

Recovery of Energetic Components from Propellant with Hydrolyzable/Degradable Binders

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Abstract

P&W Space Propulsion, Chemical Systems Division (CSD) under contract N00174-99-C-0050 issued by Naval Surface Warfare Center, Indian Head Division is currently investigating the use of hydrolyzable/degradable binders in propellant formulations. We are also developing methods for binder degradation and for the recovery of ammonium perchlorate (AP) and aluminum. In conjunction with Indian Head research efforts in new binder synthesis, CSD will evaluate other binder candidates which are deemed hydrolyzable (or degradable).

Hydroxy-terminated polyether-polyester block co-polymer was found suitable for hydrolysis in conventional aluminized or reduced-smoke propellant formulations. The ester linkage due to its reactivity toward bases is the target for binder degradation. Comparison of various bases for this purpose will be made and discussed. Procedures for isolation and recovery of AP and aluminum were developed and will be discussed. The purity and analytical methods for the recovered material will be presented.

Introduction

The increasing concern over environmental factors and emphasis on decreased life cycle costs has led to work on methods for propellant removal from rocket motors that are both environmentally sound and relatively low in cost. Under the Navy Green Energetic Materials (GEM) program, CSD has been examining a new approach to the propellant removal problem that is based on a hydrolyzable propellant binder system and a cartridge loaded grain concept. This approach allows several cost saving features that lowers both the cost of new motor manufacturing as well as remanufacture of motors that are out of service life due to propellant age.

First the cartridge loading approach allows easy propellant and insulation removal. Thus the cost of remanufacture, either at the end of the life cycle or due to line loss during initial production is minimized.

Second, removal of the grain from the motor allows for safer destruction of the propellant grain as energy intensive removal processes are not required. Approaches such as dicing the removed grain into smaller size pieces can be done without the need for large quantities of extra materials such as water.

Third, with the propellant grain separated from the hardware and amenable to size reduction, more novel degradation techniques can be explored which allow recovery of both aluminum fuel and ammonium perchlorate oxidizer for reuse.

The selected polymer binder has been shown to allow formulation of IM propellants capable of passing both slow and fast cook-off tests as well as bullet and fragment impact tests. These attributes make it even more interesting as a new binder system for tactical missiles.

Objective and Approach

The objective of this research was three-fold: 1) to identify binders that are hydrolyzable under mild conditions; 2) to develop propellants that use hydrolyzable binder while keeping or exceeding the performance of current state-of-the-art formulations; and 3) to develop material recovery procedures allowing the recovery of AP, aluminum and other ingredients.

Under IR&D, CSD has been evaluating new binders suitable for propellant applications the last few years. One class of binder in particular has been used in propellants having passed all IM tests under a contract with NAWC. Further study on this polymer reveals that its ester linkages are hydrolyzable and thus may be suitable for applications in propellant ingredient recovery for reuse. This polyether-polyester block co-polymer was used as an entry point for this study. After the binder hydrolyzability had been established and optimized, a propellant development study was conducted. During the development, formulation was optimized with respect to the processing, propellant mechanical properties, and propellant ballistic properties. Once propellant formulations were selected, propellant hydrolysis conditions were studied for the recovery of energetic components. The recovered materials were quantified and analyzed.

Gum Stocks Hydrolysis

Ester hydrolysis is a well-known chemistry since the start of modern day organic chemistry. Extensive literature search revealed nothing new. The hydrolysis in the base or acid catalyzed hydrolysis are still the ways for taking apart an ester linkage. What's added for consideration was the ester linkage degradation with organic amines. Organic amines are generally more nucleophilic and less basic than hard hydroxide ion. When an aluminized propellant is the subject for hydrolysis, organic amines may not react with aluminum as readily as aqueous hydroxide would. Thus, we stand a much better chance for aluminum recovery from the subject propellant using organic amines. The composition of the selected gum stocks being evaluated is listed in Figure 1.

