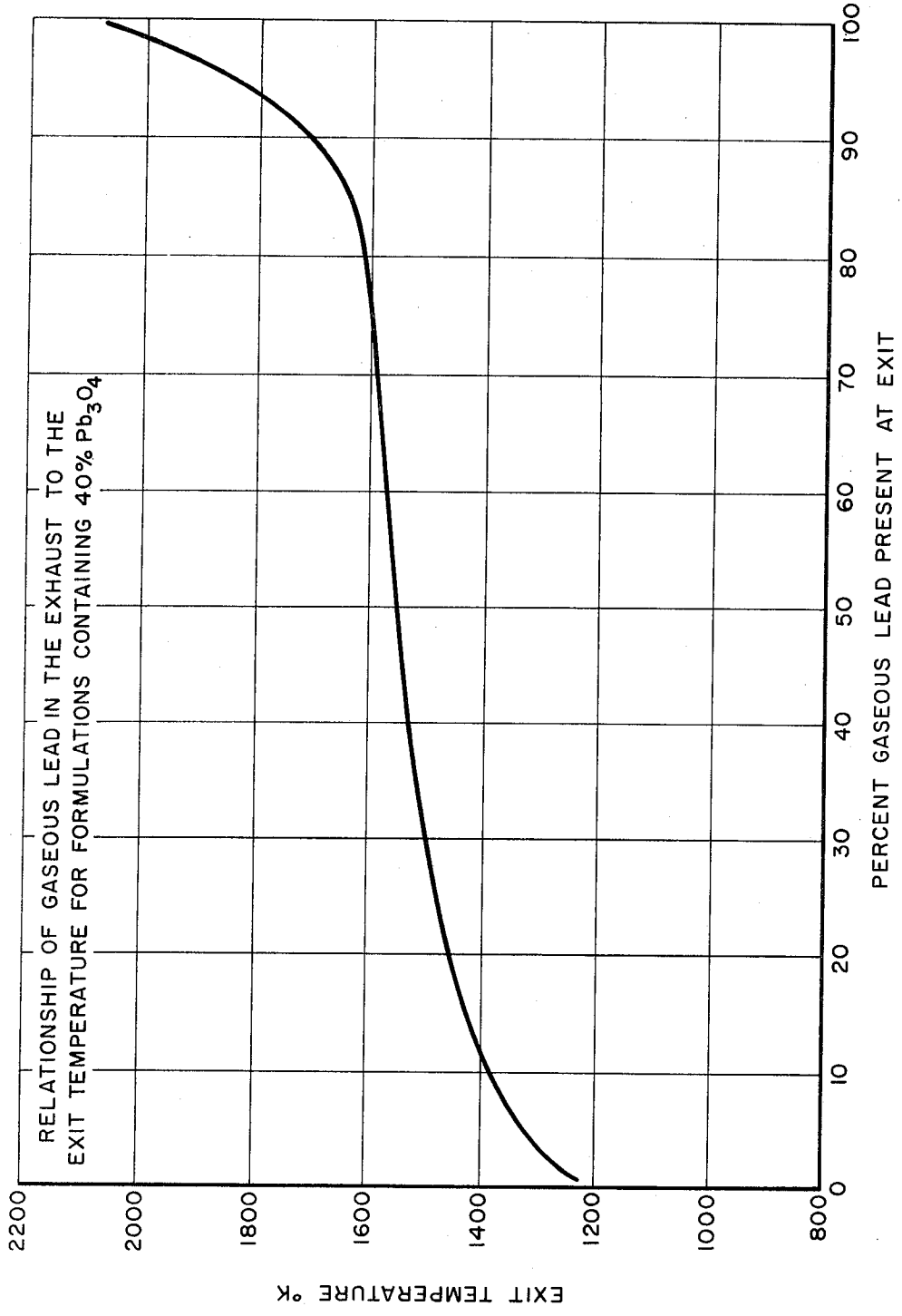
Sept. 10, 1974 D. F. MELLOW ET AL 3,834,956

SOLID PROPELLANT COMPOSITION CONTAINING LEAD AND LEAD COMPOUNDS

Filed Aug. 8, 1967



DALE F. MELLOW
RICHARD WINER
INVENTORS

BY William F. Smith

AGENT

United States Patent Office 3,834,956 Patented Sept. 10, 1974

3,834,956

SOLID PROPELLANT COMPOSITION CONTAINING LEAD AND LEAD COMPOUNDS

Dale F. Mellow, Salt Lake City, Utah, and Richard Winer, New Castle, Del., assignors to Hercules Incorporated, Wilmington, Del.

