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Optimization of low signature base bleed propellant formulations

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Optimization of low signature base bleed propellant formulations

Ehab M Youssef[1], Tamer Elshenawy[1], Hosam E Mostafa[2], Mostafa Radwan[3] and Ahmed Elbeih[2,4]

[1] Technical Research Center, Cairo, Egypt
2 Military Technical College, Kobry Elkobbah, Cairo, Egypt
3 British University in Egypt, Cairo, Egypt

[4] Email: elbeih.czech@gmail.com

Abstract: Base bleed (BB) projectile is one of the choices to minimize projectile base drag leading to 30% range extension. The secondary smoke resulting from the burning of BB is considered to be one of the drawbacks of the BB and it is an essential factor in detecting the projectile flight towards the target. Based on intensive ICT formulations results, optimization study has been carried out using design expert software to optimize the base bleed formulations that can produce minimum amount of secondary smoke with the lowest flame temperature and higher impulse. The optimized base bleed propellant formulations, that have been found, were those of 10.27 and 7.02 % for both RDX/AP and Mg/AP ratios respectively. The experimental preparation and testing of the optimized two base bleed types showed lower values of secondary smoke by 16% and 55% for RDX/AP and Mg/AP ratios respectively when tested experimentally alongside the baseline base bleed reference composition.

Keywords: Propellants, optimization, RDX, Mg, secondary smoke.

1. Introduction

Range extension of artillery projectiles has always been a basic requirement for the user in order to shoot the enemy targets at longer ranges. There are many methods to extend the projectile range some related to the weapon and others to the projectile itself. Nowadays, great attention has been paid to the base bleed unit as one of the methods used to increase the ammunition range through decreasing air resistance during projectile flight [1, 2].

Base Bleed unit is mounted at the projectile bottom containing a chemical composition in solid state called Base Bleed grain starting its burning inside the barrel. To increase base bleed efficiently, the base mass flow should be optimal and should occur during third to half of the total time of projectile flight in air. During this period of time the base drag decreases by a value ranging from 60 to 85% in supersonic speed region. Thus, the range is extended to a value ranging from20 to 30% of the total range of the projectile without base bleed [3].

Different components are combined in the composite base bleed propellant formulation which affects the propellant characteristics. Some of them are involved in chemical reactions to produce a final product or improving propellant quality. Complexity of production and final characteristics are influenced by many factors such as solid component quantities; type of binder, curing agent, particle size distributions, their shapes, quantity and type of bonding agent. Also other factors like mechanical characteristics of the propellant are very important during the propellant service life and for aging and safe life in order to withstand the high stress acting on the grain. Ingredients of composite base bleed grains are usually categorized according to their main functions which are directed to manufacture propellant with high mechanical properties and low burning rate ranging from 0.9 up to 1.5mm/s adapting with base bleed job [4-5].

The signature resulting from the burning of base bleed propellant (primary and secondary smoke) is considered to be one of the drawbacks since it is an essential factor in detecting the projectile during its flight towards the target. The high purity of AP and perfectly controlled grain performance of AP based propellant are the two important characteristic parameters that make AP as one of the most common oxidizers, the explosive salts of perchloric acid are considerably more stable and safer to handle as compared to their chlorate analogues [6]. The explosive decomposition of ammonium perchlorate that occurs during the burning process is shown in the following equation:

$$2NH_4ClO_4\text{------>}N_2 + 3H_2O + 2HCl + 5/2O_2$$

Ammonium perchlorate content in base bleed composition is about 65-75 percent, Therefore, during the propellant combustion, a large amount of HCl gas and other chlorine compounds are generated in the exhaust plume. With the moisture in air, these by-products of combustion of the propellant fuel produce an intense white smoke in the atmosphere. The exhaust gases are highly corrosive and toxic in nature and they form semi opaque clouds under humid conditions. This leads to heavy “acid rain” and depletion of the ozone layer. Another reason for developing chlorine free propellants is the need for low hazardous and minimum smoke producing propellants. Minimum smoke producing propellants are those, which eliminate both primary smoke and secondary smoke (i.e. water aerosol condensed from the atmosphere HCl with H_2O) from the exhaust plume [7]. In order to overcome the environmental problems and to avoid the detection of trajectory of the projectile, it is imperative to investigate the use of the so-called “clean burning propellants”, which eliminate chlorine as an ingredient [8]. These include Low HCl scavenged formulations (HCl scavenger added to the propellant), HCl neutralized propellant formulations, Low HCl formulations oxidized with a combination of ammonium nitrate (AN) and AP (with or without HCl scavenger) and Chlorine-free formulations. Each of these propellant formulations has its own advantages and disadvantages depending upon the chemistry involved and the physical properties of the materials used [9-21].

The main target of this work includes theoretical and practical investigation of various ways to change the chemical formulations of the prepared samples in order to decrease the smoke content emitted during firing of the ammunition based on base bleed unites. The study includes introducing various chemical additives as a partially replacement for the AP oxidizer which is the main source of emitting smoke. These chemical additives include magnesium (Mg) powder and hexahydro-l,3,5-trinitro-1,3,5-triazine (RDX). The prepared samples undergo full physical, chemical and performance characterization besides measuring smoke concentration.

2. Experimental

2.1. Theoretical thermos-chemical evaluation

Thermo-chemical calculations are used with considerable success as a fast and effective tool to investigate the characteristics of different types of propellant formulations. Since the eighties of the past century thermo-chemical calculation is an essential step for choosing propellant formulations that are candidate for a given practical application and to minimize many costly experiments which are used to evaluate the performance and properties of new propellant formulations [22-24].

Performance parameters of several propellant formulations are calculated using a chemical equilibrium computer program (ICT) thermodynamic code named after the institute of chemical technology of Germany, which is based on the chemical equilibrium and steady-state burning model and they are illustrated in tables (1) and table (2).

Table 1. Formulations depending on partial replacement of AP with Mg.

Ingredients		Formula				
		NM1	NM3	NM5	NM7	NM9
Binder	HTPB	23.933	23.933	23.933	23.933	23.933
	HMDI	1.642	1.642	1.642	1.642	1.642
	MAPO	0.4	0.4	0.4	0.4	0.4
Opacifier	C	0.025	0.025	0.025	0.025	0.025
Oxidizer	AP	73	71	69	67	65
	Mg	1	3	5	7	9
Density (g/cm^3)		1.505	1.503	1.500	1.497	1.494
Flame temperature (^{o}K)		2003	2073	2141	2204	2259
C* (m/s)		1349	1364	1378	1390	1399
Oxygen balance (O_b)		-46.04	-48.03	-50.03	-52.04	-54.03
Secondary smoke (mole number)		6.205	6.030	5.854	5.676	5.497

Table 2. Formulations depending on partial replacement of AP with RDX

Ingredients		Formula				
		NR1	NR3	NR5	NR7	NR9
Binder	HTPB	23.933	23.933	23.933	23.933	23.933
	HMDI	1.642	1.642	1.642	1.642	1.642
	MAPO	0.4	0.4	0.4	0.4	0.4
Opacifier	C	0.025	0.025	0.025	0.025	0.025
Oxidizer	AP	73	71	69	67	65
	RDX	1	3	5	7	9
Density (g/cm^3)		1.506	1.504	1.502	1.500	1.498
C* (m/s)		1340	1336	1333	1329	1325
Oxygen balance (O_b)		-46.15	-47.27	-48.38	-48.94	-50.05
Secondary smoke (mole number)		6.21	6.04	5.87	5.70	5.53

