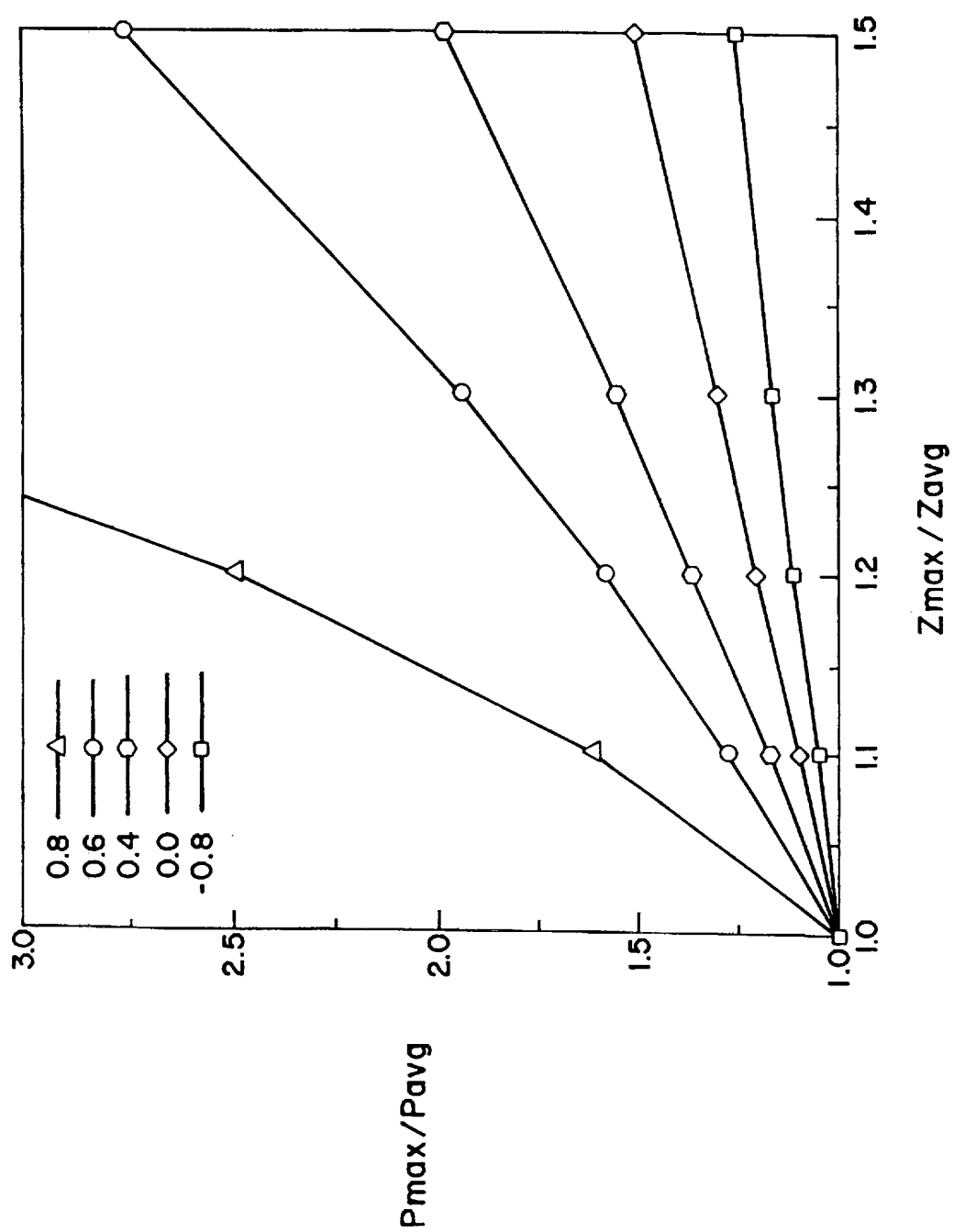


FIG. 2 (PRIOR ART)