Filed Aug. 8, 1967, Ser. No. 661,495
Int. Cl. C06b 1/07
U.S. Cl. 149—19.1 11 Claims

ABSTRACT OF THE DISCLOSURE

The use of lead and compounds thereof in high energy propellant formulations results in propellant systems having very high density-impulse and very high efficiency. This is achieved by adjusting the composition of the formulations such that the exhaust temperatures of the propellant are maintained above the vaporization temperature of the lead.

This invention relates to solid propellant compositions and more particularly to very high density-impulse and very high efficiency solid propellant compositions containing lead or compounds thereof.

The successful use of lead or compounds thereof in smokeless powder propellants to obtain plateau or mesa burning characteristics is well known. However, these propellants have the lead or compounds thereof present in low concentration and are possessed of moderate density-impulse characteristics. It is also known that investigations have been conducted concerning the use of high concentrations of lead oxide (Pb_3O_4) in double-base smokeless powder propellants (Example 1) in view of the promising increase in theoretical density-impulse indicated when compared to conventional double-base smokeless powder propellant (Example 2). The delivered Isp of the lead containing propellant, however, was not significantly increased and appreciable quantities of metallic lead remained in the fired motor chambers. These results are shown in Table I which follows and in the attached drawing, although the curve depicted in the drawing is based upon the relationship of gaseous lead in the exhaust to exit temperature for formulations containing 40% Pb_3O_4.

TABLE I

	Ex. 1	Ex. 2
Composition:		
NC (12.6% N)	17.20	
NC (13.25% N)		51.50
NG	23.30	43.00
Diethylphthalate		3.25
Ethylcentralite		1.00
2-nitrodiphenylamine	1.00	
Lead oxide (Pb_3O_4)	58.50	
Potassium sulfate		1.25
Total (weight percent)	100.00	100.00
Carbon black (added weight percent)		0.20
Candelilla wax (added weight percent)	0.05	0.02
Isp (theo.), lbf.-sec./lbm	159.6	245.2
Isp (del.), lbf.-sec./lbm	133	212
Efficiency, percent	83.5	86.5
Density, g./cc	3.11	1.60
Density Isp (theo.), lbf.-sec./lbm.×g./cc	496.4	392.3
Density Isp (del.), lbf.-sec./lbm.×g./cc	413.6	339.2
Chamber temperature, ° K	2,611	3,002
Exit temperature, ° K	1,626	1,441

Generally described, in accordance with the present invention, it has now been discovered that the use of lead and compounds thereof in conventional high energy propellant compositions results in systems having very high density-impulse (calculated as greater than 550 lbf.-sec./lbm.×g./cc.) and very high efficiency, greater than 90%. These outstanding results are obtained by formulating the propellant composition so that the exhaust temperatures of the propellant are maintained above the vaporization temperature of the lead.

More specifically, the present invention contemplates a high density-impulse solid propellant composition essentially comprising at least about 10% by weight of metal fuel and about 4 to 55% by weight of at least one material of the group consisting of lead and compounds of lead, said composition having a density of more than 2.5 g./cc. and a combustion temperature of more than 3000° K. at which temperature the lead is substantially completely vaporized.

Examples of the invention based on multiple-base smokeless powder propellant are given in Table II which illustrates several formulations incorporating various ingredients for carrying the invention into effect. Here it will be noted that the density in g./cc. was greater than 2.6, the chamber temperature in ° K. was greater than 3500, the exit temperature in ° K. was greater than 2200, and that the density Isp lbf.-sec./lbm.×g./cc. was greater than 553.