2.2. Optimization evaluation

The objective of the optimization analysis is to obtain the optimum propellant mixture, which in turn has the lowest HCl secondary smoke percentage but on the other hand has minimum flame temperature, high specific impulse and a density above 1.5 g/cm^3. The optimization study calculations have been carried out using the Design Expert software. The selected effective design factors in the optimization algorithm are mass percent of the input mixture ingredients such as RDX/ AP and Mg/AP. The response parameters that will be considered is the optimization process are the secondary smoke percent, the mixture density and the produced flame temperature as well as the specific impulse. The number of input starting points was 20 values including the combinations among composition ingredients (i.e. RDX/ AP and Mg/AP ratios) and the relevant ICT code results including flame temperature, secondary smoke and specific impulse as well as mixture predicted density. The entire input values for the design expert software used to do the optimization calculations were put into factorial design template in the Design Expert program. The goals and limiting boundary constrains were also determined according to the design requirements.

The goals, the importance and the boundary constrains of the studied factors are listed in tables (3), in which the lowest secondary smoke percent is set to be the most important objective design response, considering the boundaries and constrains of all other factors. The flame temperature of the burnt propellant is considered to be as minimum as possible, whereas the density is set to be greater than 1.5 g/cm^3. The specific impulse goal is set to be maximized, but in a lower order than that of the secondary smoke.

Table 3. The input constrains, the governing limits and the response importance of the optimization factors and response.

Name	Goal	Lower	Upper	Weight
RDX/AP (%) Mg/AP (%)	in range	0	70	3
Flame Temp. (°C)	Minimize	1600	2100	2
Density (g/cm^3)	in range	1.5	1.7	1
Sec. Smoke (mole)	Minimize	5.53	12.23	3
Impulse (N.S)	Maximize	198	215	2

The output from optimization calculations is shown in table (3) and Figures (1,3) for the RDX/AP (%). It can be seen that several combinations between RDX/AP ratios as an oxidizer and its flame temperature and its current density as well, all have an impact on the secondary smoke and the accompanied impulse. Some selected optimizations mixtures based on RDX/AP ratios are also shown in table (4), which presents six results that can be suggested for the base bleed formulations with lower secondary smoke and higher impulse as well as lower flame temperature. RDX/AP ratios of 10.27 exhibit the optimum formulation with the best desirability design parameter of unity. Therefore, this formulation has been suggested for the experimental preparation and ballistic performance test.

Table 4. Seleted optimization output results for RDX/AP ratios

RDX/AP (-)	Flame Temper.(°C)	Density (g/cm^3)	Sec. Smoke (mole)	Impulse (S)	Desirability
10.27	1600	1.51	5.51	217.2	1.00
11.65	1600	1.51	5.53	217.3	1.00
25.62	1600	1.50	5.80	214.3	0.97
26.71	1628	1.50	5.53	214.6	0.96
5.96	1668	1.51	5.53	217.9	0.95
69.99	1934	1.53	5.53	227.7	0.71

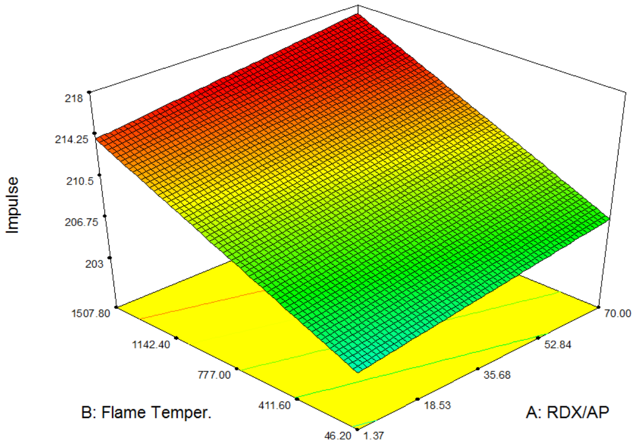

Figure 1. The optimization impulse result as a function of RDX/AP ratio and flame temperature

