(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : 0 611 141 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number : 94300922.5

(51) Int. Cl.^{5} : C06B 23/00

(22) Date of filing : 08.02.94

(30) Priority : 08.02.93 US 16381

(43) Date of publication of application : 17.08.94 Bulletin 94/33

(84) Designated Contracting States : DE FR GB IT

(71) Applicant : THIOKOL CORPORATION
2475 Washington Boulevard
Ogden, Utah 84401 (US)

(72) Inventor : Neidert, Jamie B, c/o Thiokol Corporation,
Post Office Box 707,
M/S 243, Brigham City Utah 84302-707 (US)
Inventor : Askins, Robert E,
11209 Woodcrest Drive,
Huntsville Alabama 35803 (US)

(74) Representative : Bankes, Stephen Charles Digby et al
BARON & WARREN
18 South End
Kensington
London W8 5BU (GB)

(54) Castable double base propellants with compounds containing group IIA metal ions as ballistic modifers.

(57) Propellant formulations are provided which include non-toxic burn rate modifiers. In order to produce a usable propellant formulation, it is necessary to control the burn rate of the propellant. Failure to adequately control the propellant burn rate often results in unacceptable performance of the propellant. It has been found that Group IIA metal salts, such as calcium carbonate and strontium carbonate, are capable of modifying the burn rate of propellants without resorting to lead as a burn rate additive. Accordingly, the use of from about 0.5% to about 5.0% Group IIA metal salt is taught as effective burn rate modifiers in propellants, in order provide non-toxic means for modifying the propellant burn rate.

EP 0 611 141 A1

BACKGROUND

1. The Field of the Invention

The present invention is related to methods and compositions for modifying the burn rate of solid rocket motor propellants, without the addition of expensive, toxic or polluting materials, such as lead or copper. More particularly, the present invention is related to the use of Group IIA metal ions, added in the form of Group IIA salts or similar materials, to modify the burn rate of solid rocket motor propellants.

2. Technical Background

In the manufacture of solid rocket motors, several components have been found to be required. First there must be an adequate rocket motor case. The rocket motor case forms the exterior of the rocket motor and provides the essential structural integrity for the rocket motor. The rocket motor case is conventionally manufactured from a rigid, yet durable, material such as steel or filament wound composite.

Placed within the interior of the rocket motor case is the propellant grain. The propellant forming the grain is conventionally burned to form thrust within the interior of the rocket motor case. The formation of hot gases upon burning of the propellant, and the subsequent exit of those gases through the throat and nozzle of the case provide the thrust to propel the rocket motor.

There are two major classes of propellants used in conventional applications. These include solid propellants and liquid propellants. Solid propellants are used extensively in the aerospace industry. Solid propellants have developed as the preferred method of powering most missiles and rockets for military, commercial, and space applications.

Solid rocket motor propellants have become widely accepted because of the fact that they are relatively simple to manufacture and use, and they have excellent performance characteristics. Furthermore, solid propellant rocket motors are generally more simple than liquid fuel rocket motors. For all of these reasons, it is found that solid rocket propellants are very reliable and economical.

In some applications, it is important that the rocket motor perform with reduced or eliminated smoke output. For example, in tactical rocket motors, the production of smoke causes a number of disadvantages. The smoke produced may obscure the vision of pilots or drivers of a craft or vehicle firing the tactical rocket. In addition, the production of smoke makes tracking the source of the motor easier, a serious disadvantage during military operations.

An important consideration in solid propellants, including minimum smoke propellants, is means for controlling the burn rate of the propellant, without significantly adding to the smoke output of the propellant. At the same time it is important that the propellant burn at a controlled and predictable rate without performance loss. If the burn rate of the propellant can be controlled it is possible to assure proper operation of the rocket motor, or other similar device.

If the propellant achieves an excessively high burn rate, the pressure created within the casing may exceed the design capability of the casing, resulting in damage or destruction to the device. If the propellant does not develop a sufficient burn rate, there may not be sufficient thrust to propel the rocket motor over the desired course.

Accordingly, it is conventional in the art to add materials to the propellant to control the burn rate of the propellant. Such materials are often referred to as burn rate modifiers. Burn rate modifiers are generally added in order to control the burning rate and pressure exponent of the propellant to lower the pressure exponent or to cause a "plateau" at an operable level. Plateau burning behavior (sometimes referred to as platonization) is typified by a zero, or very low, exponent over a 700 to 3000 psig range in a logarithmic plot of the burning rate versus pressure. Conversely, a mesa burning is typified by a zero slope at some point, followed by a negative burning rate at some higher pressure. When burn rate is plotted as a graph of burn rate (for example, in inches per second) on the Y-axis and pressure in pounds per square inch on the X-axis, the plateau effect results in a flattening of the burn rate curve to a slope more parallel with the X-axis, This plateau effect (platonization) is desirable in order to achieve a relatively constant burn rate pressure output over a chosen pressure range.

As used herein, the term "pressure exponent" means the slope of a curve plotted with burn rate in inches per second on the Y axis and pressure in pounds per square inch on the X axis.

In order to achieve the plateau effect described above, it has been common practice to add relatively toxic metals to the propellant. For example, lead is perhaps the most widely used burn rate modifier for certain classes of propellants. Lead, however, is known to be a hazardous, toxic, and polluting metal. Concern with lead pollution in society as a whole is on the rise, and serious health problems are known to be associated with lead poisoning and lead pollution. As a result, concern with lead in the preparation and use of propellants is high, and it is presently preferred that lead be eliminated as a component of solid propellants. The primary concern has been expressed by the United States Army because of the direct exposure of Army personnel to missile exhaust.

Accordingly, it would be a significant advancement in the art to provide methods and compositions for modifying propellant burn rates which avoided some of the significant problems encountered with conventional burn rate modifiers. It would be a significant advancement in the art to provide methods and compositions for modifying burn rates in propellants which did not rely on toxic, hazardous, or polluting burn rate additives. It would be a further advancement in the art to provide such propellants which produced a minimum of smoke output when burned. It would be another advancement in the art to provide propellant compositions which are generally insensitive.

Such methods and compositions are disclosed and claimed herein.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

The present invention is related to methods and compositions for modifying the burn rate of solid rocket motor propellants, without the addition of expensive, toxic, hazardous, or polluting materials, such as lead and copper. More particularly, the present invention is related to the use of Group IIA metal ions (generally added in the form of Group IIA metal salts), or similar materials, to modify the burn rate of a solid rocket motor propellant. Examples of such materials include calcium carbonate and strontium carbonate. The addition of such materials has been found to be effective in modifying the burn rate of certain propellants in order to provide a more usable and controllable propellant product.

The present invention has been found particularly effective in controlling the burn rate of propellants containing a combination of nitrocellulose/nitrate esters. The propellants may also include ammonium nitrate. Nitrocellulose, for example, may comprise the binder component of such propellants. Such propellants are widely used as solid rocket motor propellants.

A propellant of this general type may be formulated as follows:

Material	Percentage Range
Ammonium Nitrate	0-25
Carbon (amorphous)	0.5-1.0
Nitrocellulose (NC)	15-20
BTTN	39-54
TMETN	13-17
HMX	0-10
MNA	1-2

BTTN and TMETN are nitrate esters. BTTN is 1,2,4 butanetrioltrinitrate and TMETN is trimethylolethane trinitrate. HMX is cyclotetramethylene tetranitramine, a solid ingredient used widely in explosives and propellants. This type of propellant is known to be relatively low in smoke output and, therefore, is desirable for uses where minimum smoke is a significant benefit. In addition, formulations within the ranges set forth above are fqund to be relatively insensitive to accidental ignition (32 cards in the NOL card gap test).

The present invention is particularly adaptable to propellants of this type which are often referred to as "double base" propellants. Double base propellants have been widely used for a long period of time. The term "double base" merely indicates that two primary explosive ingredients are present (typically nitrocellulose (NC), nitroglycerin (NG), and/or other nitrate esters). Accordingly, the present invention is found to provide good results in double base propellants. As used herein, that term refers to propellants incorporating at least two nitrate esters.

One typical method of NG incorporation in this system is solventless, whereby the NG is mixed with an aqueous slurry of NC, filtered, then rolled or pasted into a powder while heating. Another method incorporates solvents such as acetone. A final method employs solid NC in a rocket chamber which is then swelled with NG or nitrate esters to then form the propellant grain.

The castable (pourable) double base discussed herein requires none of these difficult procedures. The castable double base propellant is readily cast in any device after only one mix procedure or cycle. The mix cycle involves the vacuum mixing of a preblend containing NC, TMETN, BTTN, and MNA (N-methylnitro aniline). Desired ballistic additives are incorporated, followed by the addition of curing agents, further mixing, and vacuum casting of samples.

While such propellants are widely used as rocket motor propellants, in the absence of burn rate modifiers these propellant compositions are generally found to have high burn rates/pressure exponents which render them unusable. Thus, in the absence of burn rate modifiers, it is found that the burn rate exponent is relatively constant and does not level out during operation. In addition, it is generally found that a rocket motor propellant having a pressure exponent of n=1 or greater will not operate in a stable manner.

In order to deal with this problem, the present invention teaches the addition of non-toxic, non-hazardous, and non-polluting burn rate modifiers to nitrate ester/ammonium nitrate propellants. One such burn rate modifier is calcium carbonate, however, other Group IIA metal salts also fall within the scope of the present invention. Such other salts include, for example, strontium carbonate.

It is found that the addition of from about 0.5% to about 5.0% of a Group IIA metal salt, such as calcium carbonate, to propellants of this type results in much more controllable and usable burning rates over a significant period of operation. More particularly, from about 1.5% to about 2.0% may be added. For example, using Group IIA metal salts in these amounts, a plateau is generally observed, and pressure exponents in the range of $\leqq 0.7$ can be achieved.

It is, therefore, a primary object of the present invention to provide methods and compositions for modifying propellant burning rates which avoid problems encountered with conventional burn rate modifiers.

More particularly, it is an object of the present invention to provide burn rate modifiers which are not based on lead or similar toxic materials.

It is a related object of the invention to provide methods and compositions for modifying burn rate which do not rely on expensive, toxic, hazardous, or polluting burn rate additives.