TABLE II.—HIGH DENSITY SMOKELESS POWDER FORMULATIONS

	EX. 3	EX. 4	EX. 5	EX. 6	EX. 7	EX. 8	EX. 9
Composition:							
PbO			40.0				
Pb_3O_4	40.0	40.0		41.0	53.5	9.0	34.0
Al	10.0	15.0	15.0	15.0	15.5		
U						60.0	
Zr							35.0
NC (12.6% N) plastisol	8.0	8.0	8.0	8.0	8.0	8.0	8.0
NG	20.0	18.0	18.0	20.0	20.0	20.0	20.0
AP				12.0			
HMX	19.5						
RDX		16.6	16.6				
2 NDPA	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Resorcinol				1.0			
TA	1.5	1.4	1.4	2.0	2.0	2.0	2.0
Total (weight percent)	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Isp, lbf.-sec./lbm	208.7	210.3	208.8	203.5	183.1	171.1	181.0
Density, g./cc	2.653	2.697	2.710	2.720	3.178	4.173	3.452
Chamber temp., °/K	3,577	3,856	3,810	3,869	3,835	4,001	4,012
Exit temp., ° K	2,233	2,392	2,344	2,542	2,562	2,509	2,835
Impulse × density Isp, lbf.-sec./lbm. × g./cc	553.7	567.2	566.0	553.5	581.9	714.0	624.8

Ballistic data for the propellant of Example 3 based on forty-pound charge motor firings are given in Table III which follows. Here it will be noted that the efficiency percent varied from 93.9 to 96.5 depending upon the conditioning temperature utilized.

TABLE III

Conditioning temperature, ° F	0		80		100	
Pressure, p.s.i.	675	570	901	668	992	727
Burning rate, in./sec.	0.417	0.397	0.543	0.475	0.606	0.515
Isp (del.), lbf.-sec./lbm.	191.1	189.0	198.7	195.0	199.6	192.8
Isp (theo.), lbf.-sec./lbm.	203.5	199.4	210.0	202.1	208.9	203.3
Efficiency, percent	93.9	94.7	94.6	96.5	95.6	94.8

The propellant used in the forty-pound charge motor firings described above was prepared using conventional casting technique.

Further examples of the invention based on composite propellant are given in Table IV which, similar to Table II, illustrates several formulations incorporating various ingredients for carrying the invention into effect. Here it will be noted that the density in g./cc. was greater than 2.7, the chamber temperature in ° K. was greater than 3200, the exit temperature in ° K. was greater than 2100, and that the density Isp lbf.-sec./lbm.×g./cc. was 544 or greater.

TABLE IV.—HIGH DENSITY COMPOSITE FORMULATIONS

	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15
Composition:						
Binder (C_4H_6)	9	5	6	6	4	5
Al	14	15				
PbO			34			
Zr			30	30	30	
U						65
Pb_3O_4	44	43		40	41	4
AP	33	33	30	24	22	26
TVOPA		4			3	
Total (weight percent)	100.0	100.0	100.0	100.0	100.0	100.0
Isp, lbf.-sec./lbm.	198.2	204.7	188.9	177.2	178.4	175.1
Density, g./cc	2.747	2.862	3.296	3.559	3.719	4.379
Chamber temp., ° K.	3,271	3,689	3,554	3,419	3,914	3,854
Exit temp., ° K.	2,102	2,361	2,235	2,110	2,486	2,388
Impulse × density isp, lbf.-sec./lbm. × g./cc	544.0	578.5	622.5	630.7	663.4	766.6

From the foregoing, it will be appreciated that the advantages gained through the use of the propellant of this invention in addition to the high density-impulse obtained, reside in the very high efficiency achieved. The reason that high efficiency is obtained lies in the discovery of tailoring the propellant composition so as to maintain temperatures in the rocket chamber and exit cone above the boiling point of lead (2026° K.). Efficiency losses due to condensation in the exit cone will be small but condensation in the rocket chamber will give large losses.

