



REVIEW ON TYPICAL INGREDIENTS FOR AMMONIUM PERCHLORATE BASED SOLID PROPELLANT

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ABSTRACT

Ammonium perchlorate (AP) based solid propellant is a modern solid rocket propellant used in various applications. The combustion characteristics of AP based composite propellants were extensively studied by many research scholars to gain higher thrust. The amount of thrust and the thrust profile, which may be obtained from a specific grain design, is mainly determined by the propellant composition and the manufacturing process that produces the solid propellant. This article is intended to review and discuss several aspects of the composition and preparation of the solid rocket propellant. The analysis covers the main ingredients of AP based propellants such as the binder, oxidizer, metal fuel, and plasticizers. The main conclusions are derived from each of its components with specific methods of good manufacturing practices. In conclusion, the AP based solid propellant, like other composite propellants is highly influenced by its composition. However, the quality of the finished grain is mainly due to the manufacturing process.

Keywords: ammonium perchlorate, aluminium, HTPB, solid propellant, composition.

INTRODUCTION

Ammonium perchlorate (AP) based propellant is typically used in rocket propulsion applications, such as missiles and rocket launchers. The main advantages of AP based propellants are good specific impulses, high reliability, and a relatively simple manufacturing process. Because of these performance attributes, AP based propellant is regularly used in booster applications, such as space exploration rockets, aircraft ejection, and international ballistic missiles.

In practice, there are many parameters to be considered before a solid propellant can be manufactured. The parameters include the ingredients and the steps of manufacturing. Holmes *et al.* [1] reported that there are at least ten different ingredients used in producing a solid propellant. While Ramohalli *et al.* [2] mentioned that in manufacturing propellants there would be at least 30 steps that have to be followed.

However, there are four typical ingredients for solid propellants, which basically consist of a polymeric binder (10-15 %), a curing agent as an additive (1-3.5 %), an oxidizer (65-70 %), and metal fuel (15-20 %) [3, 4]. Thus, with only these ingredients, a typical solid propellant could be produced and tested. This paper describes the four main compositions of the typical ingredients that are selected for solid propellant creation, which are Hydroxyl terminated polybutadiene (HTPB) as the binder, aluminum (Al) as the metal fuel, ammonium perchlorate (AP) as the oxidizer, and Isophoronediiisocyanate (IPDI) as the curing agent.

Hydroxyl Terminated Polybutadiene (HTPB)

The first ingredient in a composite propellant is the binder. The binder provides the structural glue or matrix in which solid loadings are held. A common binder used in a composite propellant is an elastomeric binder.

These binders include polyesters, polysulfide, polybutadiene acrylonitrile (PBAN), carboxyl terminated polybutadiene (CTPB), and Hydroxyl terminated polybutadiene (HTPB).

The HTPB binder was found in early 1970 and has been used in composite solid propellants for rockets and missile applications [5-8]. The HTPB is a yellowish liquid, polymeric binder and is normally produced by free radical polymerization. A study by K. B. Catherine *et al.* [8] used the HTPB binder that was manufactured by the free-radical polymerization of butadiene using hydrogen peroxide as an initiator. Different manufacturers may use different methods that lend different properties to HTPB. Currently it has become the best binder available because of its processability and higher energy content compared to other binders [9]. Although the CTPB binder has good mechanical properties, it has problems with aging characteristics. Most common polymers become soft at high temperatures and brittle at low temperatures. However, HTPB is able to demonstrate good mechanical properties at low temperatures and good aging characteristics.

Although HTPB is an inert binder [10, 11], curing it with isocyanate will form a polymeric binder, which has superior mechanical properties. There were only a few papers that discussed the amount of curing agents used in the respective research studies. Generally, HTPB can be cured using a different isocyanate, such as Toluene diisocyanate (TDI), Isophoronediiisocyanate (IPDI), or diphenyldiisocyanate (DDI) [7]. By far, TDI and IPDI are the most commonly applied for cast-cured propellants. The chemical TDI has a low pot life, which is approximately 30 minutes compared to IPDI, which has a pot life of three to four days depending on the storage temperature. Pot life was defined as the period of time for a propellant to begin to cure until it approaches a gel stage



or solid. Kym *et al.* [6, 12] reported that, HTPB cured with IPDI melted slowly and mildly over a range of temperatures from 330-370 °C and started to decompose at temperatures close to 500 °C. The chemical IPDI increases the burn rate at a low pressure and improves the plateau at a high pressure [6]. C.W. Fong *et al.* [13] reported that DDI cured HTPB propellants produce lower burning rates compared to other isocyanates, such as IPDI or TDI. The combustion of DDI cured HTPB propellants are more endothermic than IPDI cured HTPB propellants.