It is a further object of the invention to provide such propellants which produce minimum smoke output when burned.

These and other objects and advantages of the invention will become apparent upon reading the following detailed description and appended claims, and upon reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the manner in which the above-recited and other advantages and objects of the invention are obtained, a more particular description of the invention briefly described above will be rendered by reference to specific data presented in the appended drawings. Understanding that these drawings depict only information for typical embodiments of the invention and are not, therefore, to be considered limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

Figure 1 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 2 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 3 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 4 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 5 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 6 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 7 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 8 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 9 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 10 is a graph plotting burn rate data obtained from propellant compositions within the scope of the present invention.

Figure 11 is a graph plotting burn rate data obtained from a propellant composition within the scope of the present invention.

Figure 12 is a graph plotting burn rate data obtained from a comparison of a propellant incorporating lead oxide with a propellant incorporating calcium carbonate.

Figure 13 is a motor pressure/time trace.

Figure 14 is a plot of smoke transmissivity.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As mentioned above, the present invention is related to methods and compositions for modifying the burn rate of solid rocket motor propellants, without the addition of expensive, toxic, hazardous, or polluting materials, such as lead and copper and their related compounds.

Specifically, the present invention is related to the use of Group IIA metal ions incorporated within the propellant matrix as burn rate modifiers. Those ions are typically added in the form of Group IIA metal salts. Examples of such salts include calcium carbonate and strontium carbonate.

The Group IIA metal salts, or other similar compounds, added to the propellant formulation may have a relatively wide range of particle sizes. For example, particle sizes in the range of from about 0.5μ to about 35μ fall within the scope of the present invention and produced the desired effect when incorporated into a propellant matrix. It has been discovered, however, that particle sizes in the range of from about 2μ to about 3μ results in a particularly acceptable formulations.

Typically, burn rate modifiers comprise from about 0.5% to about 5.0% of the overall propellant. More particularly, it is found that propellants having from about 1.0% to about 3.0% produce propellants having good burning rate characteristics. Particularly good performance has been observed with from about 1.5% to about 2.0% Group IIA metal salt added.

As mentioned above, the present invention is particularly useful when used with propellant compositions based upon a combination of nitrate esters, optionally including ammonium nitrate or HMX. It should be appreciated, however, that the present invention is expected to produced beneficial results with other types of propellants, such as ammonium perchlorate-based propellants, cross-linked double base ("XLDB"), and extruded double base propellants, and minimum smoke (nitrato plasticized) propellants.

The following illustrate typical formulations falling within the scope of the present invention. Such exemplary formulations may have the following ingredients, in the following percentages (by weight):

Material	Percentage Range
Ammonium Nitrate	0-25
Group IIA metal salt (such as $CaCO_3$)	1.5-2.0
Carbon (amorphous)	0.5-1.0
Nitrocellulose	15-20
BTTN	39-54
TMETN	13-17
MNA	0-1.0
HMX	0-10

Material	Percentage Range
Nitrocellulose	20-25
BTTN	0-5
TMETN	16-20
MNA	0.7-1.2
Curative	1.5-2.5
Cure Catalyst	0.03-0.08
Group IIA metal salt	1.0-3.0
Carbon	0.3-0.7

Propellants falling within the scope of the present invention are found to provide excellent burn rate control. In particular, such formulations result in burn rate v. pressure curves which exhibit a significant "plateau." As mentioned above, the plateau effect provides the ability to control the pressure produced by burning the propellant, and allows one to construct a propellant grain which is suitable for use in a rocket motor casing.

In addition, it is found that the formulations of the present invention exhibit other beneficial characteristics. For example, the propellants of the present invention are generally low smoke. This is a significant benefit, especially when the propellant is to be used in a tactical rocket motor. Low smoke propellants make it more difficult to precisely locate the point from which the rocket motor was fired. In addition, low smoke characteristics assure that visibility is not obstructed at the point of firing.

Furthermore, these formulations are relatively insensitive. Indeed, sensitivities of <70 cards in the NOL card gap test are achievable. This increases the safety of the propellants and provides the ability to use the propellants with confidence, even in hazardous environments such as military operations. Such insensitive propellants are much less likely to be accidently detonated.

Examples

The following examples are given to illustrate various embodiments which have been made or may be made in accordance with the present invention. These examples are given by way of example only, and it is to be understood that the following examples are not comprehensive or exhaustive of the many types of embodiments of the present invention which can be prepared in accordance with the present invention.

Example 1

In this Example two (2) propellant compositions within the scope of the present invention where prepared, burned, and characterized. The propellants had the following percentage compositions (by weight):

Composition #1	
Material	Percentage
NC	15.9
BTTN	40.53
TMETN	13.51
MNA	1.7
TMXDI	1.35
AN	24.80
Calcium Carbonate	1.50
Carbon	0.7
Triphenyl bismuth (TPB/MA)	0.02
Legend in Figure 1	■

Composition #2	
Material	Percentage
NC	15.9
BTTN	40.53
TMETN	13.51
MNA	1.7
TMXDI	1.35
AN	25.0
Calcium Carbonate	1.50
Carbon	0.5
Triphenyl bismuth	0.02
Legend in Figure 1	♦

Nitrocellulose (used in these formulations as a binder as well as being one of the nitrate ester components), BTTN, TMETN, and MNA were incorporated into the propellant in the form of a preblend as described above. The preblend was prepared by dissolving or swelling the NC in acetone. After thorough mixing of all of the ingredients, all of the solvents were removed. This resulted in a lacquer preblend. TMXDI is employed in the composition as a curing agent to cross-link the NC binder. It was found that the formulations set forth above produced acceptable low-smoke propellants having good burn rate control.

The propellant formulations were burned and the burn rate of the propellant formulations was plotted against pressure produced. The results of that plot are set forth in Figure 1. It can be seen from Figure 1 that the slope of both plots plateaus, indicating that the burn rates of the propellants are modified by the addition of calcium carbonate. The burn rate v. pressure is within the range required for a usable propellant formulation.

<u>Example 2</u>

In this Example propellants within the scope of the present invention where prepared, burned, and characterized. The propellants differed in that particle size of calcium carbonate varied. Calcium carbonate with a

12 micron particle size is designated by the symbol ♦, calcium carbonate having an 8 micron particle size is designated by the symbol ■, and a composition having calcium carbonate with a 3.3 micron particle size is designated with a ◊. Each of the compositions had the following weight percentage compositions:

Material	Percentage
NC	15.81
BTTN	40.39
TMETN	13.43
MNA	2.00
TMXDI	1.35
AN	25.0
Calcium Carbonate	1.50
Carbon ($22m^2/g$)	0.5
Triphenyl bismuth	0.02

It was found that the formulations set forth above produced acceptable low-smoke propellants. The propellant formulations were burned and the burn rate of the propellant formulations was plotted against the pressure. The results of that plot are set forth in Figures 2 and 3. It can be seen from Figures 2 and 3 that the slope of the plots plateaus, indicating that the burn rates of the propellants are effectively modified by the addition of calcium carbonate. The burn rate v. pressure is within the range required for a usable propellant formulation.

Example 3

In this Example two (2) propellant formulations within the scope of the present invention where prepared, burned, and characterized. The propellants had the following weight percentage compositions:

Composition #1	
Material	Percentage
NC	21.54
BTTN	54.90
TMETN	18.30
MNA	1.96
TMXDI	1.96
Calcium Carbonate	1.0
Carbon (amorphous)	0.25
Triphenyl bismuth/MA (TPB/MA)	0.05
Legend in Figure 3	♦

Composition #2	
Material	Percentage
NC	21.38
BTTN	54.51
TMETN	18.17
MNA	1.95
TMXDI	1.94
Calcium Carbonate	1.5
Carbon (amorphous)	0.5
TPB/MA	0.05
Legend in Figure 3	■

These propellant formulations were compared to an uncatalyzed baseline propellant. It was found that the formulations set forth above produced acceptable low-smoke propellants.

The propellant formulations, along with the control, were burned and the burn rate of the propellant formulations was plotted against the pressure. The results of that plot are set forth in Figure 4. It can be seen from Figure 4 that the slope of the plots for both of the propellants within the scope of the invention plateau, whereas the plot for the control is essentially a straight line.

This once again indicates that the burn rates of the propellants are modified by the addition of calcium carbonate.

Example 4

In this Example two (2) propellants within the scope of the present invention where prepared, burned, and characterized. The propellants had the following weight percentage compositions:

Composition #1	
Material	Percentage
NC	21.38
BTTN	54.51
TMETN	18.17
MNA	1.95
TMXDI/N-100	1.94
Calcium carbonate	1.50
Carbon	0.50
TPB/MA	0.55

Composition #2	
Material	Percentage
NC	21.42
BTTN	54.63
TMETN	18.21
MNA	1.95
TMXDI/N-100	1.94
Calcium carbonate	1.50
Carbon	0.30
TPB/MA	0.05

In these examples carbon of varying particle sizes was used. The carbon used included ELFTEX-8 carbon with a particle size (surface area) of 64 m^2/g, ELFTEX-12 carbon with a particle size of 35 m^2/g, and STERLING R carbon with a particle size of 21 m^2/g.

It was found that the formulations set forth above produced acceptable low-smoke propellants. The propellant formulations, along with the control, were burned and the burn rate of the propellant formulations was plotted against the pressure. The results of that plot are set forth in Figures 5, 6, and 7. It can be seen from these Figures that the slope of the propellant plots plateau, whereas the plot for the control is essentially a straight line. This once again indicates that the burn rates of the propellants are modified by the addition of calcium carbonate.

Example 5

In this Example propellants within the scope of the present invention where prepared, burned, and characterized. The propellants had the following weight percentage compositions:

Composition #1	
Material	Percentage
NC	21.26
BTTN	54.22
TMETN	18.07
MNA	1.95
TMXDI/N-100	1.94
Calcium carbonate	2.0
Carbon	0.50
TPB/MA	0.05

Composition #2	
Material	Percentage
NC	21.31
BTTN	54.34
TMETN	18.11
MNA	1.95

In these examples carbon are varying particle sizes was used. The carbon used included ELFTEX-8 carbon with a particle size of 64 m^2/g and ELFTEX-12 carbon with a particle size of 35 m^2/g. The propellant 0.5% ELFTEX-12 carbon is designated ♦, 0.5% ELFTEX-8 carbon is designated ■, 0.3% ELFTEX-12 carbon is designated ◊, and 0.3% ELFTEX-8 carbon is designated □.