Calculations borne out by actual testing procedure have shown that compositions which burn at lower temperatures have much of the lead present in the exhaust as liquid lead. This leads to lower efficiency. The powdered or particulate metals utilized in accordance with this invention control the temperature at levels sufficiently high to maintain all of the lead present in the exhaust in the gaseous phase. The relationship of exit temperature to the concentration of gaseous lead present in the exhaut for formulations containing 40% Pb_3O_4 has been previously introduced with reference to the prior art and drawing.

The ingredients utilized in preparing the high density smokeless powder formulations include nitrocellulose (NC) having a nitrogen content of from about 12.00 to 13.25% and at least one explosive nitric ester such as nitroglycerin (NG) with or without additional crystalline high explosive oxidizing material, such as, ammonium perchlorate (AP), potassium perchlorate, cyclotetramethylene tetranitramine (HMX), cyclotrimethylene trinitramine (RDX), triaminoguanidine nitrate, hydroxylamine perchlorate, and hydrazine diperchlorate. The crystalline high explosive material is incorporated in particulate form with substantially all through a 60 mesh sieve. The lead and compounds of lead are, likewise, incorporated in particulate form with substantially all through a 60 mesh sieve. In addition to lead, the preferred compounds of lead are those having a positive partial heat of explosion, such as, lead azide, lead chromate, lead oxalate, and particularly lead oxide. The metal fuel is, likewise, incorporated in particulate form with substantially all through a 140 mesh sieve. The preferred metal fuels are those having a density of about or greater than that of aluminum, such as, aluminum (Al), uranium (U), zirconium (Zr), bismuth and thorium.

The above ingredients in substantially the following proportions by weight yield high density smokeless powder propellants as desired in accordance with this invention; from about 20 to about 30% of multiple-base smokeless powder, from about 10 to about 65% of metal fuel, and from about 4 to about 55% of lead and compounds of lead. When high explosive oxidizer material is included in the multiple-base smokeless power propellant from about 10 to about 25%, by weight, of the total composition is utilized. Moreover, crosslinking agents, such as, the diisocyanates may be included as a binder component. Crosslinking agents such as polyglycoladipate-2,4-tolylene diisocyanate, tolylene-diisocyanate, and hexamethylene diisocyanate are preferred, ordinarily not exceeding about 5 to 10% by weight of the total composition. Also, conventional additives, such as 2-nitrodiphenylamine (2-NDPA), triacetin (TA), resorcinol, and the like may be simply incorporated in the composition in small amount, ordinarily not exceeding about 10% by weight of the total composition. All the foregoing compositions may be manufactured using conventional procedures.

The ingredients utilized in preparing the high density composite formulations include the usual polymeric binder systems, such as polybutadiene (C_4H_6) as shown in the examples, oxidizers, metal fuels, lead and compounds of lead, with or without plasticizers.

The oxidizers, metal fuels, lead and compounds of lead and the particle sizes thereof include those set forth for the high density smokeless powder propellant.

The above ingredients in substantially the following proportions by weight yield high density composite propellants as desired in accordance with this invention; from about 4 to about 20% of polymeric binder, from about 20 to about 40% of high explosive oxidizer, from about 10 to about 70% of metal fuel, and from about 4 to about 55% of lead and compounds of lead. When plasticizer material is included in the composite propellant, from about 2 to about 10% by weight of the total composition is utilized. Difluoramine plasticizers are preferred as shown in Examples 11 and 14 where as low as 3 to 4% by weight of 1,2,3-tris[1,2-bis(difluoroamino)ethoxy] propane (TVOPA) gave an increase in excess of 30 volumetric impulse units over comparable Examples 10 and 13. An epoxy crosslinked-carboxy terminated polybutadiene binder system was used as the binder in Examples 10 and 14 and is preferred in view of the excellent mechanical properties imparted to the composition. Other hydrocarbon binder systems, however, would give comparable volumetric impulse. Binder systems and plasticizers based on fluorocarbons may also be utilized in view of their higher density and indicated improved volumetric impulse as compared to the hydrocarbon binders. Also, conventional additives, such as, the various compounding ingredients commonly employed in making composite propellants, as, for example, oxidation inhibitors, reinforcing agents, wetting agent, surfactants, ballistic modifiers, radar attenuators, burning rate modifiers, and the like, may be simply incorporated in the composition in small amounts, ordinarily not exceeding about 10% by weight of the total composition. All of the foregoing compositions

may be manufactured using conventional procedures.