Function	Wt. %
Polymer	
Crosslinker	
Curative	80
Plasticizer	19.95
Cure catalyst	0.05

Figure 1. Formulation for Hydrolyzable Gum Stocks

The gum stocks were cured at 140°F for 7 days. The cured material was cut into ca. 1.0 gram pieces for hydrolysis studies. Aqueous sodium hydroxide hydrolysis of gum stocks in boiling solution for overnight is summarized in the Figure 2. The slow rate of hydrolysis can be attributed to low solubility of organic polymer in water thus the contact between the hydroxide ion and ester site of the polymer is limited.

NaOH Concentration	1 N	3 N	6 N
% Wt. Loss	0	10	28

Figure 2. Relative Rates of Hydrolysis of Polymer in Aqueous NaOH

When the hydrolysis was done in methanolic media, the hydrolysis rate improved substantially. The ability of an organic solvent to bring two reactants together is evident in improved reaction rates. The results are shown in Figure 3. Even in 0.5 N NaOH, a 0.61-g sample of cured gum stocks was hydrolyzed completely after an overnight reaction in boiling methanol solution. At the end each reaction, there were white solids at the bottom of the flask. Sodium salts of acids (from hydrolyzed ester) and sodium hydroxide are suspected to be the main components of the solids. The liquid layer showed some oily organic material when quenched with a large volume of water while the solids are soluble in water.

NaOH Concentration	0.5 N	1 N	3 N	6 N
% Wt. Loss	100	100	100	100

Figure 3. Relative Rates of Hydrolysis of Polymer in Methanolic NaOH

Acids such as sulfuric, perchloric, and hydrochloric were tried with concentrations from 1N to 6N. The only thing that showed some gum stocks degradation is 6 N HCl at boiling for 18 hours. It is deemed the conditions for acid-catalyzed gum stock hydrolysis are too harsh and the reaction is not efficient. Di-n-butylamine and n-butylamine were excellent amines that reacted with cured gum stocks in methanol solution. The reaction formed only methanol soluble products (As opposed to the sodium salts in methanolic NaOH). To a 0.5-gram piece of cured gum stock polymer in 50-ml of methanol was added about 20 mmoles of amine. The contents then were brought to boiling overnight. The solution became homogeneous and the solid polymer was taken apart and dissolved in methanol completely. The possibility of total recovery of aluminum from a propellant sample is greatly enhanced due to this technical advance. The amine/polymer reaction is shown in Figure 4.

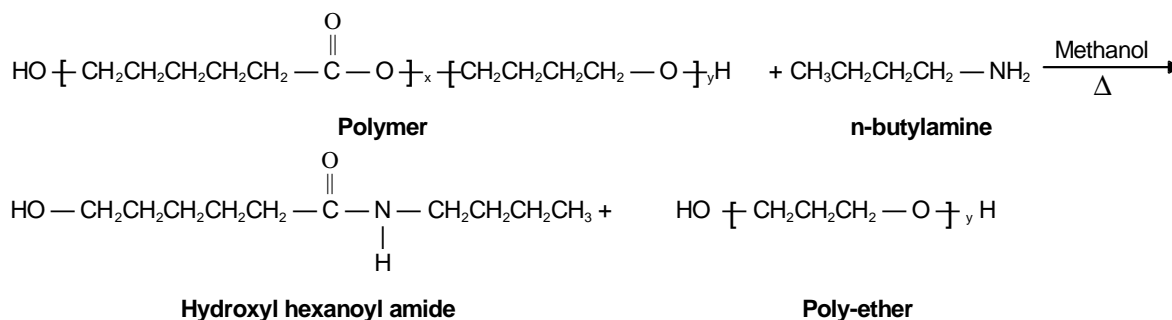


Figure 4. n-Butyl amine/Polymer Reaction

Propellant Hydrolysis

Formulation selection: Two aluminized propellant formulations were selected for hydrolysis study. Both formulations use the polymer binder shown to be hydrolyzable in the gum stock hydrolysis tests. One formulation (Formulation A) was developed under CSD's IR&D while the second (Formulation B) was developed under an NAWC contract.

One reduced-smoke formulation was also developed (Formulation C) for hydrolysis study. The formulation was developed jointly by researchers at Indian Head and CSD. Again, the polymer for this propellant is the same as the one used in the gum stock hydrolysis tests.