It was found that the formulations set forth above produced acceptable low-smoke propellants. The propellant formulations, along with the control, were burned and the burn rate of the propellant formulations was plotted against the pressure. The results of that plot are set forth in Figure 8. It can be seen from this Figure that the slope of the propellant plots plateau, whereas the plot for the control is essentially a straight line. This once again indicates that the burn rates of the propellants are modified by the addition of calcium carbonate.

Example 6

In this Example propellant within the scope of the present invention where prepared, burned, and characterized. The composition had the following weight percentage compositions:

Material	Percentage
NC	20.27
BTTN	51.70
TMETN	17.23
MNA	1.90
TMXDI	1.84
Calcium Carbonate	1.50
Carbon	0.5
TPB/MA	0.05
HMX	5.0

It was found that the formulation set forth above produced acceptable low-smoke propellant. The propellant formulation was burned and the burn rate of the propellant formulation was plotted against the pressure. The results of that plot are set forth in Figure 9. It can be seen from Figure 9 that the slope of the plot plateaus, indicating that the burn rates of the propellants are modified by the addition of calcium carbonate.

Example 7

In this Example propellant within the scope of the present invention was prepared, burned, and characterized. The composition had the following weight percentage compositions:

Material	Percentage
NC	19.17
BTTN	48.90
TMETN	16.30
MNA	1.85
TMXDI	1.74
Calcium Carbonate	1.50
Carbon	0.5
TPB/MA	0.05
HMX	10.0

It was found that the formulation set forth above produced acceptable low-smoke propellant. The propellant formulation was burned and the burn rate of the propellant formulation was plotted against the pressure. The results of that plot are set forth in Figure 10. It can be seen from Figure 10 that the slope of the plot plateaus, indicating that the burn rates of the propellants are modified by the addition of calcium carbonate.

Example 8

In this Example propellant within the scope of the present invention was prepared, burned, and characterized. The composition had the following weight percentage compositions:

Material	Percentage
NC	15.89
BTTN	40.53
TMETN	13.51
MNA	1.70
TMXDI	1.35
Strontium Carbonate	1.50
Carbon	0.5
TPB	0.02
Ammonium nitrate	25.00

It was found that the formulation set forth above produced acceptable low-smoke propellant. The propellant formulation was burned and the burn rate of the propellant formulation was plotted against the pressure. The results of that plot are set forth in Figure 11. It can be seen from Figure 11 that the slope of the plot plateaus, indicating that the burn rates of the propellants are modified by the addition of calcium carbonate.

Example 9

In this Example a minimum smoke composite propellant within the scope of the present invention where prepared, burned, and characterized. The composition had the following weight percentage compositions:

Material	Percentage
Binder (inert polymers and curing agents)	6.16
BTTN	15.23
TMETN	7.62
MNA	0.5
Calcium Carbonate	1.50
Carbon	0.5
Al_2O_3	1.0
HMX	20.26
RDX	47.24

It was found that the formulation set forth above produced acceptable composite/double base propellant. The propellant formulation was burned and the burn rate of the propellant formulation was plotted against the pressure. The results of that plot are set forth in Figure 12 and is compared to a lead containing formulation. It can be seen from Figure 12 that the slope of the plot plateaus, indicating that the burn rates of the propellants are effectively modified by the addition of calcium carbonate.

Example 10

Figure 13 illustrates 70-grain motor traces for a formulation with 1% calcium carbonate compared to a formulation containing LC-12-15, which is a lead-copper complex of beta-resorcyclic acid. Neither formulation contained a classic combustion stability additive (i.e. ZrC, or Al_2O_3 which have historically increased card gap sensitivity by 30 cards or more). The motor with calcium carbonate exhibits smooth combustion, whereas the leaded version is erratic. This appears to indicate that calcium oxide is generated during combustion, which in turn stabilizes performance.

Example 11

Figure 14 illustrates a comparison of smoke output from a propellant within the scope of the present invention with a lead-containing propellant. It will be appreciated that the smoke outputs are similar, indicating that the present invention provides a minimum smoke formulation without the need for the use of toxic burn rate modifiers. This formulation (1.5% calcium carbonate) was determined to be 50 cards in the NOL card gap test.

Summary

In summary, the present invention provides methods and compositions for controlling the burn rate of solid rocket motor propellants. More particularly, the burn rate of nitrate ester/ammonium nitrate/HMX propellants have been shown to be controlled by the addition of Group IIA metal ions, particularly in the form of calcium carbonate and strontium carbonate.

By formulating the propellants as taught by the present invention it is possible to avoid some of the significant problems encountered with conventional burn rate modifiers. In particular, the present invention provides compositions and methods for modifying burn rate without the use of lead, copper, or similar materials. The burn rate is modified by the addition of calcium carbonate, or similar materials, which are not toxic, hazardous, or polluting.

The propellant formulation produced is a minimum smoke propellant which is also generally insensitive. Thus, the major objects of the present invention are met by the compositions and methods of the present invention.

Claims

1. A solid propellant comprising at least two nitrate esters and a burn rate modifier comprising at least one Group IIA metal salt.

2. A solid propellant as claimed in claim 1 wherein said burn rate modifier comprises calcium carbonate.

3. A solid propellant as claimed in claim 1 wherein said burn rate modifier comprises strontium carbonate.

4. A solid propellant as claimed in any preceding claim comprising from 0.5% to 5.0% Group IIA salt.

5. A solid propellant as claimed in claim 4 comprising from 1.0% to 3.0% Group IIA salt.

6. A solid propellant as claimed in claim 5 comprising from 1.5% to 2.0% Group IIA salt.

7. A solid propellant as claimed in any preceding claim wherein a sufficient quantity of Group IIA salt is added to produce a plateau of the burning rate v. pressure curve of the propellant.

8. A solid propellant as claimed in any preceding claim which also includes ammonium nitrate.

9. A solid propellant as claimed in claim 1 wherein the Group IIA metal salt comprises particles having a particle size in the range of from 0.5μm to 35μm.

10. A solid propellant as claimed in claim 9 wherein the Group IIA metal salt comprises particles having a particle size in the range of from 0.5μm to 3μm.

11. A solid propellant as claimed in any preceding claim wherein one of said nitrate esters is nitrocellulose.

12. A solid propellant as claimed in any preceding claim wherein one of said nitrate esters is 1, 2, 4 butane-trioltrinitrate.

13. A solid propellant as claimed in any preceding claim wherein one of said nitrate esters is trimethylolethane trinitrate.

14. A solid propellant as claimed in any preceding claim wherein one of said nitrate esters is nitroglycerin.

15. A solid propellant as claimed in any preceding claim which has a pressure exponent less than or equal to approximately 0.7.

16. A solid propellant as claimed in any preceding claim further comprising from 0.5% to 1.0% carbon.

17. A solid propellant as defined in any preceding claim further comprising up to 2.0% N-methylnitro aniline.

18. A rocket motor including a controlled burner rate propellant as claimed in any preceding claim.

19. A method for modifying the burn rate of a solid propellant containing at least two nitrate esters, comprising the step of adding to the propellant an effective quantity of Group IIA metal calcium carbonate and strontium carbonate.

20. A method as claimed in claim 19 wherein Group IIA metal salt is added such that it comprises from 0.5% to 5.0% by weight, preferably 1.5% to 2.0% by weight, of the propellant.

21. A method as claimed in claim 19 or claim 20 wherein a sufficient quantity of Group IIA salt is added to produce a plateau of the burning rate v. pressure curve of the propellant.

22. A method as claimed in any one of claims 19 to 21 wherein said Group IIA salt has a particle size in the range of from 0.5μm to 3μm.

23. A method as claimed in any one of claims 19 to 22 wherein a sufficient quantity of Group IIA salt is added that combustion is stabilized.