The advantages of the present invention are multifold. A comparison of density Isp for various state of the art smokeless powder propellants as compared to the high density propellants of the present invention is given in Table V which follows:

TABLE V

Propellant	Isp (theo.), lbf.-sec./lbm.	Density, g./cc.	Density ISP (theo.), lbf.-sec./lbm. × g./cc.
Ultra-high energy (beryllium hydride fuel)	309.3	1.34	414.0
High energy (beryllium fuel)	289.1	1.72	497.0
Conventional (aluminum fuel)	269.8	1.81	487.4
High density-impulse:			
(40% Pb_3O_4, 10% Al fuel)	208.7	2.65	553.7
(40% Pb_3O_4, 15% Al)	210.3	2.70	567.2
(53% Pb_3O_4, 16% Al)	183.1	3.18	581.9

It is evident from the foregoing, that the present invention provides an outstanding improvement in the art. In the past, primary emphasis in propellant development programs has been placed on the development of propellants with maximum specific impulse. However, for volume limited and booster applications, the density of the propellant becomes as significantly important as the specific impulse. For example, for missiles with missile weight large compared to the propellant weight (low mass fraction) the performance is proportional to the density to a power approaching one. That is to say, most first stage rockets could increase range and pay load by direct substitution of the high density-impulse propellant of this invention without requiring change in motor configuration or hardware. Alternatively, the use of the present invention could reduce significantly the size of the motor case required for certain applications or be particularly advantageous in such applications (rocket assisted projectiles) where the volume limitations are particularly rigid.

It will be seen, therefore, that this invention may be carried out by the use of various modifications and changes without departing from its spirit and scope, with only such limitations placed thereon as are imposed by the appended claims.

What we claim and desire to protect by Letters Patent is:

1. A high density-impulse solid propellant composition containing a combination of about 4 to 55% by weight of at least one particulate metal of the group consisting of lead and compounds of lead with at least about 10% by weight of a particulate metal fuel other than said lead and said compounds of lead in intimate admixture in the composition to provide said composition with a density of more than 2.5 g./cc. and a combustion temperature of more than 3000° K. at which temperature the said lead and the said compounds of lead are substantially completely vaporized.

2. The composition of claim **1** wherein the lead oxide is PbO.

3. The composition of claim **1** wherein the lead oxide is Pb_3O_4.

4. The composition of claim **1** wherein the solid propellant is a multiple-base smokeless powder propellant and contains about 10 to 65% by weight of the metal fuel.

5. The composition of claim **4** wherein the smokeless powder propellant contains about 5% to 10% by weight of a diisocyanate crosslinking agent.

6. The composition of claim **4** wherein the smokeless powder contains about 10 to 25% by weight of particulate high explosive.

7. The composition of claim **6** wherein the smokeless powder contains about 5 to 10% by weight of a diisocyanate crosslinking agent.

8. The composition of claim **1** wherein the solid propellant is a composite propellant and contains about 10 to 70% by weight of the metal fuel.

9. The composition of claim **8** wherein the composite propellant contains about 4 to 20% by weight of polymeric binder.

10. The composition of claim **9** wherein the composite propellant contains about 2 to 10% by weight of plasticizer.

11. The composition of claim **10** wherein the plasticizer is a difluoramine plasticizer.

References Cited

UNITED STATES PATENTS

3,228,338	2/1969	McEwan et al.	149—37 X
2,945,751	7/1960	O'Neill	149—38 X
3,033,716	5/1962	Preckel	149—38 X
3,033,717	5/1962	Preckel	149—38 X
3,138,499	6/1964	Camp et al.	149—38

STEPHEN J. LECHERT, JR., Primary Examiner

U.S. Cl. X.R.

149—20, 37, 38, 98, 92, 76, 18