FINAL REPORT

Evaluation of Metal Bound Porphyrins and Porphyrazins as Lead Salt Replacements as Ballistic Modifiers in Minimum Signature XLDB Propellants

SERDP Project WP-2140

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Table of Acronyms

AMU	Atomic Mass Unit
AN	Ammonium Nitrate
DSC	Differential Scanning Calorimetery
ips	Inches per second
I_{sp}	Specific Impulse
MSP	Metal Salt Paste
Pc	Phthalocyanine
psi	Pounds per square inch
Psia	Pounds per square inch absolute

1. Abstract

In an effort to reduce exposure to lead from minimum smoke propellants to both manufacturing operators and military personnel, alternate metal ions are being investigated in the roll of ballistic modifiers in these propellants. Lead citrate has long been the burn rate modifier of choice due to its ability to reduce a propellant's burn rate over a specific pressure range in many minimum smoke propellant formulations. Other metal ions have been investigated as burn rate modifiers, but have found to either reduce service life or significantly reduce propellant cure times causing the propellant to solidify before it is cast. Investigations were directed to porphyrins and porphyrazins as alternate chelating agents for various metal ions testing the hypothesis that the chelating anion would affect a more desired response to the issues of shelf life degradation and pot life while allowing the metal ion to perform as a burn rate modifier. In addition, several bismuth salts were investigated for their potential to perform as burn rate modifiers in minimum smoke propellant. For these studies a minimum smoke formulation whose ballistics are difficult to tailor due to its high concentration of ammonium nitrate, was chosen.

2. Project Objective and Scope

This project investigated the usefulness of metal-bound porphyrins, metal-bound phthalocyanines (porphyrazins), and several bismuth salts for their effectiveness as replacements for lead salt burning rate modifiers in minimum smoke propellants. Specifically, their effectiveness in modifying the ballistics of an AN-based propellant was determined. This work is expected to potentially lead to more tailorable AN-based formulations for future tactical rocket motor applications.

3. Background

On the battlefield, a visible smoke trail from a recently fired tactical rocket motor provides the enemy with an approximate position of the launcher and its associated personnel. It is important in a theater of war, therefore to use propellants in rocket motors that make the least amount of smoke to avoid having their launch position discovered.

Solid propellants for rocket motors can be classified either as Smoky, Reduced Smoke or Minimum Smoke. Smoke made by rocket motors is either primary or secondary. For example the Reusable Solid Rocket Boosters (RSRB) for the space shuttle contained a smoky propellant which produced both primary and secondary smoke. Primary smoke is the result of metals or organic compounds that when burned produce particulates while secondary smoke is a result of atmospheric water chelating on to a chlorine ion.

When burned in the shuttle motors, powdered aluminum (Al) which produces the particulate aluminum oxide and ammonium perchlorate (NH_4ClO_4) produces a chloride ion making a significant amount of smoke. For reduced smoke propellants compounds that would cause primary smoke are removed. Minimum Smoke or Minimum Signature propellants are made with ingredients that by their nature or low concentrations in the propellant have little or no potential to make smoke.

Traditionally minimum smoke propellants are made with nitrate esters such as nitroglycerine and/or nitramines. It has long been known that lead salts can favorably modify burn rates in this

type of propellant. Lead, however, is highly toxic and it is therefore desirable to find an alternate modifier. This would significantly reduce lead exposure to those who make the propellant and those who use it. Since many transition metals are known to catalyze the degradation of nitrate ester based energetic materials it is believed that encapsulating transition metal ions in larger complex molecules will mollify or negate their less than desirable effects on nitrate esters while being useful as burn rate modifiers.