FIGURE 1

EFFECT OF CARBON CONTENT ON CDB/AN
BURNING RATES WITH CALCIUM CARBONATE

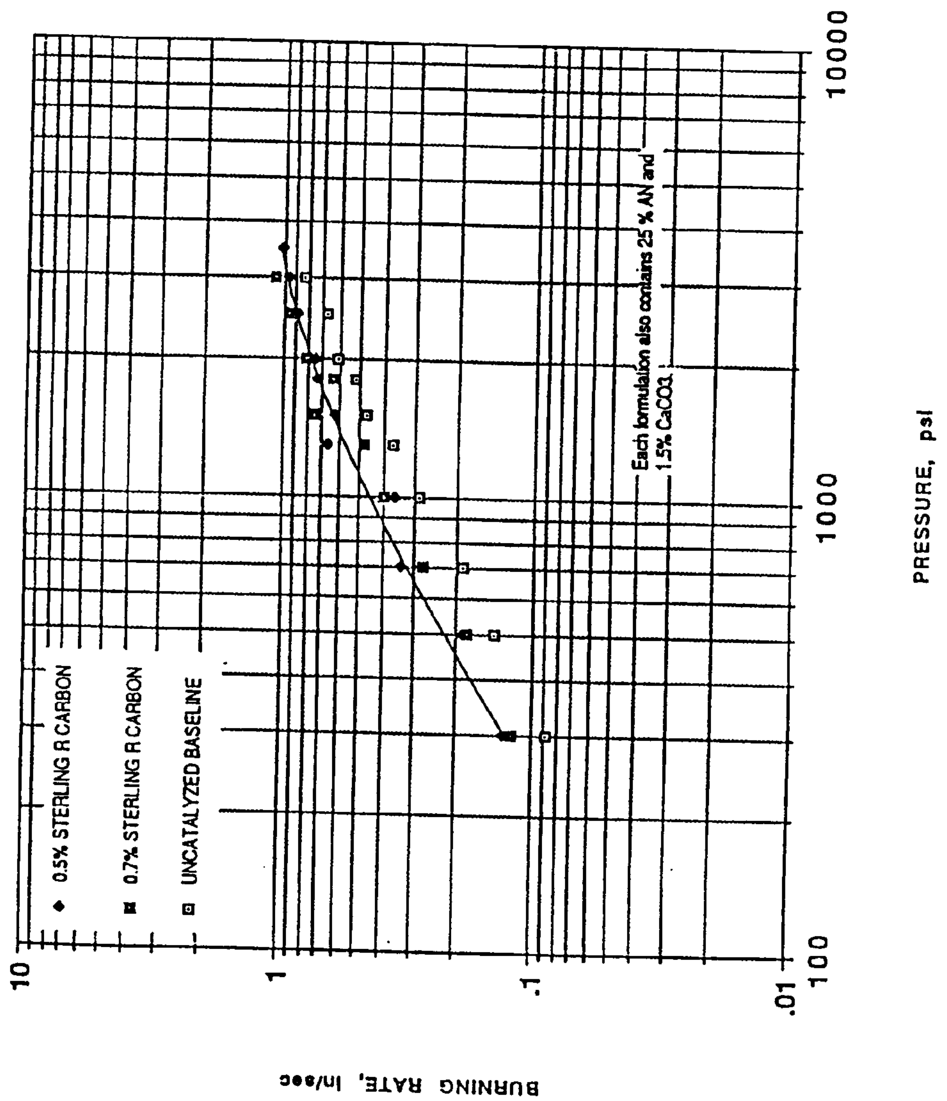


FIGURE 2

BURNING RATE RESPONSE IN CDB/AN PROPELLANT WITH PARTICLE SIZE OF CALCIUM CARBONATE

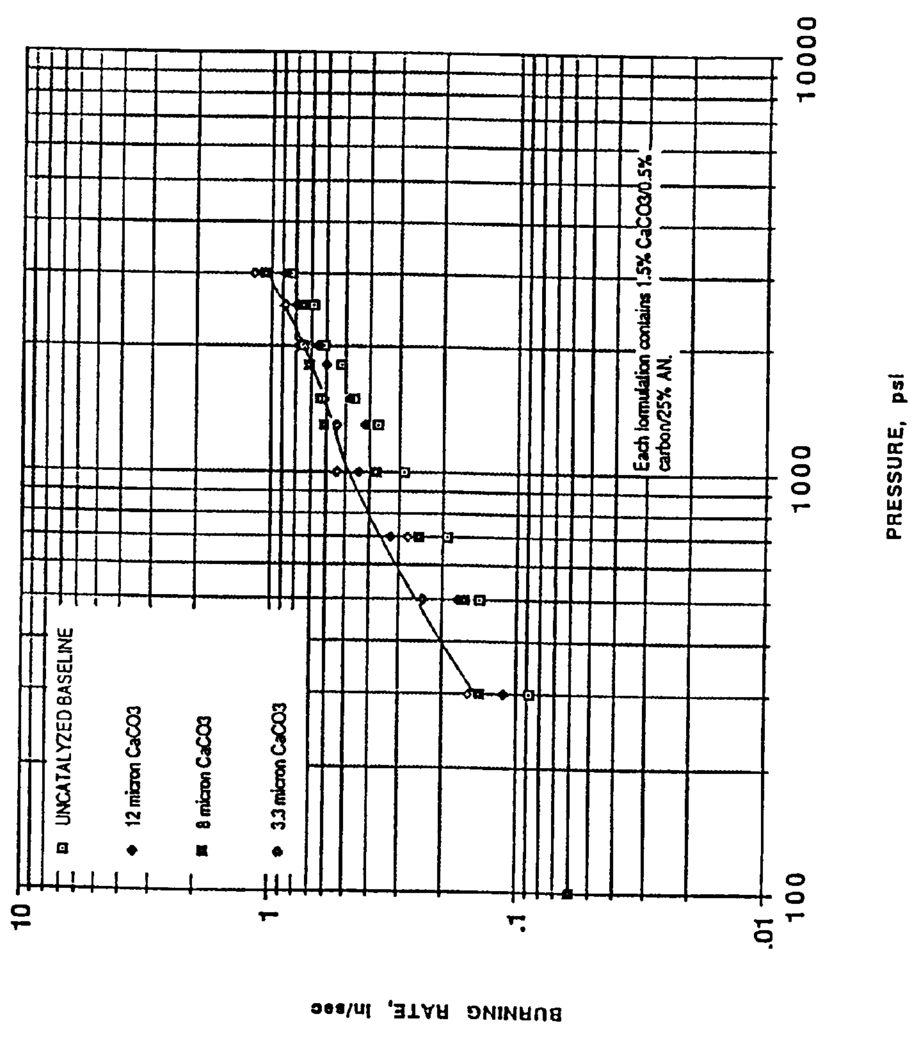


FIGURE 3

EFFECTS OF VERNIER CHANGES IN CALCIUM CARBONATE PARTICLE SIZES ON BURNING RATES IN CDB/AN PROPELLANT