The mechanical and ballistic properties of all these propellants were characterized and the results tabulated in Figure 8. The ballistic data on Formulations A and C and are based on strand burning while that of Formulation B is based on 4-lb motors.

Function	Wt. %
Polymer Crosslinker Plasticizer Curative	15.65
Oxidizer; AP	65
Fuel; Aluminum	19
Other Additives	0.35

Figure 5. Formulation A

Function	Wt. %
Polymer Crosslinker Plasticizer, inert Plasticizer, energetic Curative	15.65
Oxidizer; AP	65
Fuel; Aluminum	19
Other Additives	0.35

Figure 6. Formulation B

Function	Wt. %
Polymer Crosslinker Plasticizer Curative	15.65
Oxidizer: AP	83
Combustion Stabilizer	1
Other Additives	0.35

Figure 7. Formulation C

Propellant ID	Isp; Calc.	Modulus	COR Stress	COR Strain	Burning Rate	Exponent
Formulation A	261.3 sec	404 psi	233 psi	82 %	0.23 ips@1000	0.263
Formulation B	261.8 sec	292 psi	111 psi	50 %	0.252 ips@1000	0.273
Formulation C	243.6 sec	566 psi	173 psi	54 %	0.23 ips@1000	0.336

Figure 8. Mechanical and Ballistic Properties of Selected Propellants

AP and Aluminum Recovery and Analysis: It is known that AP reacts with sodium hydroxide to form ammonia and sodium perchlorate. With the presence of an organic amine, AP will become contaminated with perchlorate salt of this organic amine. To minimize complications in the recovery of AP, it is advantageous to have it separated from the propellant before hydrolysis.

AP separation from the bulk propellant can be achieved by the soaking of propellant in a solvent in which AP is soluble. Simple soaking is time consuming and requires large quantity of solvent. Soxhlet extraction, provides fresh solvent to the propellant sample on a continuous basis, was thus developed for this purpose.

The propellant was cut into approximately ¼-inch squares and then subjected to soxhlet extraction to remove AP and other soluble ingredients from propellant. AP can be recovered from extract solution by recrystallization. The AP-depleted propellant is then subjected to n-butylamine/methanol degradation for the recovery of aluminum.

A 7.25-gram of Formulation B propellant sample was placed in a thimble of a soxhlet extractor with 130-ml of methanol in the bottom flask. After 5 hours of extraction, the AP-depleted propellant pieces weighed 2.25 grams (vacuum dried overnight). This is 31.03% of the original propellant weight compared to a theoretical 28.78 % for this formulation (aluminum + binder + curative). This AP-depleted material then was subjected to degradation with methanol (50 ml)/n-butylamine (1.5 g; 20 mmol) at boiling. In 4 hours, the polymer disintegrated and the solution was clear with aluminum settled at the bottom of flask. The aluminum was collected and washed several times with hot methanol and dried. The dried aluminum weighed 1.35 grams (18.6 % vs. 19.0 % theoretical). AP was recovered from the methanol solution by recrystallization from toluene. After drying in vacuum, 4.1-gram (4.7-gram theoretical; 87% yield) of AP was recovered. This procedure was scaled up to 40-gram propellant samples.

The average of two large-scale runs showed aluminum was recovered in quantitative yield and AP recovery is 95.0%. The purity of recovered aluminum and AP was determined. Scanning electron microscopy (SEM) pictures were taken of the recovered aluminum. It showed the recovered aluminum has the same size and shape as that of starting MD-101. Infrared Micro Spectroscopy (IR μ S) was taken on the recovered aluminum and there is no indication of organic materials (polymer residue) on the surface. The recovered AP was analyzed by Ion Chromatography. As indicated in Figure 11, two recovered AP lots are compared to the standard and also to a blank solution. The recovered AP is better than 99% in purity.