2 / 8

**FIG. 3**

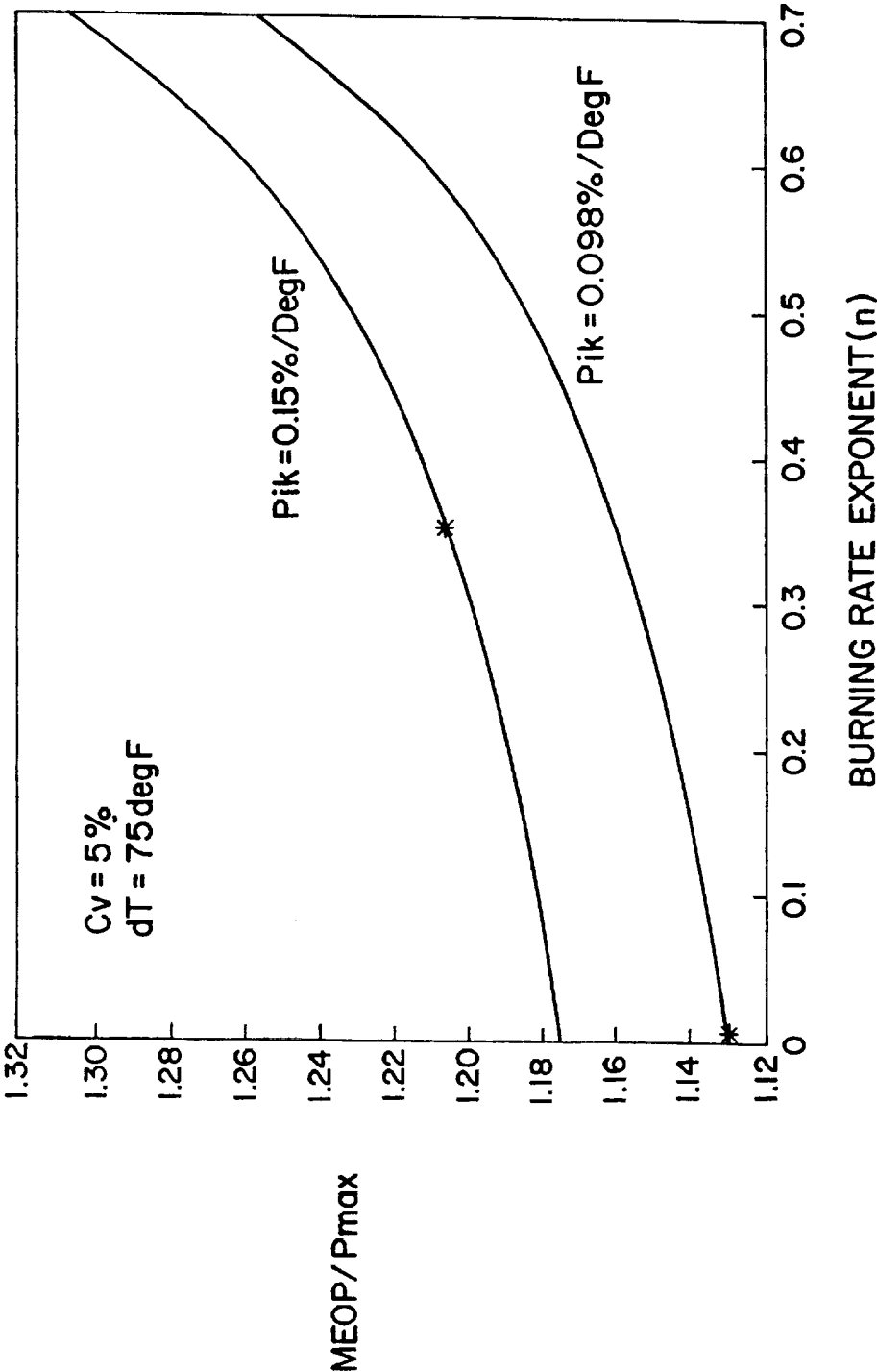


FIG. 4

4 / 8