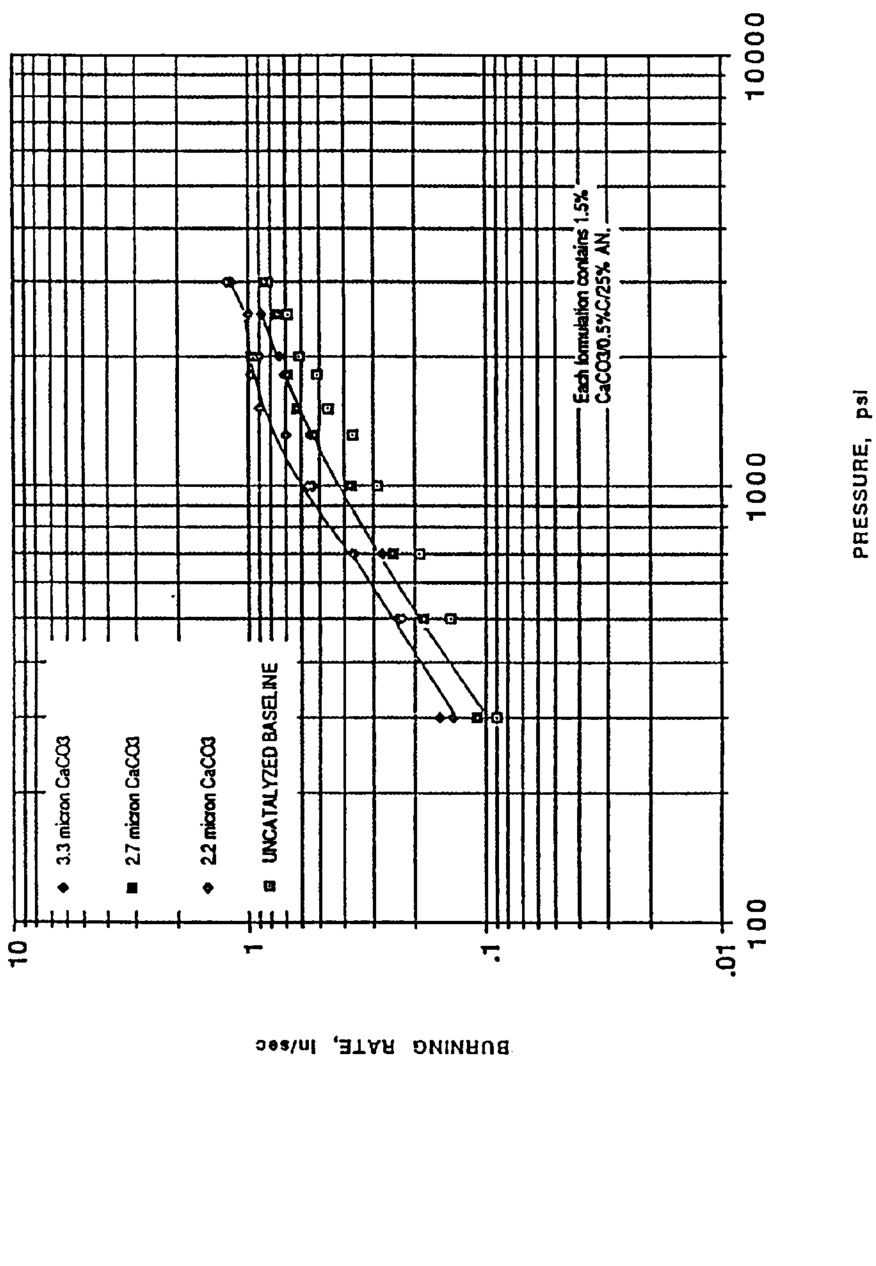


FIGURE 4

EFFECT OF CALCIUM CARBONATE
CONCENTRATION ON
CDB/UNFILLED BURNING RATE

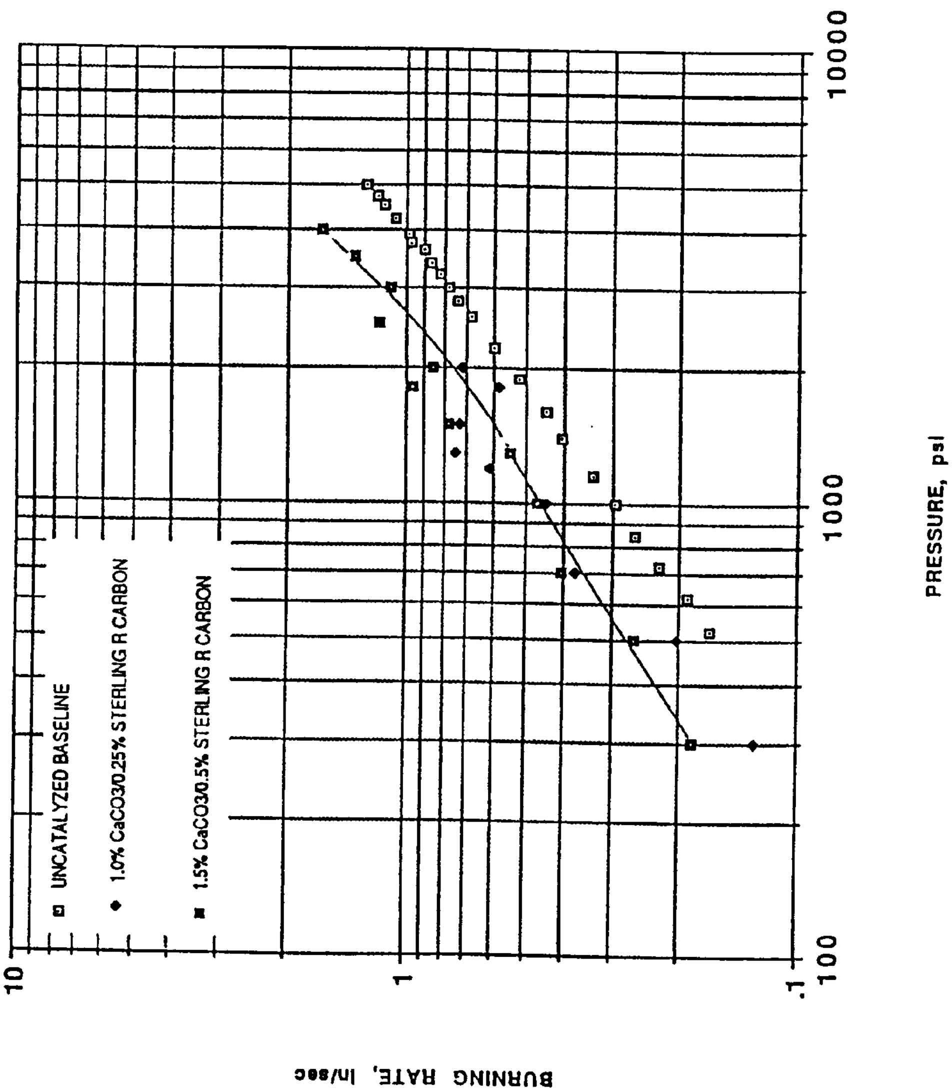


FIGURE 5

BURNING RATE COMPARISONS WITH
1.5% CaCO3 AND ELFTEX-8 CARBON

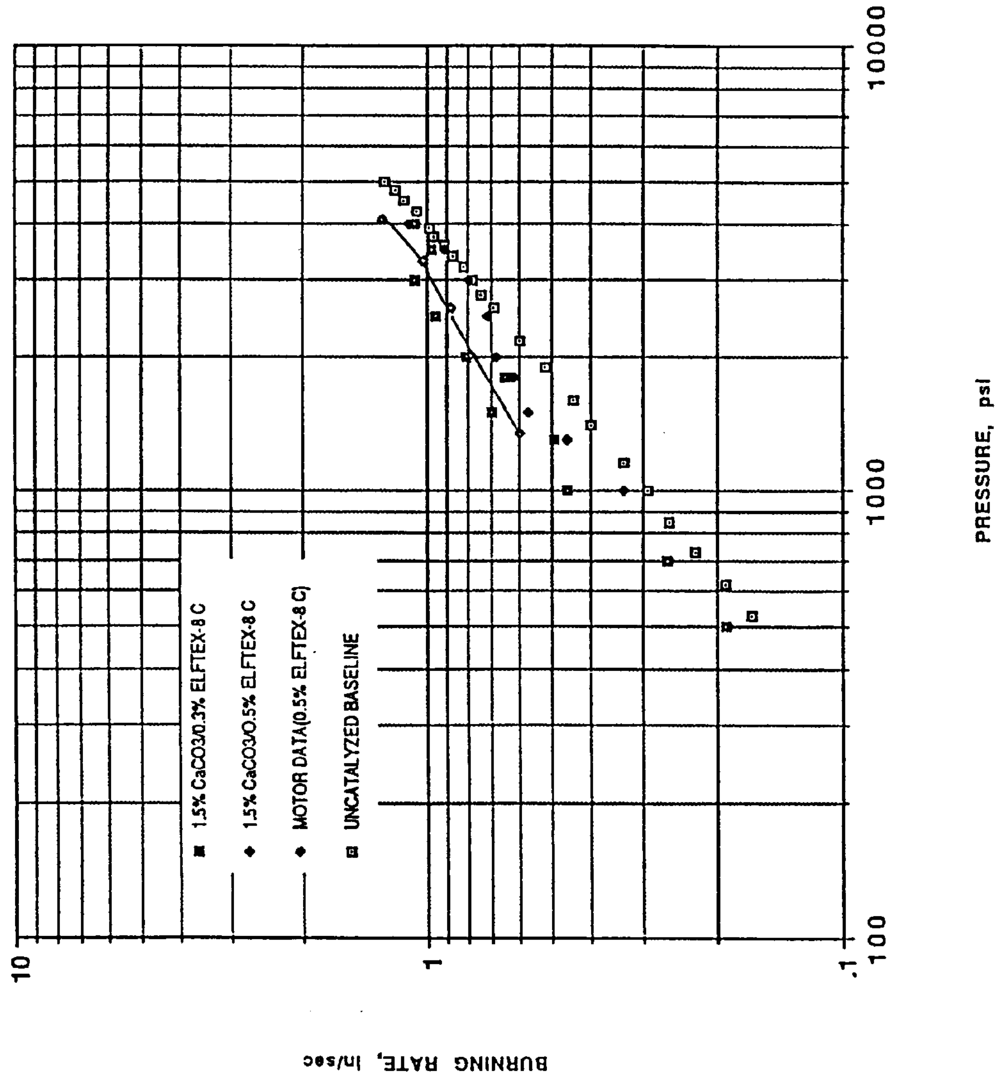


FIGURE 6

BURNING RATE VARIATIONS WITH
1.5% CaCO3 AND ELFTEX-12 CARBON

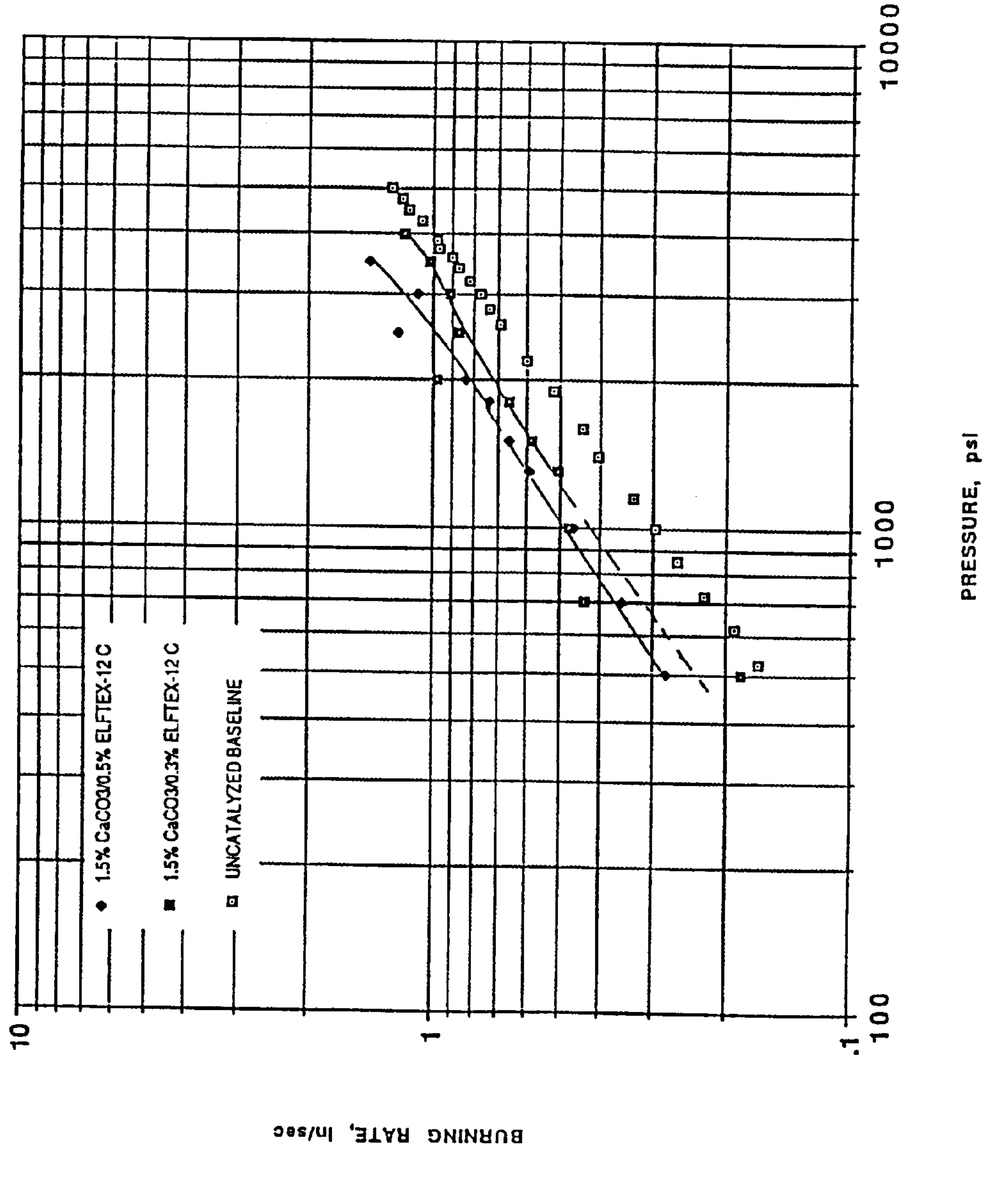


FIGURE 7