Aluminum (Al)

The second ingredient in composite propellants is metal fuel. Metal fuel was added in composite propellants to enhance performance by increasing the combustion temperature. Twenty five years ago, almost every element in the periodic table was tested to investigate the possibilities for propellant formulation [9]. These included beryllium, zirconium, boron, magnesium, and aluminum (Al). Beryllium (Be) has a high heat of combustion and a low molecular weight combustion, but it has a highly toxic oxide that can cause fatal effects compared to Al. For Zirconium (Zr), combustion efficiency is poorer than Al, and it has lower energy compared to Al and Be. The problem for boron is that it is too expensive relative to aluminum when compared to performance. The addition of magnesium (Mg) to a propellant would tend to decrease rather than increase the performance (Isp) [9].

Compared to others, Al is the best metal fuel because of the high heat of combustion, low cost, ready commercial availability, low degree of toxicity, and relatively high combustion efficiency. Aluminum has the symbol Al and atomic number 13. Aluminum is soft, durable, and lightweight with an appearance ranging from silvery to dull grey. In the usual form, Al is powder or dust and can damage the lungs if inhaled [14]. But in coarser forms like the powder, it is less dangerous. For a composite propellant, Al usually constitutes around 5% to 25% of the propellant weight [6] and acts as a metallic fuel and additive to enhance the performance of a rocket motor. The decomposition of Al produces a high combustion temperature. The combustion temperature increases approximately 15% by the addition of 10% of aluminium [15]. Al has a high heat capacity [16], which releases a large amount of energy that significantly expands the gases in the combustion chamber. As the gases expand, the pressure rises and forces the exhaust gases to escape through the nozzle. This is known as exit velocity. The higher exit velocity, in turn, raises the specific impulse of the motor.

However, a problem also arises from increasing the amount of Al. Although the combustion temperature increases, the molecular mass of the combustion products also increase due to the formation of aluminum oxide. As a result, the performance of rockets is significantly reduced [10]. Recently, rocket scientists have studied nanosizing or Ultra FineAluminum (UFAL)]. The UFAL was produced by an electro explosion [17] of aluminum wire in an inert medium, specifically argon, at nearly

atmospheric pressure. Ultra FineAluminum has a particle size of 0.1 μm compared to the typical aluminum used in propellants at 30 μm. The advantages of UFAL are the ability to give high burning rates, the complete combustion, and higher energy propellant. The disadvantages of UFAL are the high cost and decreases in the energy of the propellant combustion because of the low content of metallic aluminum (high content of the oxide) [17].

Ammonium Perchlorate (AP)

Another ingredient in composite propellant is the oxidizer, which can be referred to as the material that whose function is the supply of oxygen or oxidizing materials for deflagration of a solid propellant [18]. Some of the most common oxidizers include ammonium nitrate (AN), potassium nitrate (KNO₃), potassium perchlorate (KClO₄), sodium nitrate (NaNO₃), and lithium perchlorate (LiClO₄). Nevertheless, these oxidizers produce a much lower Isp compared to AP, except for LiClO₄, which is slightly lower than AP [9]. The problems with LiClO₄ are hygroscopic and expensive. Although AN is hygroscopic, it was applied when rocket motors need to obtain low burning rates, low flame temperatures, and smokeless exhaust [18].

The proven and widely used oxidizer is ammonium perchlorate (AP), which replaced potassium perchlorate as an oxidizer in the late 1940's [19]. At room conditions, AP is a powder of white crystalline material with a density of approximately 1949 kg/m³. Like other perchlorates, AP is a powerful oxidizer and was used as an oxidizer in various types of propellants and pyrolants (energetic materials that generate hot flames upon combustion) [10]. Two major reasons for AP's widespread use are its stability, resulting in safe munitions, and its ability to control a propellant's burning rate.