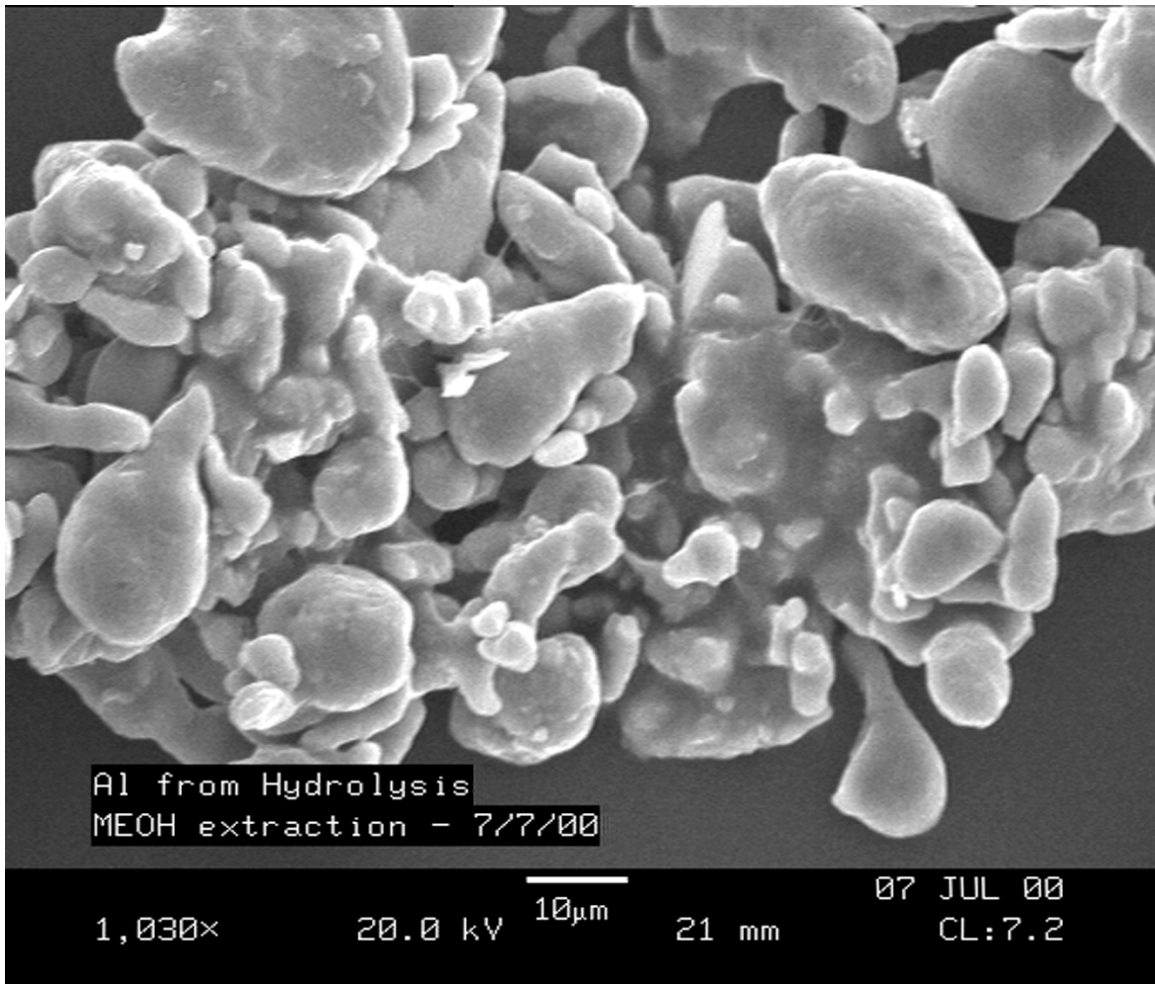


Figure 9. SEM Picture of Recovered Aluminum

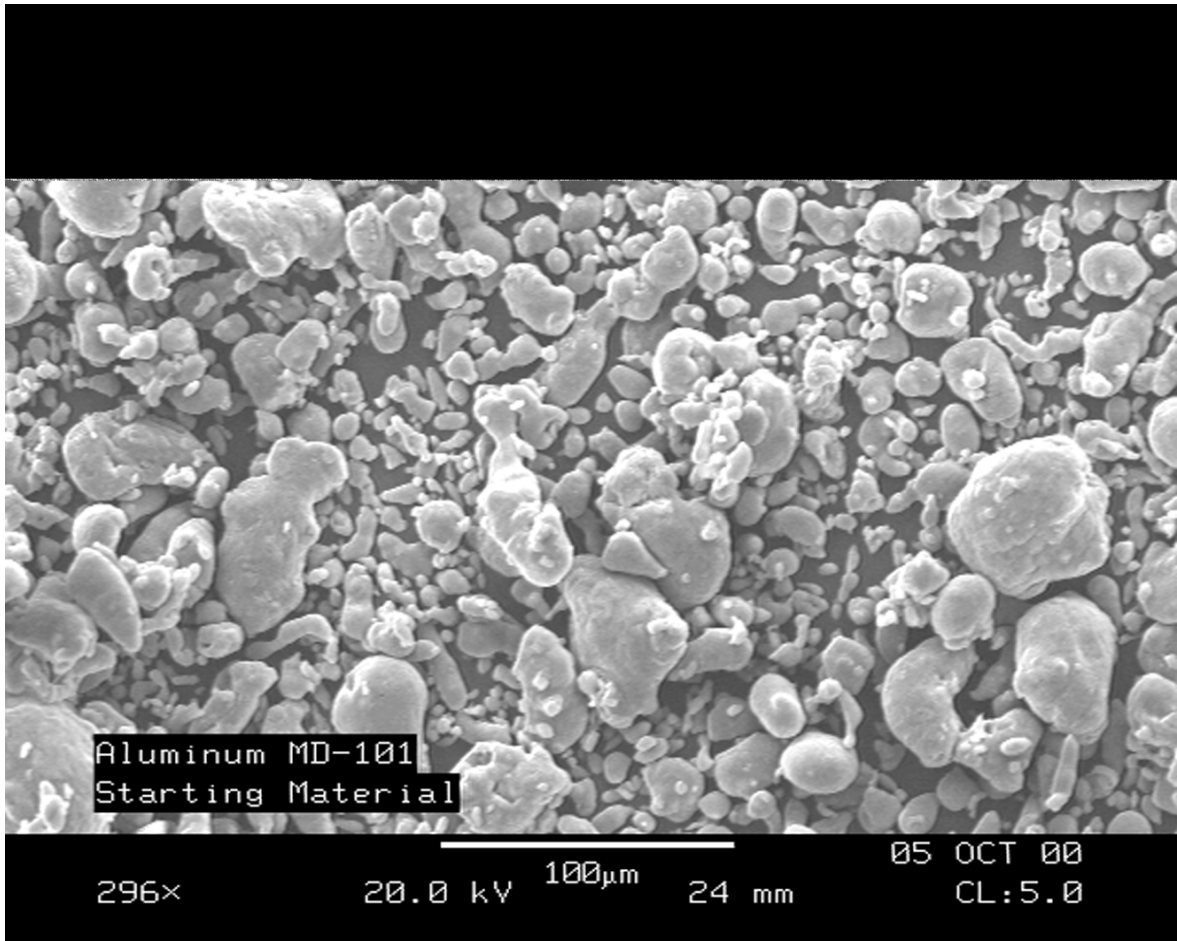


Figure 10. SEM Picture of Starting Aluminum

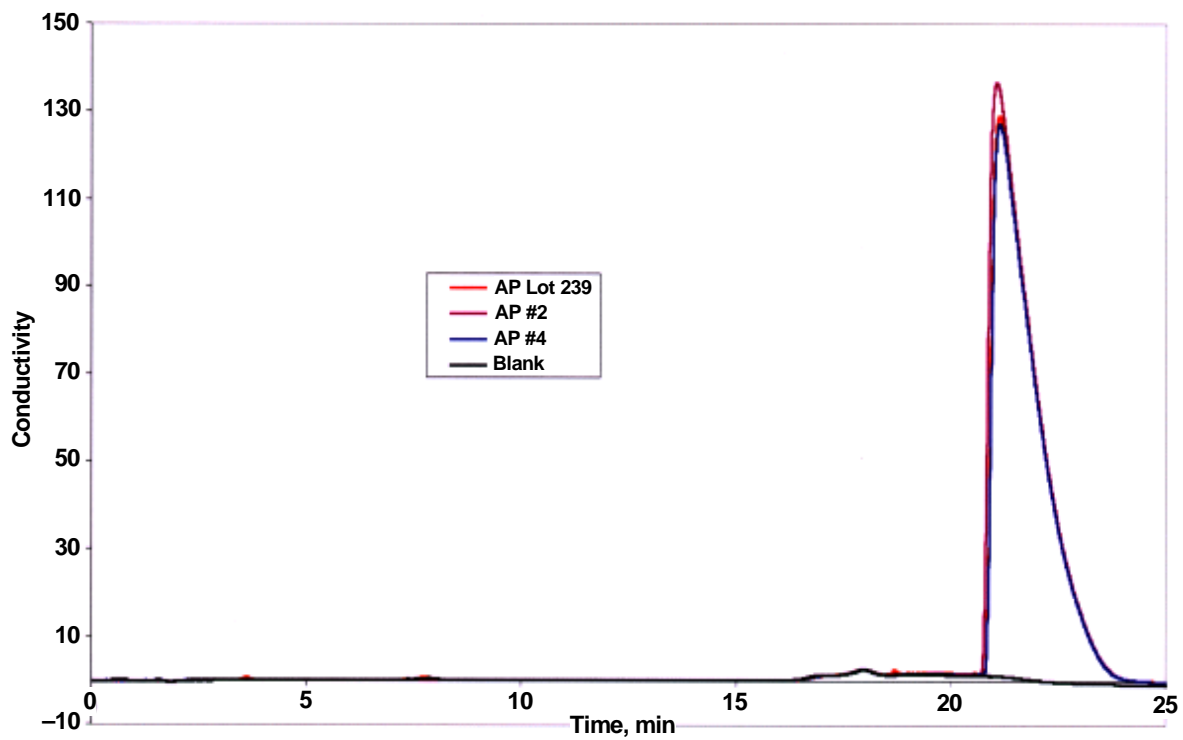


Figure 11. AP Ion Chromatogram

Summary

The need for pollution prevention technologies for application to insensitive munitions energetic materials has generated a flurry of research activities in recovery, recyclability and reuse of energetic ingredients in propellants. We have been in the forefront in the research and development for these “green” processes and propellants. Through this funded effort, we have improved the possibilities that the recovered solids (AP and aluminum) are in reusable form. The summary of technical advances and their impact on the program is summarized in Figure 12.

Technical advances	Impact to the program