BURNING RATE VARIATIONS WITH
1.5% CaCO3 AND STERLING R CARBON

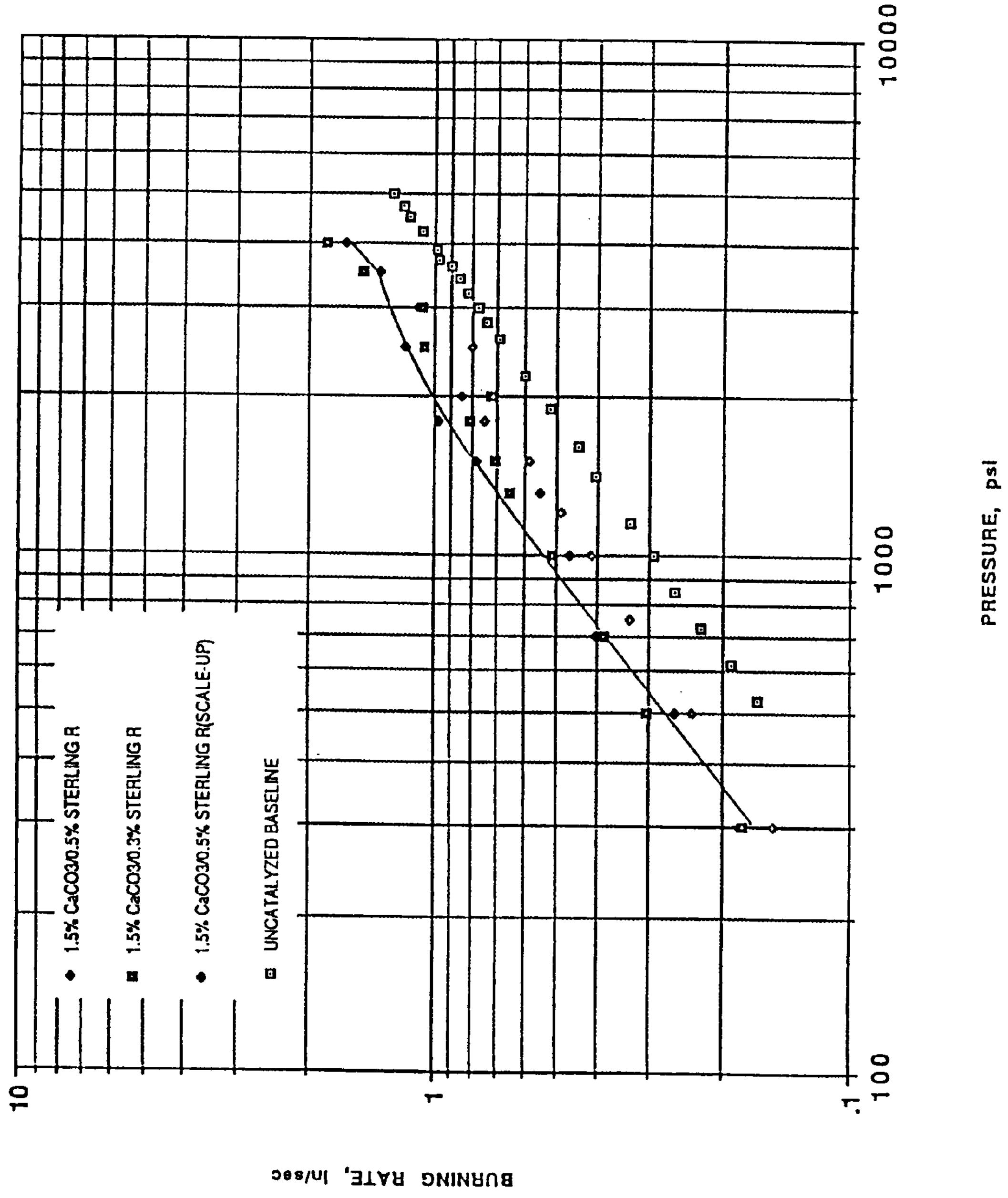


FIGURE 8

BURNING RATE VARIATIONS WITH 2% CALCIUM CARBONATE IN CDB/UNFILLED PROPELLANT

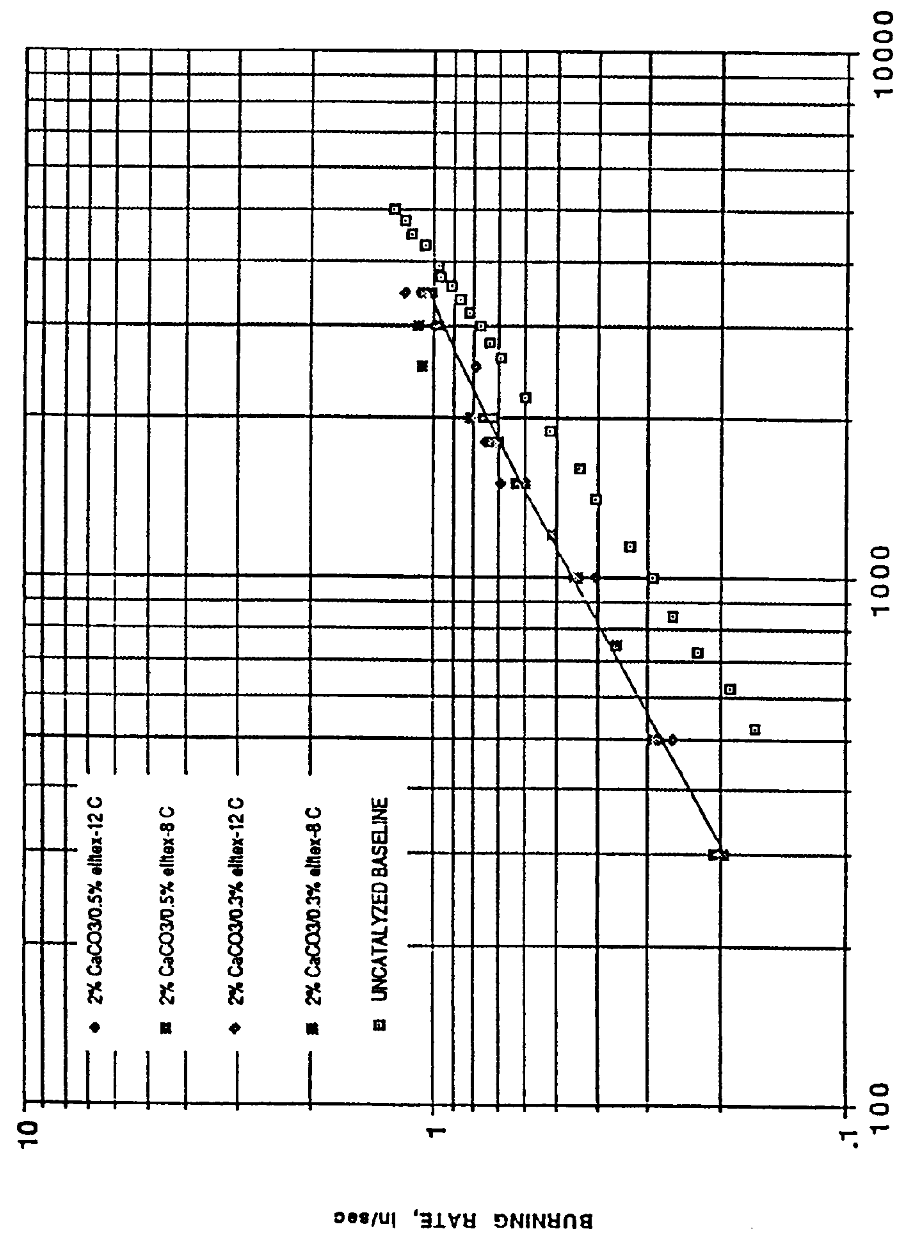


FIGURE 9

BURNING RATE RESPONSE WITH CALCIUM CARBONATE IN CDB/HMX (5% HMX) PROPELLANT

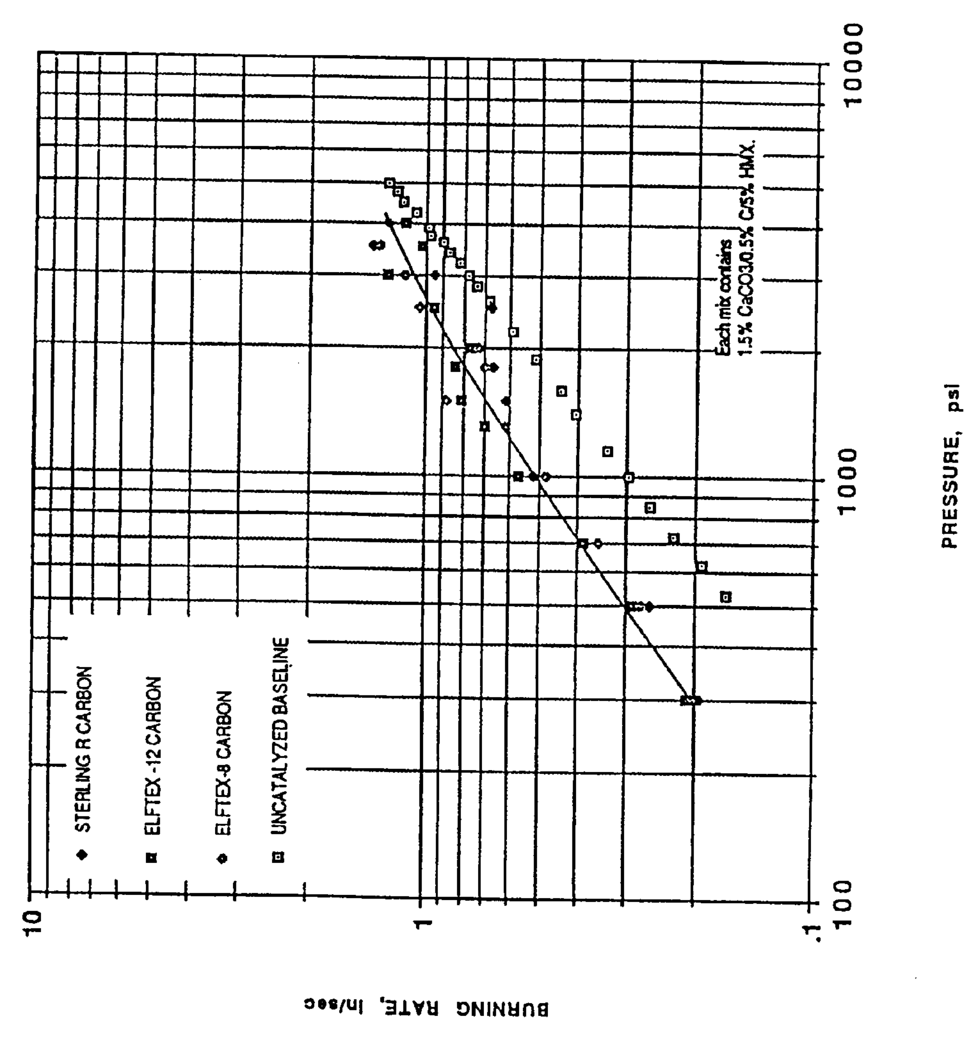


FIGURE 10