The particle sizes of AP can affect the manufacturing process and burning rate of a propellant. R.R miller *et al.* [1] reported a burning rate increase with decreasing particle size of AP. Sizes below 40 micrometres are considered hazardous because of easy ignitability and sometimes detonation [14]. For the application of composite propellants, AP usually constitutes around 59% to 90% of the propellant weight [4, 9]. Theoretically, the performance of AP/HTPB propellant will decrease significantly when using a mass fraction of AP higher than 90% [9].

Additives

Another ingredient that is added in the composite propellants is additives. A small amount of additives are added in composite propellants for many purposes, such as altering the curing time, improving rheology properties for easier casting (plasticizers), altering burning rate (burn rate modifiers), improving bonding (bonding agents), improving the physical properties, or improving aging characteristics. D.H. Meyer [9] reported that small quantities of additives do not affect the performance (Isp) of the propellant.



Pot life varies from 1 to 5 hours and depends on curators, temperature and curing catalyst. Plasticizers were added to control the pot life. They were added to the propellant mixture to increase the plasticity and flow behaviour [7]. Increasing the level of plasticizer will reduce the viscosity of the binder. R. C. Matthew *et al.* [20], state that by adding 0.2% Tepanol (to act as a plasticizer) and two drops of Silicone Oil (a defoaming agent), the ease of production and physical strength of the propellant were increased without affecting the burn rate. While Rm. Muthiah *et al.* [21] reported that the most suitable plasticizers used with HTPB are DOA and IDP due to the ability to improve the process ability and pot life of HTPB propellants. Works by several other researchers [6,7,22,23] used DOA as a plasticizer for composite propellants and accounts for around 1% to 5% of the propellant weight.

Previous studies have reported that a composite solid propellant burning rate can be modified by addition of small quantities (< 3%) [10] of burn rate modifiers to its composition. Lower burning rates could be achieved by adding a small amount of nitramine [24]. Studies by Kumar Ishitha and P.A. Ramakrishna [25] have found that a higher n (pressure exponent) and burning rates observed with addition of iron oxide as compared to a propellant with copper chromite. Trevor D. Hedman and *et al.* [26] investigated the addition of iron (III) oxide (Fe_2O_3) and copper (II) oxide (CuO) to an AP/HTPB propellant. The ignition delay of coarse AP particles was found to significantly decrease with the presence of catalyst at 1 atm. However, it has been shown that beyond the 20 atm low pressure deflagration limit for AP, the effect of the catalyst on the single crystal burn times of the AP is unknown.

Reena Dubey *et al.* [27] studied the effect of bimetallic nanocomposites of MnCo, MnNi and MnZn to the burning rate of AP/HTPB composite solid propellant. Their analysis revealed that these additives can be used as efficient catalysts for enhancing the burning rates with the MnCo is the best catalyst in terms of burning rate enhancement. Shigeyuki *et al.* [28] reported that the addition of a ferric oxide catalyst enhances the burning rate and sustains the steady-state combustion. Works by Liang *et al.* [29] reported that the burning rate of AP composite propellants can be reduced by adding Ammonium oxalate (AO). It has the ability to increase the decomposition temperature and the activation energy of AP, which leads to a decrease in burning rates. Unfortunately, AO is a highly hygroscopic chemical and has the ability to absorb humidity from the air. As a result, the propellants produced have poor mechanical properties. Mehilal *et al.* [3] in their study found that lower content of 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB), i.e. 1.5% to 2% was very effective in reducing the pressure index value however beyond this content, the pressure index increases to standard composition.

CONCLUSIONS

Ammonium perchlorate based solid propellants have drawn attention from many scientists for several reasons. Many scholars spend money and time to study the best compositions or ingredients to maximize the potential of AP based propellants. In conclusion, it has been found that every component plays a vital role for different aspects of the formulation. Therefore, before the propellant can be extensively manufactured, a thorough study should be conducted to ensure the best ingredients are used. The manufacturing techniques used to produce the propellant also play an important role in ensuring the final product fits the minimum requirements.

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