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Comparison of Propellants and the Processing Methods

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Abstract: This paper is a historical review of propellant types and of processing methods that have been used in the USA in last 50 years. Both castable and extrudable propellants are discussed. A wide range of oxidizers are discussed from the use of potassium perchlorate in very early solid propellants to the more recent use of nitramines. The wide range of propellant binders that has been used over the decades are discussed, and merits of the systems described. Discussion of cure systems, and even bonding agents, are included when appropriate.

Key words: propellant; oxidizer; binder; processing method

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1 Introduction

Fundamentally there is little difference in the goals for gun propellants and for rocket propellants. Both require the maximum practical energy from the available chemical components.

The history of black powder and its centuries of use as a gun propellant are well known. It is still being used in gun applications, and as launch charges for display fireworks today. Black powder also has a history of use as pressed solid propellant grains in small rockets, such as those propelling battlefield signal flares. Large grains are not practical with black powder because there is no actual binder, potentially leaving interstitial voids leading to malfunctions.

Nitrocellulose has been the basis of most gun propellants for over a century, and the propellants based on it manufactured at many locations. Nitrocellulose requires a solvent for processing as a "single-base" propellant, and this can create porosity. Single-base is used as small grains and flakes. Double-base propellant uses nitroglycerin and/or other energetic plasticizers to soften and swell the nitrocellulose, making the resultant propellant extrudable at elevated temperatures. Triple-base propellant adds nitroguanidine and is also extrudable when warm. Extrusion forces are around 30 MPa, thus limiting the potential grain sizes. These propellants have served well in various military conflicts, and for sporting purposes.

However, nitrocellulose-based propellants are not truly castable, and therefore never succeeded in widespread use. The only technique available is to prepare granules of a base composition, transfer into the rocket chamber containing the mandrel, and then pour or imbibe the energetic plasticizer into the interstitial void space. The "cure" process is simply heating the mixture until all the plasticizer has been absorbed into the granules, and has welded the solvent-swollen grains into a homogeneous mass. Operating temperature ranges are rather limited for these rockets.

Alternate chemical systems for rocket propellants were desired, and initial work on alternates to nitrocellulose began in the USA during World War II. It was well recognized that nitrocellulose was a self-oxidized propellant, and that near-term candidates would have to be of the composite propellant type, combining a binder-fuel with some form of inorganic oxidizer, and often including ballistic additives for burning rate control, and for additional energy.

2 Description of systems

These various systems will be described in approximate chronological order. In a number of cases work proceeded simultaneously at different companies. The work was the goal to have systems that did not undergo embrittlement when cooled to −54 ℃ and which retained strength, and did not

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slump or flow at 74 ℃. This temperature range eliminated remeltable binders such as asphalt, and led to intensive polymer evaluation and development efforts.

2.1 Asphalt-based

Asphalt is a residual material from petroleum refining operations, in addition to some naturally occurring deposits in the world. It becomes a relatively fluid material when heated beyond its softening range, and has long been used as a road paving material containing rock, grave, and sand fillers. Thus it was logical that it received early evaluation as a composite propellant binder. When properly formulated with plasticizers such as oils, and fabricated into an end-burning grain, it became a practical Jet-Assist-Take-Off (JATO) rocket (also called Rocket-Assist-Take-Off (RATO) motor). Temperature ranges were limited, and the rocket required storage with the nozzle end up. In any other storage position, the propellant grain would slowly slump and flow, eventually blocking the nozzle and the aft-end igniter, leading to blow-up upon ignition. In fact, the JATO could not be remain installed in an airplane for extended times. Horizontal mixers were used for production of this type of propellant, and require long mix times. The relatively high temperatures required to melt the asphalt increased the hazards of working with this binder. The incorporation of more oil resulted in lower processing temperatures, but increased the tendency to cold flow.

2.2 Polyester resin based

Aerojet, Rohm and Haas and others, developed a binder system based on peroxide-cured polyester/styrene resin, similar to ones used in glass fiber reinforced composites. This resulted in a cross-link, cured resin binder that had high strength, but low elongation, and a tendency to be brittle. Oxidizers used with this binder included both ammonium perchlorate and potassium perchlorate, as well as ammonium nitrate. In addition to the temperature limitations imposed by the brittleness of the binder, there was always the risk of autoignition resulting from cure exotherm. This risk did not disappear until polymers using totally endothermic cure systems were developed. In addition, the styrene content of the binder ensured the rockets created large clouds of black smoke, making a smokeless, or low smoke system impossible.

2.3 Polysulfide polymers

Jet Propulsion Laboratory, Thiokol, Grand Central Rocket Co., Rocket Power, Inc., and probably other manufactured propellants based on the Thiokol developed liquid polysulfide polymers, cross-linkable into rubbery products. Initially these were rather viscous, with a high specific gravity resulting from the high sulfur content of the polymer. The heat of formation of these polymers was less negative than for some other polymers. This resulted in adequate specific impulse, and practical density-impulse values for a number of missiles, and for a wide range of sounding rockets. In addition, at equivalent weight loadings of AP, and equivalent surface areas of AP, polysulfide-based propellants usually have higher burning rates and slightly higher burning rate exponents than do most other propellants. Depending on the application, this will be either a positive factor or a negative factor. The propellant could be readily prepared, with an adequate pot-life, and cast in motors of many hundreds of pounds.