BURNING RATE RESPONSE WITH CALCIUM CARBONATE IN CDB/HMX (10%) PROPELLANT

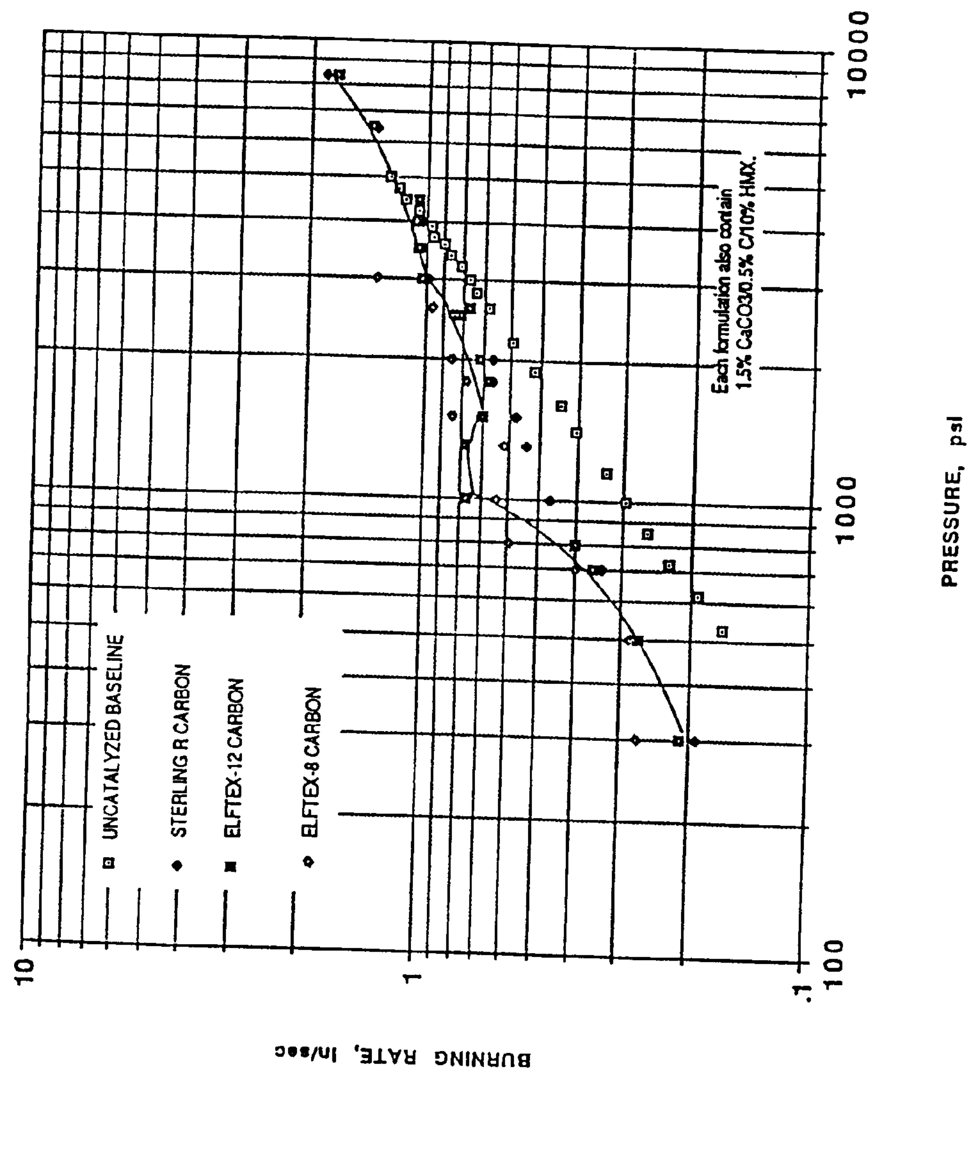


FIGURE 11

BURNING RATE RESPONSE WITH STRONTIUM CARBONATE IN CDB/AN PROPELLANT

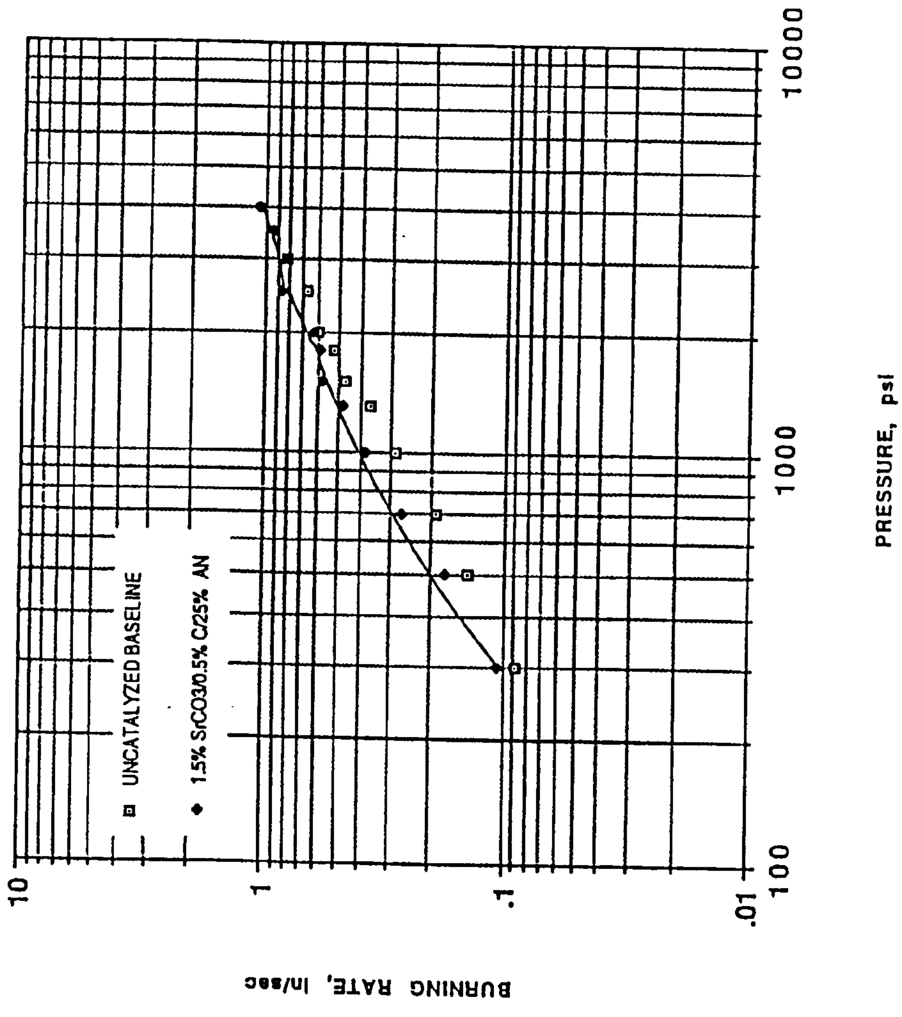


FIGURE 12

BURNING RATE COMPARISONS BETWEEN LEAD OXIDE AND CALCIUM CARBONATE IN A COMPOSITE MS PROPELLANT

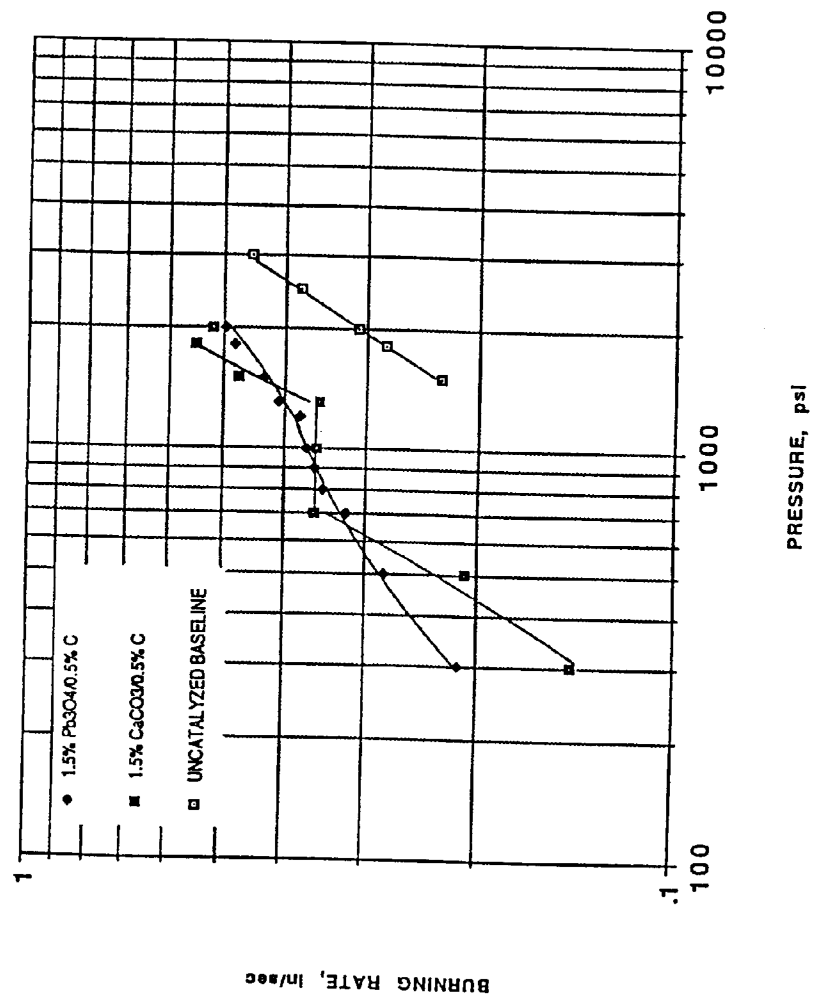


Figure 13.