AP extraction with methanol	AP can be isolated before its in contact with hard bases which would convert AP to sodium or potassium perchlorates with release of ammonia.
Use of organic amines in place of sodium hydroxide for binder degradation	Aluminum can be recovered in original size and shape. This makes the processes useful in both aluminized and non-aluminized propellants. The use of hard bases would convert aluminum to useless aluminum oxide.

Figure 12. Summary of Technical Improvements and Impact

AP and aluminum generally make up 85% or more of total propellant weight. Our target is to recover the solids in reusable form with as little processing requirements as possible. While the rest of materials make up approximately 15% of total weight. Binder and curative comprise a big portion of that 15%. We very much would like to recover them for reuse. However, it takes chemical reactions to break up the binder into small pieces so the aluminum would fall out of polymeric networks and be recovered.

Theoretically, when the reaction is complete, the “poly-ether” part of the polymer is free from amides (as shown in Figure 4) and recoverable. In reality, one needs to consider the following factors: 1) The poly-ether will be in with a host of other compounds such as butylamine, hydroxyl hexanoyl amide, triphenylbismuth, aziridine and its derivatives, octyl alcohol (from plasticizer), phthalyl amide (from plasticizer), etc. It would be a tremendous undertaking for isolation of small amount of inexpensive material; and 2) In order to recover aluminum, one only needs to have the reaction go far enough to have the metal fall off from the polymer network. Whether the degradation reaction is complete or not is not of importance.

Acknowledgment

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