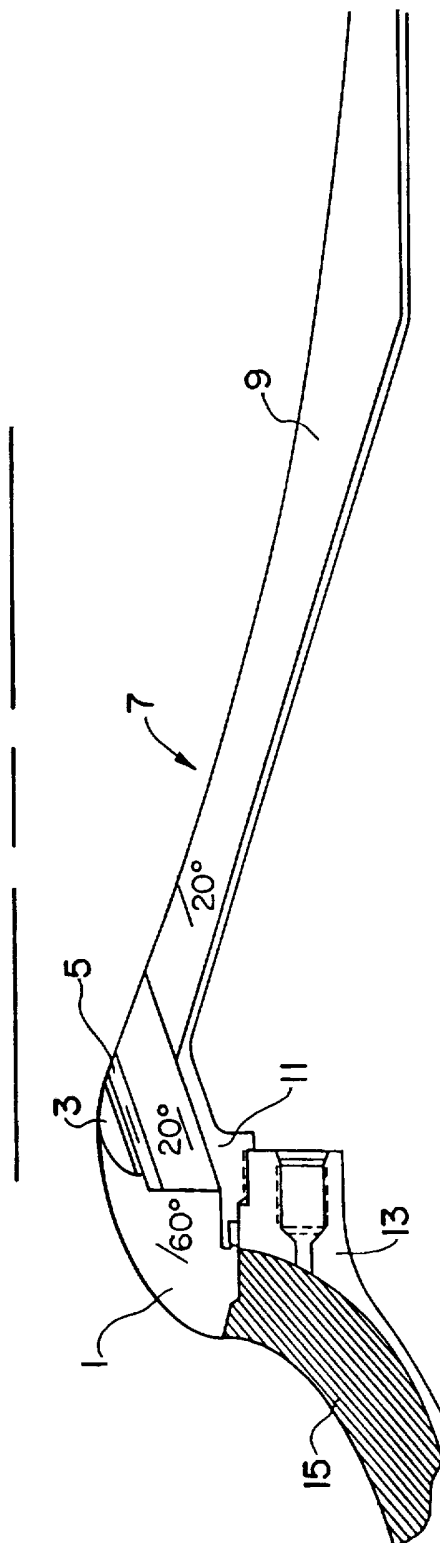
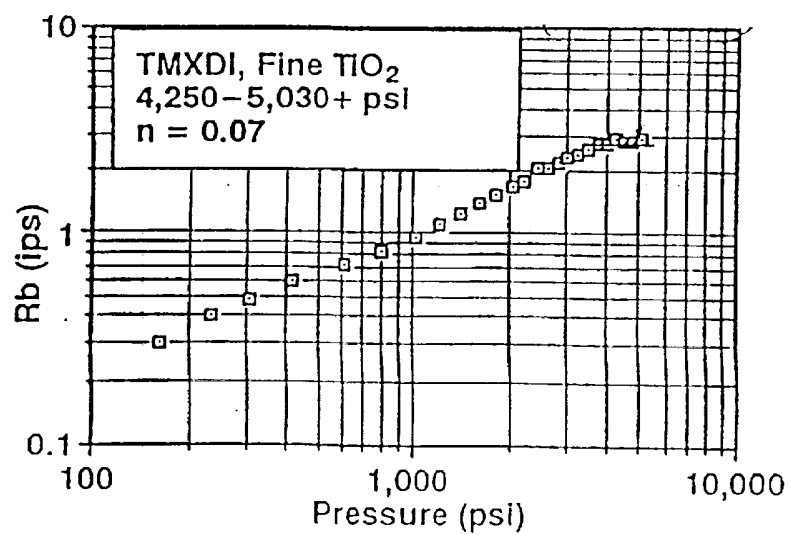