MOTOR TRACE FOR CDB/UNFILLED PROPELLANT SHOWS EXCELLENT COMBUSTION STABILITY WITHOUT ADDED STABILIZER

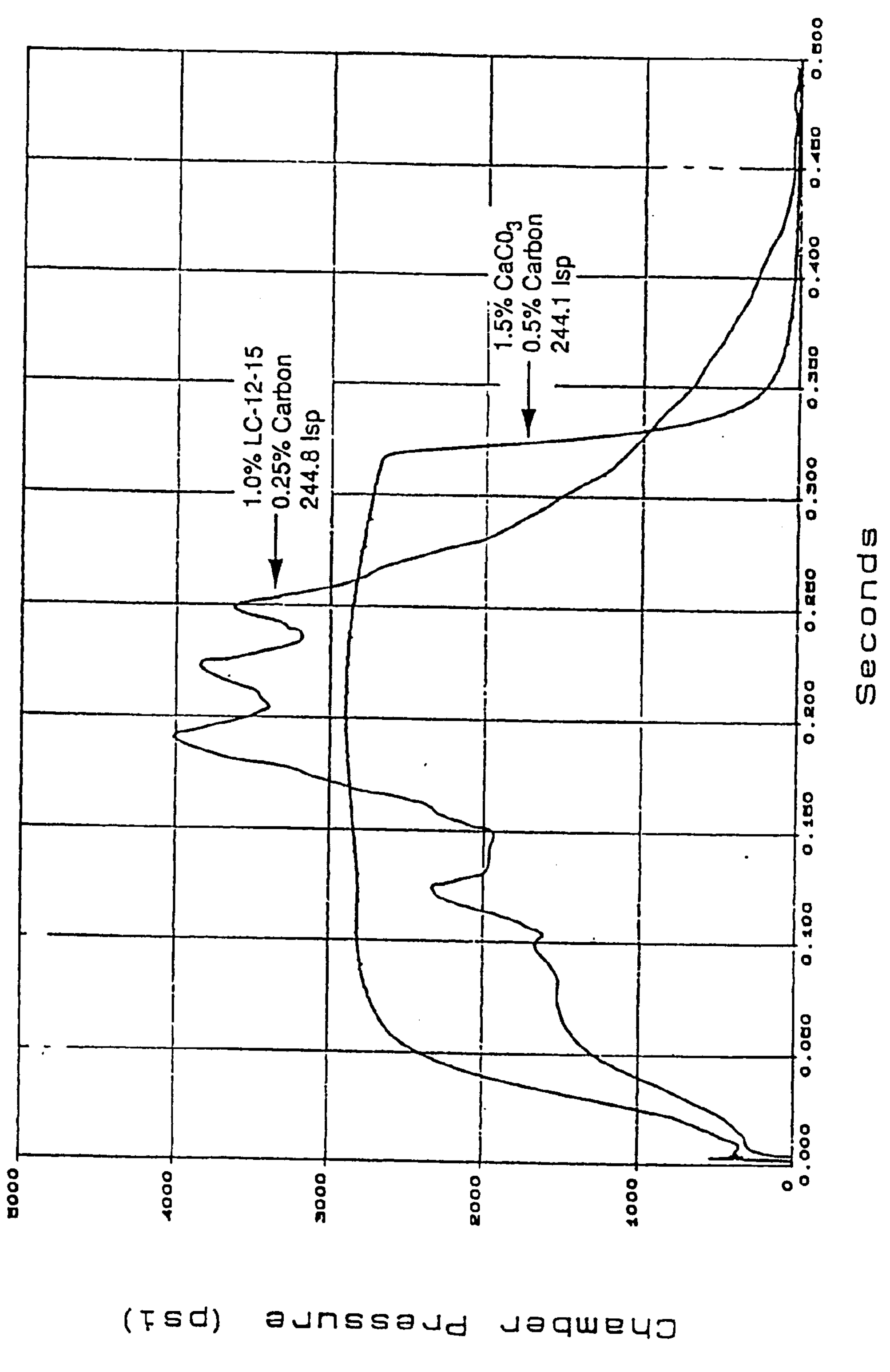
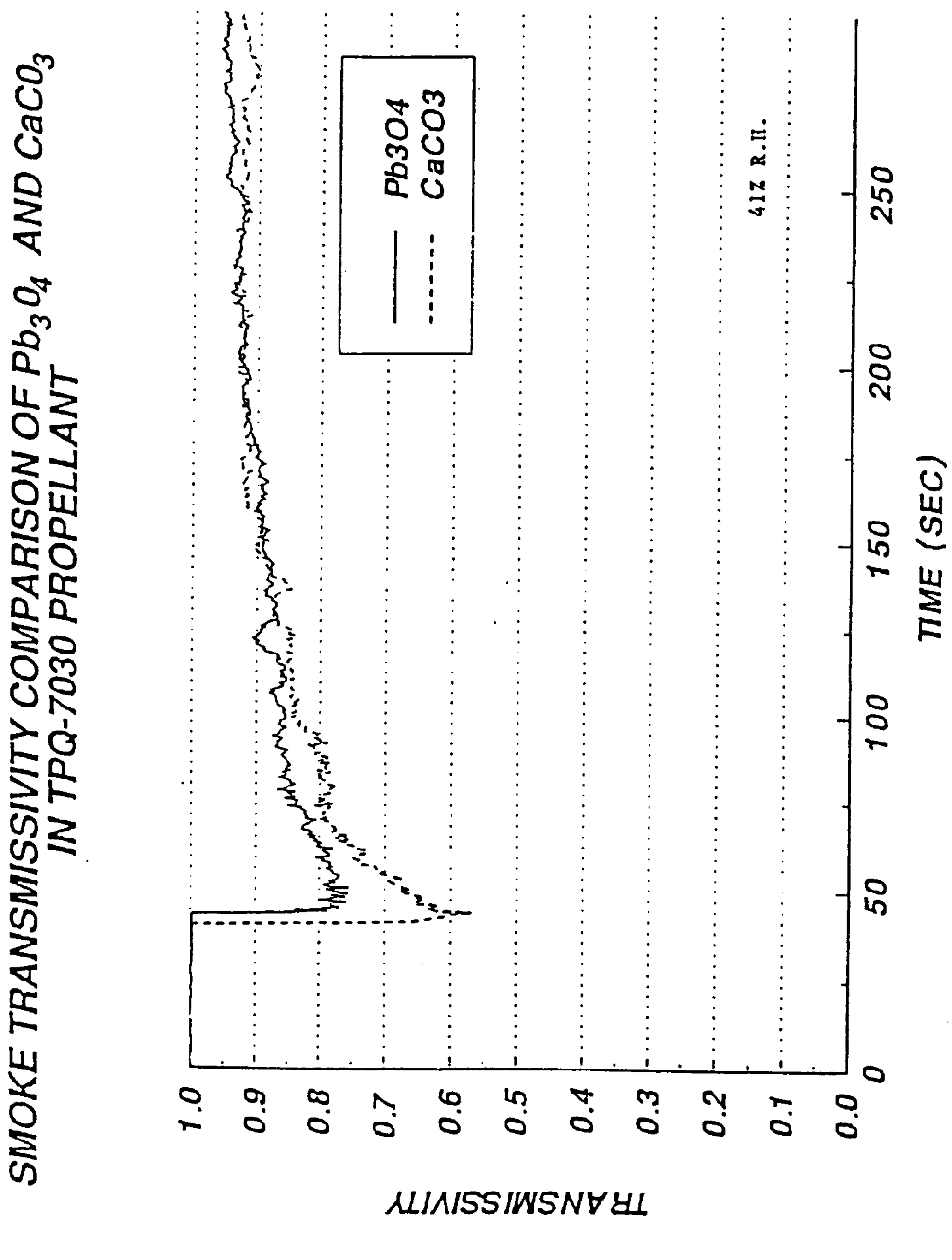


Figure 14.


SMOKE TRANSMISSIVITY COMPARISON OF Pb_3O_4 AND $CaCO_3$
IN TPQ-7030 PROPELLANT
TRANSMISSIVITY
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
250
TIME (SEC)
Pb3O4
CaCO3
41% R.H.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 0922

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	US-A-3 009 796 (R.F. PRECKEL)	1,2,4-7, 11,14, 15, 18-21,23	C06B23/00
Y	* column 3, line 25 - column 4, line 69; examples 23,31 *	12,13,17	
X	CHEMICAL ABSTRACTS, vol. 083, no. 10, 8 September 1975, Columbus, Ohio, US; abstract no. 82295a, J. KANEKO ET AL. 'Solid propellant chemical composition containing smokeless explosive material.' page 201 ;	1,3-6, 11,14, 16, 18-20,23	
Y	* abstract * & JP-A-7 504 721 (ASAHI CHEMICAL INDUSTRY CO., LTD.) 24 February 1975 & CENTRAL PATENTS INDEX, BASIC ABSTRACTS JOURNAL Derwent Publications Ltd., London, GB; AN 75-20239W & JP-A-7 504 721 (ASAHI CHEMICAL IND. CO.) 24 February 1975 * abstract *	12,13,17	
Y	US-A-3 873 386 (D.E. ELRICK) * claims *	12,13,17	

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TECHNICAL FIELDS SEARCHED (Int.Cl.5)
C06B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 May 1994	Schut, R

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	CHEMICAL ABSTRACTS, vol. 106, no. 20, 18 May 1987, Columbus, Ohio, US; abstract no. 158905r, Z. LAZIC ET AL. 'Multifactorial analysis of technological conditions for the manufacture of double-base rocket fuels with high combustion rates.' page 150 ; * abstract * & NAUCNO-TEH. PREGL. vol. 36, no. 8 , 1986 pages 28 - 34	1,18,19	
X	CHEMICAL ABSTRACTS, vol. 069, no. 18, 28 October 1968, Columbus, Ohio, US; abstract no. 68698p, S. DELI ET AL. 'Methane-proof and non-methane-proof industrial explosive of high brisance and increased storability.' page 6426 ; * abstract * & HU-A-154 740 (BANYASZATI KUTATO INTEZET) 29 May 1968	1,2,9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
X	US-A-3 841 929 (J.M. CRAIG) * column 2, line 43 - line 52 * * column 3, line 61 - column 5, line 50; claims *	1,18,19	
A	US-A-4 216 039 (E.M. PIERCE) * claims *	1-23	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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