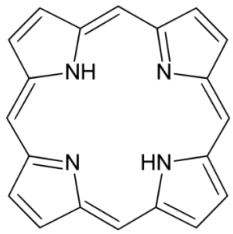


Figure 1) Chemical Structure of Porphine

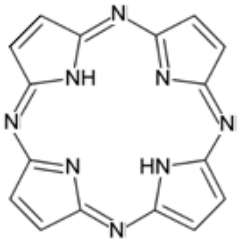


Figure 2) Chemical Structure of Porphyrazine

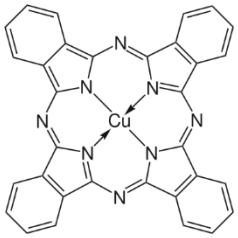


Figure 3) Chemical Structure of Copper Phthalocyanine (CuPc)

A porphine, simplest of the porphyrin family of compounds, is a flat, heterocyclical molecule that is constructed from four pyrole molecules with 4 mezo carbon atoms bonded to the α carbons in the pyrole, see Figure 1. Porphyrazine molecules are similar to porphyrins but have meso nitrogen atoms in place of four meso carbon atoms. The β carbons in a porphyrazine can be used for substitution. If a benzene ring is substituted at the β carbons on a porphyrazine the structure is known as a phthalocyanine. The nitrogen atoms at the center of all of these structures can centrally hold metal ions via direct bonding and/or chelation such that a metal ion's orbitals can extend above and below the plane of the macro organic structure. For example, the structure of copper phthalocyanine (CuPc) which is a commercial dye is depicted in Figure 3. It is hypothesized in this work that holding the metals in such a manner may reduce or prevent the interaction between the metal ions and nitrate esters that causes the degradation of nitrate esters while still functioning as a ballistic modifier. It is also hypothesized that bismuth (Bi) salts, due to their periodic proximity to lead (Pb) might be a satisfactory, less toxic substitute for lead salts (Pb) as a burn rate modifier.

4. Materials and Methods

Porphyrazins are usually synthesized with specific groups substituted to the molecule for a particular research venue and are not commercially available. Due to funding restrictions, synthesis of sufficient amounts of any of the target molecules was not economically feasible and therefore not included as part of this project. Since phthalocyanines are a benzene ring substituted porphyrazines and since there are many commercially available metal bound phthalocyanines it was decided to utilize them for this project instead of pure porphyrazines. Porphyrins, phthalocyanines, and bismuth salts investigated as potential ballistic modifiers were therefore purchased from commercial manufacturers, Acros and Sigma Aldrich. A list of these chemicals and their manufacturers can be found in Table 1.

Table 1) List of Compounds Investigated

Compound	Manufacturer
Phthalocyanine (Pc)	Acros
Silver Phthalocyanine (AgPc)	Sigma Aldrich
Cobalt Phthalocyanine (CoPc)	Sigma Aldrich
Copper Phthalocyanine (CuPc)	Acros
Iron Phthalocyanine (FePc)	Acros
Magnesium Phthalocyanine (MgPc)	Acros
Manganese Phthalocyanine (MnPc)	Sigma Aldrich
Nickel Phthalocyanine (NiPc)	Acros
Lead Phthalocyanine (PbPc)	Sigma Aldrich
Zinc Phthalocyanine (ZnPc)	Acros
Cobalt (II) meso-Tetraphenylporphyrin	Sigma Aldrich
Copper (II) meso-Tetra (4-carboxyphenyl) porphyrin	Sigma Aldrich
Bismuth Subnitrate	Sigma Aldrich
Bismuth Citrate	Sigma Aldrich
Bismuth Nitrate Oxide	Sigma Aldrich
Bismuth Oxide Carbonate	Sigma Aldrich
Bismuth Oxide	Sigma Aldrich
Bismuth Subnitrate	Sigma Aldrich

Formulations using these materials were generated for AN based propellants using a specific impulse range and amount of smoke produced as selection criteria. All materials were tested for thermal stability and compatibility with minimum smoke propellant ingredients. Ingredients that were found to thermally degrade below temperatures that the propellant is generally exposed to during processing or incompatible with energetic ingredients were removed from the list of investigated materials. The remaining ingredients were incorporated into AN based, minimum smoke, slurry cast propellant formulations by way of metal salt pastes. The slurry propellant was tested for pot life and sensitivity to impact, friction and electrostatic discharge. Cured propellants were tested for shelf life stability via MNA depletion, sensitivity to impact, friction and electrostatic discharge. Mechanical properties and burn rates were measured and pressure exponents calculated for propellants that showed promise.