FIG. 5

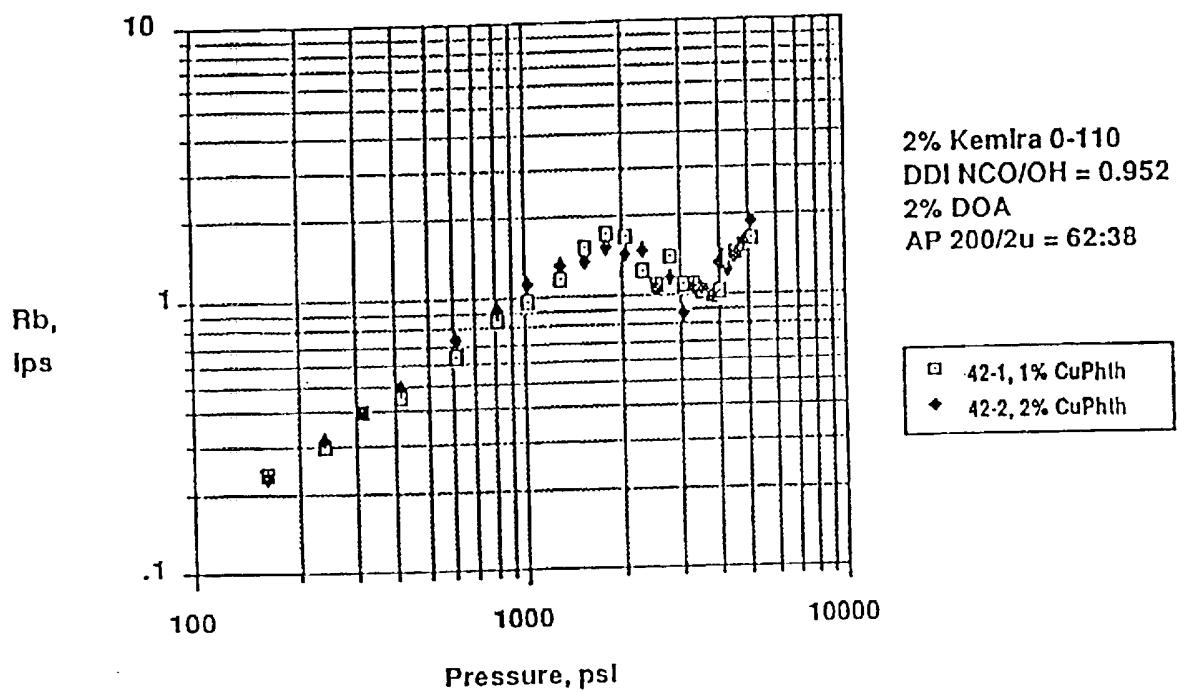
5 / 8

Figure 6



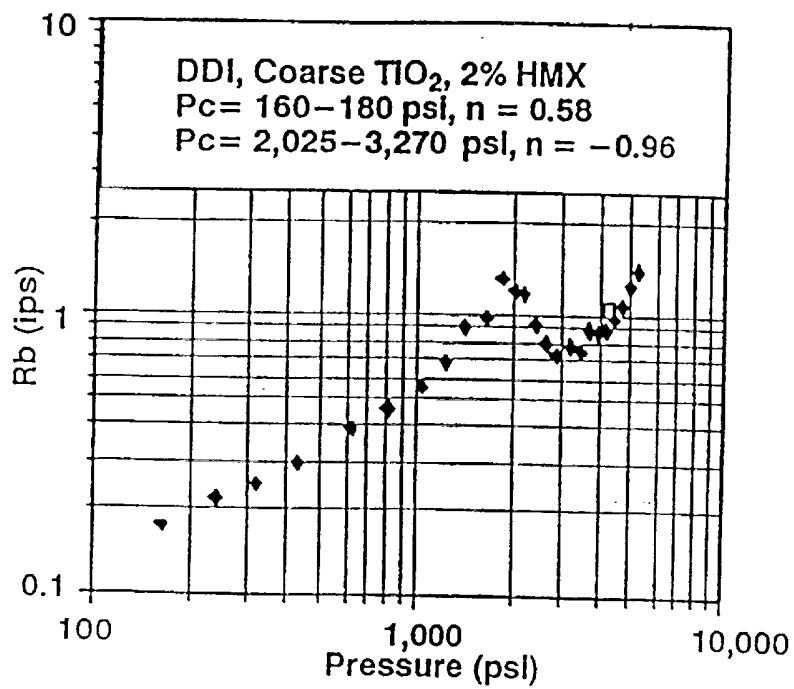
6 / 8

Figure 7



7 / 8

Figure 8



8 / 8

Figure 9