The cure system did, however, still have an exotherm, requiring careful control of over temperature and time. Some accidental ignitions in ovens did occur, resulting in injury and death. The introduction of the LP-205 polymer having significantly reduced sulfur content decreased this risk, while increasing the potential specific impulse by having more hydrogen in the binder. The inclusion of LP-205 greatly improved the low temperature capability of these propellants, but only marginally met the −54 ℃ requirement. The use of these propellants has declined over the years, but remained in occasional use for specialty applications until a few years ago. One factor in the decline was the steadily increasing cost of the LP-205 polymer to almost prohibitive levels.

Both ammonium perchlorate and potassium perchlorate were used as oxidizers. Mixing and casting could be done with any of the equipment available at the manufacturers.

2.4 Butyl rubber

Butyl rubber has a long history of use in products requiring sustained exposure to high temperatures. As a result of this capability, Grand Central Rocket prepared butyl rubber-based perchlorate propellants on open roll mills and made them into grains formed by adhesively laminating die-cut sheets held together in a press while the adhesive and the propellant cured. Low-temperature properties of the resulting propellant were better than the polyester-based compounds, but the process was labor intensive, shape limited, and required intensive process control to reproducibly eliminate the interlaminar voids, and to precisely duplicate the mix-to-mix burning rate. This class of propellants was another step in the historical development of propellants, but by no means was it a final solution. Neither burning rate, nor specific impulse levels offered significant improvement from other competing approaches.

A modest number of space motors were made with a fully hydrogenated butyl rubber because it could be sterilized at about 150 ℃ to ensure no earth-borne germs, etc. were carried into space.

2.5 Butadiene-methylvinylpyridine

Phillips Petroleum Company was funded by the United States government to develop low-temperature polymers for rockets. The Rocket Fuels Division used this butadiene 2-methyl 5-vinylpyridine (BdMVP) specialty copolymer for extrudable propellants, obtaining glass transition points below −54 ℃, although elongation was only a few percent at that temperature. Free-standing grains not bonded to the case wall performed well in ammonium nitrate-oxidized 450 kg thrust grains.

O. D. inhibited gas generator grains were also produced and employed in a number of applications. Burning time of these was often measured in minutes. These grains were made with ram extrusion presses after the propellant had been mixed in horizontal-blade Baker-Perkins mixers. Occasional mixer fires resulted from oxidizer becoming trapped inside bearings, and eventually igniting from friction.

The use of ram extruders limited the diameter or cross-sectional area of the grains. Some work was done with modular grains, having a star-point core opening, but the difficulties of eliminating all voids within the adhesives could not be overcome to enable this process to compete with the castable propellants coming into the industry. Some of the test firings became rather spectacular when the motors failed from over-pressure due to bondline failure.

Phillips custom made special lower molecular weight versions of the basic BdMVP polymer were limited in success, became very difficult to process at adequately high oxidizer loading. Neither the castable, nor the extrudable polymers were smoke-free, although the solids in the exhaust were dry and non-sticky, not building up on turbine blades, unlike such polymers as butadiene-styrene.

2.6 Polybutadiene-acrylic acid (PBAA)

The PBAA random polymer developed by American Synthetic Rubber was a very significant improvement in liquid polymers for propellants, and several companies began using it. This polymer with good castability, was readily cured with epoxides, accepted solids loading up to 80% or 85% based on ammonium perchlorate and aluminum. PBAA-based propellants offered improved specific impulses with good density impulses and were used in several tactical and other missiles. Low temperature properties continued to be improving, but still did not have the best possible properties at −54 ℃. High temperature properties were acceptable, but some strengthening there was desired.

2.7 Polybutadiene-acrylic acid-acrylonitrile (PBAAN)

PBAAN represented an improvement in strength of the polymer, and in the high temperature and aging properties. Low temperature properties were slightly better, more or less ensuring its use in tactical missiles. It has seen extensive use in the solid boosters for the USA Space Shuttle, where its competition is from HTPB-based systems. Burning rate range is slightly lower than for polysulfide-based propellants, but the exponent is lower, making grain design easier. The propellant can be mixed by horizontal-blade, vertical-blade, or continuous processing mixers. The pot-life is adequate for casting most motors, even if multiple mixes are required.

PBAAN continues in use after almost 40 years, where the service temperature limits are not demanding.

2.8 Carboxy-terminated Polybutadlene (CTPB)

Two versions of this polymer were developed: HC-434 from Thiokol (now Rohm and Haas), and the higher molecular weight Butarez family from Phillips Petroleum. Only the HC-434 is still in production, and only in specialty applications. Originally these polymers found widespread applications in both tactical and strategic missiles, particularly because they had excellent low temperature properties. Elongations of 40% to over 50% at maximum stress can be obtained with Butarez-based formulations at −54 ℃. The glass transition point of Butarez based propellants is about −73 ℃.

