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Development of Green Propellants for Short Range Solid Rocket : an Overview

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***Abstract*— Choice of propellant primarily depends upon tactical applicability and deployment pattern of the weapon system. Solid propellants are preferred in short rockets as it provides major advantages of simplicity and quick deployment time as compared to its liquid counterpart. It has physical features like to quick response time and high reliability make solid propellant first tactical and technical choice for short range rocket. Solid rockets may be propelled by double base, composite or modified double base solid propellant. All these propellants cause smoky exhausts and unsuitable for environment and health hazards for the crew members. Development of green propellant is underway globally for rockets including short range rockets. The works on the green propellant have opened up new avenues and posed challenges for the high energy materials research community. The mechanical and ballistic properties of these formulations should be judiciously evaluated test fired and improved for further recommendation to use in the existing or new weapon systems. The same is equally applicable to short range solid rockets.**

Keywords*— Ammonium Perchlorate, Chemical Decomposition, Composite Propellant, Double Base Propellant, Exhaust Plume, Hydroxyl Terminated Polybutadiene, Modified Double Base Propellant, Nitrocellulose, Nitroglycerine, Oxidizer, Solid Rocket, Specific Impulse, Thrust and Warhead.

I. INTRODUCTION

Short range refers to the rocket having a maximum range of 50 km. These rockets are primarily used for military purposes and can be launched through tubes mounted on shoulder and fired from man portable weapon up to a range of 4 km. The rockets are also fired from vehicle mounted multiple launcher tubes up to a range of 50 km. Solid propellants are preferred in these rockets as it provides many advantages as compared to its liquid counterpart. Simplicity and ease of handling are the factors being very important in battle field scenario, leading to its preference. Propellant is a balanced source of chemical energy ignition of which develops adequate thrust quickly to propel warhead to the target. Time of flight of the rockets vary from few seconds to few minutes.

Main ingredients of solid propellant contain homogeneous mixture of nitrocellulose and nitroglycerine. Small amount of additives are also added to improve mechanical properties and burning characteristics. Composite solid propellant contains polymer fuel binder, oxidizer and metal additives. In case of rocket propellants, composite propellants have acquired greater significance because of advantage of wide range of tailor made mechanical properties and superior strain capability. It also develops higher specific impulse (up to 245s). Another class of solid propellant known as Composite Modified Double Base solid propellant is cast from a mixture of ammonium perchlorate crystals, aluminum powder and liquid hydroxyl terminated polybutadiene. Compositions of the ingredients are fixed to meet specific requirements. Chemical decomposition of solid propellant due to ignition produces various oxides of nitrogen, sulfur, chlorine, hydrogen and gases like hydrochloric and sulfuric acid. All these products are harmful to environment and human body and the damage has both short term and long term effect [1]. The concept of green energetic materials [2] for defence and space applications is acquiring importance. It is expected to become mandatory requirement in near future to save our planet. From the invention of basic solid propellant (gun powder) to modern propellant, China has always taken lead to develop weapon system. Chinese scientist Xin [3] has reported green propellants, explosives, and related processing technologies for futuristic rocket application.

II. INGREDIENTS OF SOLID PROPELLANT

Solid propellant forms the part of low explosive due to its high thrust producing capability with negligible detonating power. It is a balanced source of potential energy containing necessary ingredients for combustion and conversion of this energy into useful kinetic energy [4]. Its ingredients include both fuel and oxidiser and hence it is independent of atmospheric oxygen for its combustion. It makes solid propellants to meet specific requirements for military as well as space applications (during booster phase). Solid propellant, based on its ingredients is classified [5] as single base, double base and composite propellant. Single base propellant contains nitrocellulose only. It has poor mechanical properties making it unsuitable for any practical application other than for experimental purposes. Double base propellant is a homogeneous mixture of nitrocellulose and nitroglycerine with small amount of additives. The propellant is capable of generating specific impulse up to 220s. Additives are added to improve physical properties and to meet manufacturing and operational requirements.