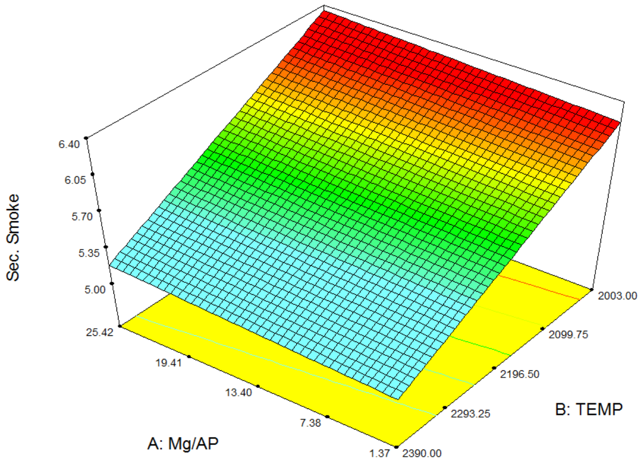

Figure 2. The secondary smoke optimization result as a function of Mg/AP ratio and flame temperature.

Similarly, the Mg/AP base bleed mixture optimization has been performed in the same way as that of the RDX/AP mixture. The optimization boundries and design improtance are shown in Table 3, while figures. (2, 4) show the contour surface relation connecting the input base bleed formulation with relevant ballistic characteristics (i.e. flame temperature, impulse, ...).

First five optimization results with the largest desirability values arranged descendingly are listed in table (5).The first row in the table with Mg/Ap ratio of 7.04 has been selected for experiment preparation and testing.

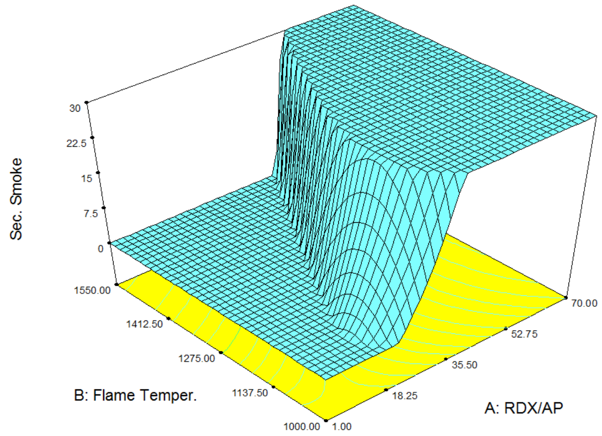

Figure 3. The secondary smoke optimization result as a function of RDX/AP ratio and flame temperature.

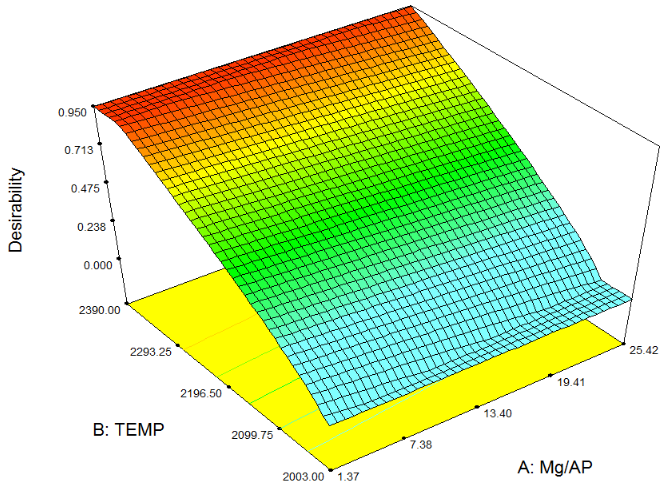

Figure 4. The optimization desirability result as a function of Mg/AP ratio and flame temperature

2.3. Materials

2.3.1. Polyurethane matrix system. The Polyurethane matrix used in this study consists of aHydroxyl-terminated polybutadiene (HTPB, of Iverise Co.Brazil) as prepolymer having a hydroxyl value of 0.84 meq/gramandhexamethylenediisocyanate (HMDI,Aldrich chemical Co. England) as a curing agent with an NCO equivalence value of 11.83 meq/gram. Chemical bonding agent Tris-1- (2, Methyl Aziridinyl) Phosphine Oxide (MAPO, Arsynco Inc, New Jersey, USA) were used as received.