Missile applications have included stages 1 and 2 of the Minuteman missile based on CTPB with AP and aluminum, and versions of the Sparrow tactical missile. Many other specialty applications, such as aircrew escape systems continue because of the low temperature properties and good processability, including the lack of a need for a bonding agent when cured with a mixed epoxide-imine cure system.

2.9 Polyvinylchloride-based propellants

This class of propellant was and is utilized by Atlantic Research, particularly with burning rate enhancement wires lengthwise in the grain, to mace a family of sounding rocket motors, as well as very short burning time launch motors for shoulder-fired missiles. The propellant is based on mixing finely powdered PVC granules with a plasticizer and with stabilizers, adding the oxidizer and mixing until a readily pourable slurry is created, containing ammonium perchlorate, and/or potassium perchlorate as the oxidizer. The slurry is put into the mold or rocket motor case, then heated to 140 ~ 150 ℃ until the plasticizer and PVC granules fuse together into a rubbery matrix. The process is irreversible, but is not truly a chemical cross-linking of the polymer. Instead, the solvation process is analogous to the solvation process with nitrocellulose and nitroglycerin in double-base propellants.

The resulting propellant has rather good specific impulse and density impulse, partly because the chlorine con-tent in the polymer acts as an oxidizer. The resulting propellant is very effective in "wired" end-burner configurations in sounding rockets. The propellant delivers reasonably good impulse, fast burning rate, and rather clean combustion, but has a relatively high burning rate exponent, even with ammonium perchlorate.

The slurry is readily processable, even in the simpler and less powerful mixers, but must be transferred via a deaeration device to ensure lack of bubbles in the propellant. Bubbles create tremendous stresses during the cool-down from the curing temperature, and become significant weak spots in the grains, potentially leading to failures.

2.10 Polyurethanes

The polyurethane family is another of the polymeric families with a long and continuing history. In the earliest days, natural polyols, such as castor oil, were chemically cured with toluenediisocyanate (TDI). Unfortunately, the toxicity problems of TDI were not well known in the early days and the author has known people who developed severe skin reactions to even minuscule amounts of TDI in the air. TMXDI (Trimethylxylenediisocyanate) has a much lower vapor pressure and is much more suitable for use.

The evolutionary development of the HTPB (hydroxyl-terminated polybutadiene) polymers originated by Sinclair and the development of the isophoronediisocyanate (IPDI) curative have resulted in a propellant family that encompasses greater formulation diversity than was previously possible. This wide, diverse, family of rocket propellants includes highly aluminized formulations, as well as formulations with minimal primary smoke but with secondary smoke because the oxidizer is ammonium perchlorate.

The family also includes those formulations, which have no secondary smoke because they generate few, if any, water vapor condensation molecules in the exhaust stream. These formulations usually use either RDX or HMX as the oxidizer, and balance potential energy versus the transition from class 1.3 to class 1.1 hazard categories, with 1.3 being far more desirable. Problems encountered along the development sequence have included the reality of erratic potlife when using ferric acetyl acetonate (FeAA) as the active catalyst. The problems associated with FeAA, and its variability are mostly eliminated by using a catalyst system based on triphenylbismuth (TPB).

As a summary for this class of propellant, the current HTPB polymer allows the creation of a wide range of propellants, with most of them having the lower slope characteristic of HTPB, combined with adequately fast burning rates, and a 'decent' to 'very good' specific impulse values. The low specific gravity of the polymer encourages the creation of high specific impulse formulas, and creation of high density-impulse formulas. Overall, this propellant system is approaching 30 years of age, and is still a good choice for a starting point on formulation work. This binder is naturally hydrophobic, rejecting water as a result of the curing process.

Polyglcol adipates (PGA) and similar polymers are being increasingly used, and provide practical systems in combination with nitrate-ester plasticizers.

Improved organic compounds that can act as an oxidizer continue to be developed and created. Two examples are hexanitrohexaazaisowurzitane (CL-20) and ammonium dinitramide.

Other present ingredients being tailored to use inside a rocket motor include the hydroxy-functional glycidylazide polymer (GAP), and CL-20. GAP and the thermoplastic AB polymers, such as those based on BAMO/AMMO oxetanes are some of the present routes to thermoplastic, reprocessable binders.

3 Concluding comments

Many things were tried in a "shotgun" manner, without developing a theoretical basis for the attempts. Some were successful. Some were of limited success, and others were totally unusable. Still, the years were exciting and informative.

推进剂及工艺方法的比较

摘要: 回顾了近50年来美国所用的推进剂类型及工艺方法,介绍了可浇铸和可挤压型推进剂,讨论了很多氧化剂,包括早期固体推进剂中所用的高氯酸钾直至现在所用的硝胺。介绍了近二十年来推进剂所用的粘合剂和固化系统。

关键词: 推进剂; 氧化剂; 粘合剂; 工艺方法