Introduction of composite propellant has put double base propellant in the back seat. Composite propellant is the heterogeneous mixture of solid fuel, usually Aluminum and oxidizer, usually ammonium perchlorate (AP) held together in a matrix like binder [6]. Availability of high purity AP at low cost and perfectly controlled grain performance of AP

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based propellant are the two important characteristic parameters that make AP as one of the most common oxidizers. Thus AP-based propellants are likely to continue for large scale manufacturing of solid propellant not only for rocket but also for other ammunitions. Polybutadiene is the most effective binder which improves the physical properties. This high density mixture generates higher specific impulse up to 250s. Composite propellant can be cast from a mixture of ammonium perchlorate crystals and aluminum powder. In this mixture liquid hydroxyl terminated polybutadiene (HTPB) is added as curing and ballistic agent and it is called Composite Modified Double Base propellant. It is capable of generating specific impulse up to 260s. HTPB is most preferred additive [7] because of its moderate (70^0C) curing temperature and capability to generate better specific impulse [8]. Additionally it imparts good mechanical strength at low cost.

III. SOLID PROPELLANT FOR SHORT RANGE ROCKET

Choice for type of propellant primarily depends upon tactical applicability and deployment pattern of the weapon system. For rockets in man portable anti tank role or truck mounted multi barrel area weapon role solid propellant is preferred; whereas for larger and longer range, the choice goes to liquid propellant [9]. Liquid-fueled [10] rocket typically pump separate fuel and oxidiser components into the combustion chamber, where they mix and burn. Complex design of liquid propellant rocket [11] with moving parts like pumps and valves makes it cumbersome and thus less reliable. It also requires longer preparation time and thus preferred in static launch role.

Simplicity in weapon system design and ease of manufacture are the two factors favour selection of solid propellant. Ammunitions with solid propellant are basically supplied in ‘ready for use’ condition [12]. In short range rocket solid propellant is preferred being more convenient to use and provides quick deployability [13]. In addition to high specific impulse development capability, the solid propellant retains its usefulness even on prolonged storage [14] and deployment in field condition.

Weapon system designed with solid propellant requires quick response time and provides high reliability and both these factors are very important in any military operation. Solid propellant offers limited toxicity and health hazards to the troops while in storage. It has adequate structural strength which remains unchanged [15] under varying temperature, humidity condition, prolonged storage, transportation and handling. It also provides good mechanical strength. Numerical modeling of dielectrical breakdown in solid propellant is employed to predict its breakdown strength [16].

All the above physical features added to quick response time and high reliability make solid propellant first tactical and technical choice for short range rocket. It is observed that during field deployment some propellant failures have occurred [17]. These are case breach, debonding; propellant structural failure, combustion instabilities etc. However, better processing and quality checks have since been adopted to eliminate these problems.

IV. ENVIRONMENTAL AND HEALTH HAZARDS WITH SOLID PROPELLANT

When solid propellant burns to lift a space shuttle, the result is that a highly acidic, chlorinated, aluminized exhaust plume that is not very good for the ozone layer.

Compositions of combustion products depend upon the ingredients of solid propellant that has been stuffed in the motor casing to meet the tactical requirement. Smoky exhaust invariably contains oxides of nitrogen, sulfur dioxide, hydrogen sulfide and other toxic metallic elements. Quantity of composition however depends upon the mixture ratio of the ingredients. The smoke affects health of crew members when exposed for longer during operation and handling of the weapon system. Nitroglycerine vapour present in the exhaust enters human body through vapour inhalation, absorption through impermeable cloth and intact skin and also absorption through digestive tract [18]. On ignition, chemical decomposition of AP based oxidizers produces nitrogen (N_2) and hydrogen chloride; reacting with atmospheric moisture which turns hydrochloric acid (HCl). Solid propellant contains up to 75 % AP and thus produces a large amount of HCl. The exhaust gases are highly corrosive and toxic in nature and they form semi-opaque clouds under humid conditions. The impact of HCI pollution has been studied around the launch area. Release of less than 1 % HCl by weight in the rocket exhaust is the prime goal of research and development activities [19] in solid rocket propellant industry.

V. GLOBAL DEVELOPMENT OF ENVIRONMENTAL FRIENDLY SOLID PROPELLANT

For short range solid rocket the number of launches is so small that the total effect on environment and on the health of crew members may not be appreciable. Space shuttles considered to be highest emitter of exhaust smoke add less than 0.25% of the total Cl present in atmosphere [20]. This tiny amount decreases the yearly average of global ozone by just 0.0065%. This reduction is far less than even the variation in ozone levels due to natural phenomena like volcanic eruptions and solar flares. In this account environmental imbalance due to exhaust plumes short range solid rocket would be negligible. As far as crew members are concern, openness of battle ground and frequent change of firing position undermine the health hazards. However, green propellant is a consideration on two accounts; firstly continuous exposure to toxic smoke does pose a threat to health and secondly, the smoke reveals the position of firer making him vulnerable to enemy counter fire.