5. Results and Discussion

5.1. Testing

Lead salts used in propellant for burn rate modification are not directly added to the mix bowl, but are incorporated in a metal salt paste (MSP). The standard method of making a paste is to first grind the salt to the correct particle size and then mix it with polymer and carbon black to make a viscous paste. The final step is to pass the paste through a roller mill to produce a paste of uniform consistency. The amount of lead in the paste and hence lead in the propellant is critical to the propellant's ballistic performance.

One issue of initial concern was the ratio of chelated or bound metal ions to non-metals in the investigated compounds. For example dry lead citrate has a molecular weight of 999.70 atomic mas units (AMU's) while lead phthalocyanine has a mass of 719.72 AMU's. In lead citrate the percent of lead in the molecule is 62.2% while in lead phthalocyanine it is 28.8%. It would therefore take a little over twice the lead phthalocyanine to equate to the lead in lead citrate. It was therefore desirable to determine percent of metal in the investigated materials so that calculations could be made that would yield a molar equivalency in metal ions to that of lead as a starting point. The molar amount of lead in the selected propellant formulation was determined and molar equivalent weight amounts for the investigated materials were calculated from that.

Table 2 displays the ratio of metal ion to porphyrin or phthalocyanine for each of the purchased metal bound porphyrin or phthalocyanine. It can be seen from this data that the weight ratio of cationic metal to anionic organic chelate is significantly smaller than that of the ratio of lead to citrate in lead citrate. Using the moles of lead added in the standard propellant mix for this project as a basis, the equivalent amounts of the candidate ingredients were calculated and normalized relative to the amount of lead normally used in a propellant. For example, it would require 1.611 times as much MgPc as it would lead citrate to obtain the same level of magnesium as lead in the final propellant. This is an issue in that adding more ballistic modifier to the propellant would require the removal of energetic materials thereby negatively affecting the propellant impulse.

Table 2) Relative weights of Metal Phthalocyanine and Bismuth Salts

Compound	Molecular Weight (AMU's)	Metal Ion % in molecule	Equivalent Weights
Lead Citrate	999.85	61.1	1.00
Silver Phthalocyanine (AgPc)	620.39	17.39	3.57
Cobalt Phthalocyanine (CoPc)	571.46	10.31	6.03
Copper Phthalocyanine (CuPc)	576.08	11.03	5.64
Iron Phthalocyanine (FePc)	568.38	9.83	6.33
Lead Phthalocyanine (PbPc)	719.72	28.79	2.16
Magnesium Phthalocyanine (MgPc)	536.85	4.53	13.73
Manganese Phthalocyanine (MnPc)	567.46	9.68	6.42
Nickel Phthalocyanine (NiPc)	571.21	10.28	6.05
Zinc Phthalocyanine (ZnPc)	577.91	11.31	5.50
Cobalt (II) meso-Tetraphenylporphyrin	671.65	8.77	7.08
Copper (II) meso-Tetra (4-carboxyphenyl) porphyrin	852.3	7.46	8.34
Bismuth Carbonate Oxide	509.97	81.96	0.76
Bismuth Citrate	398.08	52.50	1.18
Bismuth Nitrate Oxide	286.98	72.82	0.85
Bismuth Oxide	465.96	89.70	0.69
Bismuth Subnitrate	1461.99	71.47	0.87

To determine the effects of the various ballistic modifiers on motor impulse via changes in formulation, a series of calculations were performed using the NASA Glen Chemical Equilibrium with Applications (CEA) computational software. This software calculates complex mixture properties and compositions for chemical equilibrium from propellant input information. Of the various applications that the software provides the one of interest for this project is theoretical rocket performance, which generates a theoretical Specific Impulse (I_{sp}) plus a listing in mole fractions of chemical species in the exhaust. Input files are generated using the percentage of an ingredient in the propellant formulation, each ingredient's heat of formation, density and the initial temperature of the ingredients. The input file also contains the type of problem to be run, a standard case type and the pressure at which the calculations were to be made. In all of the calculations the problem was "Rocket Motor", the case was MS-1103 and the

pressure was 1000 psia. Output files contain various calculated parameters such as propellant density, pressures and temperatures in the chamber, throat and exhaust as well as performance parameters such as CSTAR and I_{sp} and a list of exhaust species.