2.3.2. Military fillers. AP was prepared in Abu zabal Co., Egypt with different grain size and used as recieved. RDX was obtained from Eurenco, Paris, France and recrystalized in our laboratories with an average particle sizes of about 15 µm. Mg was obtained from Kaha Co. Egypt with grain size from 45-75 µm.

Table 5. Selected optimization output results for Mg/AP ratios

Mg/AP (-)	Flame Temper. (ºC)	Density (g/cm^3)	Sec. Smoke (mole)	Impulse (S)	Desirablity
7.04	2050	1.50	4.77	222.83	0.95
50.44	2260	1.51	5.18	222.83	0.95
25.74	2110	1.50	5.12	222.83	0.95
44.06	2223	1.52	5.17	222.83	0.95
5.62	1998	1.51	5.18	222.83	0.95

2.4. Preparation of base bleed propellants

The base bleed propellant was prepared in stainless steel vertical mixer of 12 kg capacity. HTPB and MAT4, burning rate modifier, Mg and/or RDX, if exist, are weighed according to the required formulation and well mixed at 50ºC for 15 minutes. Inside the mixer with a double jacket, temperature is raised up to 60ºC through 10 minutes. The dried oxidizer is divided into four equal portions and added to the slurry in series under continuous stirring within 10 minutes at 60ºC.Temperature of the slurry should be decreased to 40ºC and the accurately calculated amount of curing agent (HMDI) is carefully weighted and added. The stirring for 15 minutes takes place at this temperature to insure homogeneity of the paste under vacuum. Then vacuum is released with continuous stirring for 5 minutes. The mixture was then casted and cured at 60 ±2˚C for (3-4) days under vacuum. The cured HTPB binder system was prepared with NCO/OH ratio of 0.83. The prepared propellants were contained 74 wt% fillers and 26 wt% binder system and are designated as AP-HTPB, AP-RDX-HTPB and AP-Mg-HTPB.

2.5. Heat of explosion

The heat of explosion (HEX) of the propellant is directly tied to its energetic level based on the representative ratios of the various ingredients. It is measured as the heat released when a material ignites and burns in a PARR bomb calorimeter pressurized to 25 bar by an inert atmosphere (nitrogen gas) illustrate.The measurement is made after the products have been cooled to near room temperature by noting temperature rise of the calorimeter water jacket; HEX is calculated from this temperature rise using the effective heat capacity of the calorimeter body and water jacket. Strictly speaking then, HEX is defined as the absolute value of the total energy released during constant volume combustion of a material in an inert atmosphere [25].

2.6. X-ray inspection of samples

The quality of the prepared samples was done after curing the samples and 2 inch motor were tested through X- ray unit to assess the inner homogeneity, cracks, air bubbles, porosity and foreign matters**.**

2.7. Density of samples

The propellant density is measured at 20ºC using Pyckno-meter (density crucible) and silicon oil. The samples of the propellant used to measure the density are being cut in regular and equal shape.

2.8. Ignition temperature of samples

This test is used to determine the spontaneous ignition at which the propellant ignites or decomposes. It is measured by progressive heating regularly increasing the temperature by 5ºC every minute to determine the maximum temperature at which the propellant can with stand during its manufacture and use.

2.9. Hardness and tensile mechanical properties measurements

The stress-strain relation and modulus of elasticity for the prepared samples is measured by the aid of Zwick (model 1487) testing machine. It has remote control (DAPMAT) software, which could acquire recording, analyzing, storing and printing test data. The tensile test was carried out for at least three times for each prepared formulation using JANNAF specimen and the mean value of the obtained results is recorded. Also hardness shore A is measured using the hardness tester Zwick (model 3102) at ambient temperature (25ºC).