Of late, the solid propellant industry has come under increased scrutiny from the environmentalists. Concern has also been given to the hazards of health of troops handling solid rockets and exposed to the smoky exhaust. Overall scenario has compelled to change the conventional thinking. This has lead to paradigm shift of initial research and development, production, testing and disposal. Numerous efforts have been initiated for the design and development of green propellants, predominantly aimed at eliminating/reducing chlorine from the exhaust. Major thrust has been centered on reduction of HCl in exhaust plumes within acceptable limit. This type of propellant is popularly

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known as scavenger propellant as the propellant is capable of scavenging chlorine from the combustion products. This propellant would be a boon to shouldered fired rockets to hide its place of launch. Minimum smoke producing propellants [21] which are being developed are capable of eliminating Al_2O_3 (primary smoke) and water aerosol condensed from the atmosphere (secondary smoke).

Various green propellants have been reported [22-25] which include low HCl scavenged formulations (HCl scavenger added to the propellant) type, HCl neutralized propellant formulations type, low HCl formulations oxidized type with a combination of AN and AP (with or without an HCl scavenger) and chlorine-free formulations. Solid propellant with reduced HCl emissions could be formulated by adding sodium nitrate ($NaNO_3$), an HCl scavenger, or Mg for acid neutralization to the propellant compositions [26-28].

In both the cases AP serves as oxidizer, but the mechanism of reducing exhaust HCl is different. In $NaNO_3$ scavenged propellants, the Na from nitrate oxidizer reacts with chlorine generated from AP in the combustion process. Thus it forms harmless NaCl salt instead of HCl. The extent of acid reduction in the exhaust by this type of propellants is in the range of 1-3%. But in this process, there is a loss of specific impulse up to 15-20s. In another green composition Al is replaced by Mg which gets oxidized to form MgO during combustion. By reaction with moisture it forms $Mg(OH)_2$. HCl and $Mg(OH)_2$ react and forms harmless $MgCl_2$. Hence HCl gets neutralized by Mg and we get acid free exhaust [29, 30]. The extent of acid reduction by Mg neutralized propellants is in the range of 1-10 %. For this type of propellant, the manufacturing process remains the same as conventional propellants. However, precaution needs to be taken to ensure that Mg is kept as dry as possible. The specific impulse of this Mg based propellant is close to Al based propellant but the density is considerably lower.

Ammonium nitrate is being considered as green oxidiser however its performance is below AP. Besides low energetic, ammonium nitrate is a hygroscopic solid which undergoes phase transformation at room temperature involving a significant volume change and burns at a slow rate [31].

VI. CONCLUSION

Presently development of environmental friendly composite propellants has been the main objective of defense research without compromising the performance. There is a need to develop the best possible solution in terms of cost, safety and reliability as well. The challenge for future solid propellants for space and defense application is not only to meet the tactical and technical requirements but also to comply with the stringent environmental regulations. Therefore, the research efforts is directed to develop green propellant in order to reduce hydrogen chloride gas emission from motor exhaust plumes, so that formation of HCl is within acceptable limit.

The works on the green propellant in general and energetic oxidizers in particular have opened up new avenues and posed challenges for the high energy materials research community. The mechanical and ballistic properties of these formulations should be judiciously evaluated test fired and improved for further recommendation to use in the existing or new weapon systems. The same is equally applicable to short range solid rockets. However, more research needs to be focused for new generation of eco-friendly propellant before its regular application.

Recently ammonium dinitramide (ADN) and hydrazinium nitriformate (HNF) have been introduced [32, 33] as energetic and green oxidisers. Both the oxidisers have the potential to be used in solid composite propellant systems. These have relatively less O_2 balance compared to AP; these have substantially higher heat of formation than AP. Moreover, they undergo highly exothermic combustion reactions near the surface unlike nitramines, leading to efficient heat feedback to the deflagrating surface enhancing the burning rates. However, severe hygroscopicity of ADN and higher sensitivity of HNF, particularly mechanical stimuli are cause of concern. Despite initial encouraging results in terms of high specific impulse [34-36] and environmental benign, the long-term stability and ageing mechanisms of such complex formulations are yet to be thoroughly examined. Hence these oxidizers need to undergo refinement and rest fires to smoothen the rough edges before going for mass production stage.

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