Table 3) I_{sp} Calculations for Various Ballistic Modifiers*

Ballistic Modifier	**I_{sp} at 75% Weight of Lead (Lb-Sec/Lb)**	**I_{sp} at 100% Weight of Lead (Lb-Sec/Lb)**	**I_{sp} at 125% Weight of Lead (Lb-Sec/Lb)**	**I_{SP} Range**
Lead Citrate	228.6	227.6	226.6	NA
Silver Phthalocyanine (AgPc)	227.0	225.4	223.7	-0.6 to -3.9
Cobalt Phthalocyanine (CoPc)	227.2	225.6	224.1	-0.4 to -3.5
Copper Phthalocyanine (CuPc)	227.3	225.9	224.4	-0.3 to -3.2
Iron Phthalocyanine (FePc)	227.1	225.6	224.0	-0.5 to -3.6
Lead Phthalocyanine (PbPc)	227.6	226.3	224.9	0 to -3.1
Magnesium Phthalocyanine (MgPc)	227.1	225.6	224.0	-0.5 to -3.6
Manganese Phthalocyanine (MnPc)	226.8	225.1	223.4	-0.9 to -4.4
Nickel Phthalocyanine (NiPc)	227.1	225.5	223.9	-0.5 to -3.7
Zinc Phthalocyanine (ZnPc)	225.5	222.5	220.2	-2.1 to -7.4
Bismuth Oxide Carbonate	229.7	229.0	228.4	+2.1 to 0.8
Bismuth Citrate	230.2	229.7	229.2	+2.6 to 1.6
Bismuth Nitrate Oxide	230.3	229.9	229.5	+2.7 to+1.9
Bismuth Oxide	228.6	227.6	226.6	+1.0 to -1.0
Bismuth Subnitrate	230.5	230.1	229.8	+3.5 to 2.8

*All values for I_{sp} in (lb_f-sec/lb_m)

Calculations were based on replacing lead citrate in a min-smoke, ammonium nitrate based propellant formulation on a weight to weight percent basis as well as weight percent levels of +/- 25%. The same calculations were done with the five bismuth salts studied in this work. Both sets of calculations are collected in Table 3. Using the I_{sp} produced by the standard amount of lead, 227.6 lb_f-sec/lb_m as the comparison point, it can be seen that all of the metalo-phthalocyanines fall short in I_{sp} even when their relative amount in the propellant is changed by +/- 25%. This is due to the low metal to molecule weight ratio as compared to lead citrate (See Table 2). The bismuth salts all display an increase in I_{sp} with the exception of Bismuth (III) oxide (Bi_2O_3) at 100% and 125% the weight of added lead. This is due to their not only having a

higher metal weight to molecule weight but also to the fact that each of the molecules contain some oxygen that can participate in propellant combustion. This is especially true for the two bismuth nitrate salts which understandably add more I_{sp} to the propellant than any of the other materials in this study.

It was found that the I_{sp} of the metalo-phthalocyanine pastes were comparable to a lead citrate based propellant (when the weight% of the metalo-phthalocyanine was 75% of that in the lead based propellant when compensation was proportionally made in the AN and lacquer weight percent to accommodate the removal or increase of the metalo-phthalocyanine). This result can be attributed to the metal to chelator weight ratios. One mole of lead citrate is 61.1% lead and 38.9% citrate by weight where as one mole of lead phthalocyanine is only 29% lead. It is observed that most of the metals chosen have AMU's between 54.94 and 65.93 resulting in a weight % range of metal to chelator between 10% to 11%. Outliers in the group of purchased phthalocyanines are Magnesium phthalocyanine (5% Mg to Pc) and Silver Phthalocyanine (17% Ag to Pc).