2.10. Practical evaluation of signature

The measurement of secondary smoke HCl gas concentration in the exhaust plume represents the percentage of secondary smoke or its concentration. Detection of the HCl gas concentration in the gaseous products of combustion are carried by Gas analyzer device (Gasmetdx4030) was used for identification of both organic and inorganic compounds with low levels of detection (0-300 ppm) without need of changing of the rounded electronic sensor which can also resist corrosion, contamination and can operate for several hours with battery. About 0.5 gram of different propellant compositions was burned in the combustion chamber and the device determines the percentage of each product including HCl gas. Advantages of this technique was that no sample preparation to be done as the sample was injected into the device with a built in pump through a particle filter, this device can detect up to 25 gases less than 30 seconds.

2.11. Ballistic performance evaluation

Propellant samples casted in steel cylinders undergo machining to secure the functional dimensions then loaded in the testing motor after isolation found. The pressure and time history is recorded for each test. Firing generally takes place on static benches and an efficient data acquisition ware is used to measure the motor performance through pressure transducer and then the propellant performance analysis can be done. Greatly different results may occur in flight, as predictable with appropriate computer programs

3. Results and Discussion

The results of optimized compositions using ICT-code and Design expert optimization software were practically prepared using the optimum ingredients illustrated in table (6) in addition to the baseline reference of B.B. composition

The table 6 explains that the base bleed composition NR7 contains 7% RDX, and composition NM5 containing 5% Mg respectively, do not make a significant change in density, heat of explosion and ignition temperature as the percentage of RDX and Mg were too small percentage to make touchable change in these properties.

In case of NR7, the value of maximum stress (σm) and strain increased by (7%) and (27%) respectively. This is reasonable, as nitramine based compounds are able to enhance the bonding behavior of propellant matrix, which in turn affect mechanical properties especially strains at various temperatures. Mechanical properties offered high stress, high hardness and high strain with low values of young's modulus because NCO/OH ratio was <1, so free OH groups were available in the matrix especially, RDX had three nitramine groups could make H-bonding with the free OH groups increasing the mechanical properties. The burning rate decreases by (14%) as the grain size of RDX is somewhat larger than that of AP.

Table 6. Selected base bleed formulations characteristics

Property	Formula		
	Ref.	NM5 Mg/AP	NR7 RDX/AP
Heat of explosion (°C)	819	816	815
Density (g/ cm^3)	1.51	1.5	1.5
Ignition temperature (°C)	310	306	308
Hardness (shore A)	55	60	59
Stress (Kg_f/cm^2)	10.5	12.3	11.3
Strain (%)	33	31	45.5
Burning rate (mm/s)	1.1	1.4	0.9
Secondary smoke (ppm)	276	233	124

For sample NM5, the value of the maximum stress (σm) increases by (15%), strain has a slight decrease by about (6%) but still satisfy good value, the sample satisfy the hardness required with slight increase above the required value of base bleed applications. Mg acts as a fuel giving rise to an increase in burning rate by (20%) as it contributes to the additional energy of the product propellant and still found in the required region of properties used in this application.

The two samples NR7 and NM5 offer a good value of the maximum stress (σm) and satisfy the minimum values required. The other properties as density, heat of explosion, ignition temperature and burning rate comply with the optimum balance of properties for base bleed applications.

The compositions RDX/AP and Mg/AP have been chosen in our research as the optimum compositions in their own families satisfying its optimized properties of base bleed application decreases the secondary smoke by 16 %, and 55% respectively.

4. Conclusions

Based on intensive ICT thermochemical calculation code and design expert optimization software, two different base bleed compositions have been recommended as the optimum compositions that decrease "HCl" secondary smoke by 16% and 55% for both RDX/AP and Mg/AP compositions respectively. This decrease in the secondary smoke has a direct impact on the easiness of detection of the projectile during its flight towards the target.

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