Table 4) STANAG Smoke Calculations

Compound	STANAG Smoke Value
Lead Citrate	0.106
Silver Phthalocyanine (AgPc)	0.063
Cobalt Phthalocyanine (CoPc)	0.067
Copper Phthalocyanine (CuPc)	0.076
Iron Phthalocyanine (FePc)	0.075
Lead Phthalocyanine (PbPc)	0.062
Magnesium Phthalocyanine (MgPc)	0.055
Manganese Phthalocyanine (MnPc)	0.070
Nickel Phthalocyanine (NiPc)	0.070
Zinc Phthalocyanine (ZnPc)	0.070
Bismuth Oxide Carbonate	0.036
Bismuth Citrate	0.075
Bismuth Nitrate Oxide	0.033
Bismuth Oxide	0.036
Bismuth Subnitrate	0.083

Upper limits for minimum smoke propellants and calculations to determine the amount of smoke made by propellant combustion was found in the North Atlantic Treaty Organization (NATO) Standardization Agreement (STANAG) No. 6016 Edition 1. Calculations for a particular

formulation of minimum smoke propellants were made first by determining the condensable combustion products taken from the list of mole fraction exhaust components generated by the NASA Glen software program. The calculations that incorporated phthalocyanines and bismuth salts at 125% the normal weight of lead citrate were used. The weight percent of each condensable specie was divided by its density, these numbers were totaled and their exponent was taken and subtracted from 1.

The lead citrate value from these calculations was found to be 0.106 while the resultant value for all phthalocyanine samples examined were between 0.062 and 0.070, see Table 4. This would indicate that adding more phthalocyanine modifier to the formula could be done without making more smoke than a lead based modifier. But it is observed that because of the relative weight of the phthalocyanine the I_{sp} of the propellant would be lowered further. On the other hand more of either of the bismuth nitrate species could be added to the propellant to enhance the I_{sp}.

5.2. Thermal Stability

Thermal Stability measurements were performed on a Differential Scanning Calorimeter (DSC) between RT and 450°C at a ramp rate of 10°C/min on each of the phthalocyanines. Since the propellant cures at 140F (60°C) it was decided that the metalo-phthalocyanines should be thermally stable at least to that temperature. Samples of the ballistic modifier were placed in an aluminum pan and put on one (sample) probe of the machine while an empty pan was placed on the other (control) probe. The sample and control were heated at a rate of 10°C/hour up to 400°C. Differences in temperature between the two probes indicated either exothermic (increases in the temperature of the sample pan) event or endothermic (decreases in the temperature of the sample) event. Stability would be the result of having no significant endotherms or exotherms below the target temperature. Since thermal events are not usually definitive points, the endotherm or exotherm is extrapolated from the slope before and after the event. Figures 4-19 show DSC results on the various phthalocyanines.

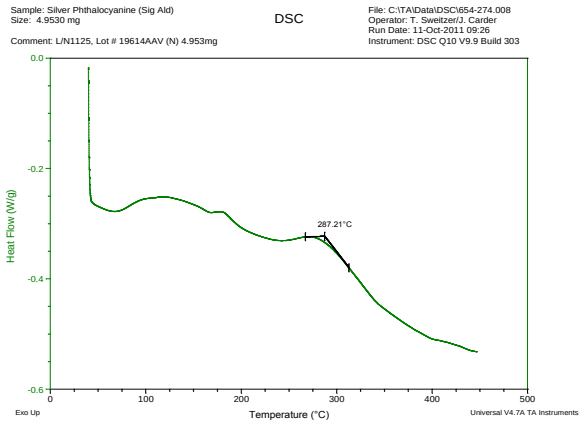


Figure 4) DSC of Silver Phthalocyanine

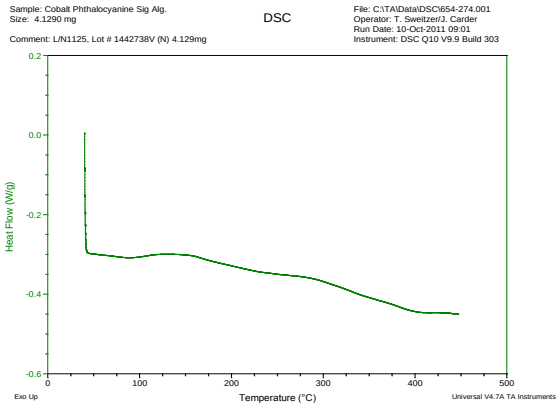


Figure 5) DSC of Cobalt Phthalocyanine

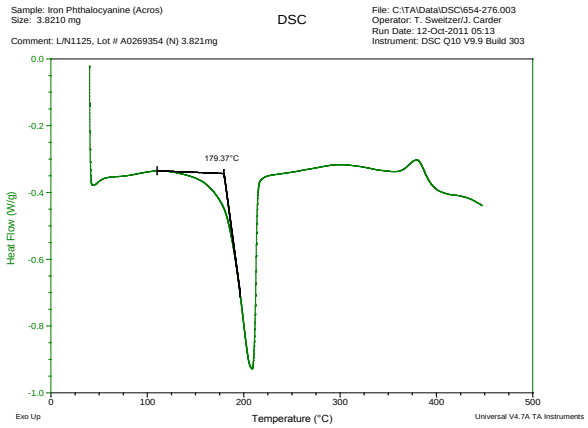


Figure 6) DSC of Copper Phthalocyanine

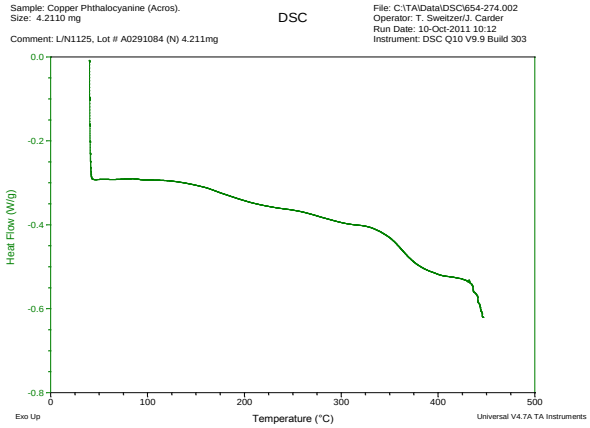


Figure 7) DSC of Iron Phthalocyanine

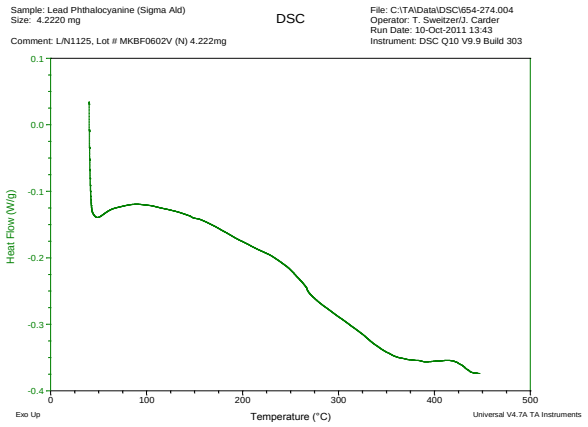


Figure 8) DSC of Lead Phthalocyanine

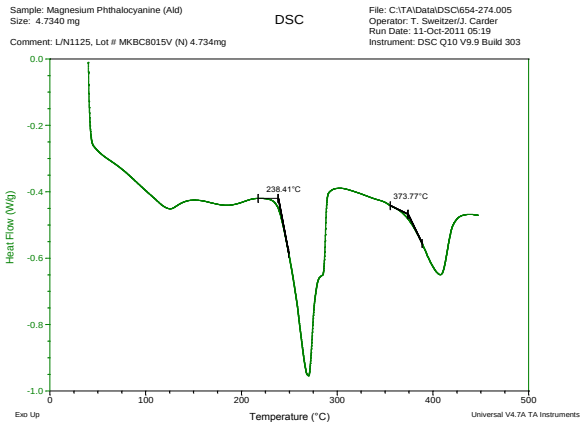


Figure 9) DSC of Magnesium Phthalocyanine

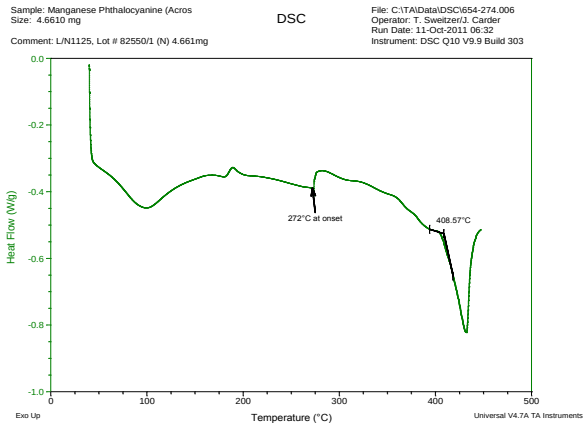


Figure 10) DSC of Manganese Phthalocyanine

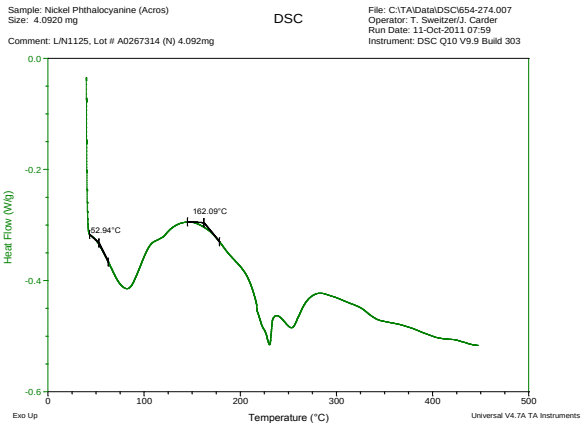


Figure 11) DSC of Nickel Phthalocyanine

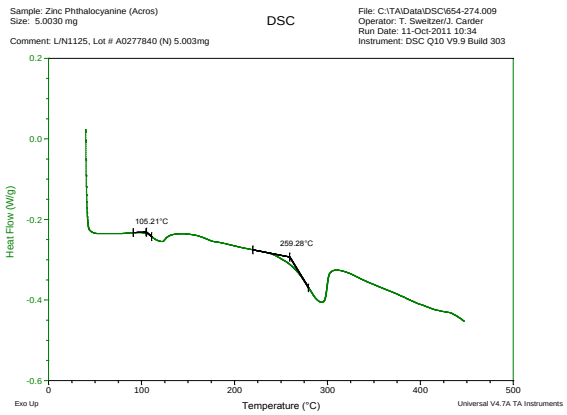


Figure 12) DSC of Zinc Phthalocyanine

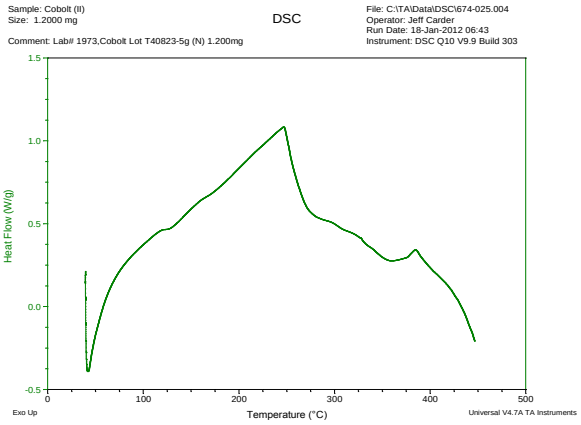


Figure 13) DSC of Cobalt (II) meso-Tetraphenylporphyrin

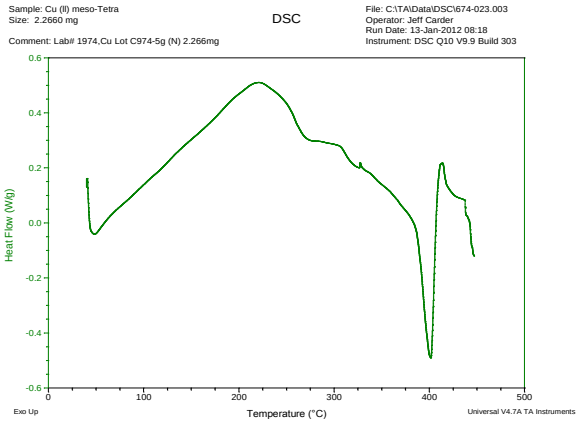


Figure 14) DSC of Copper(II)meso-Tetra(4carboxyphenyl)porphyrin

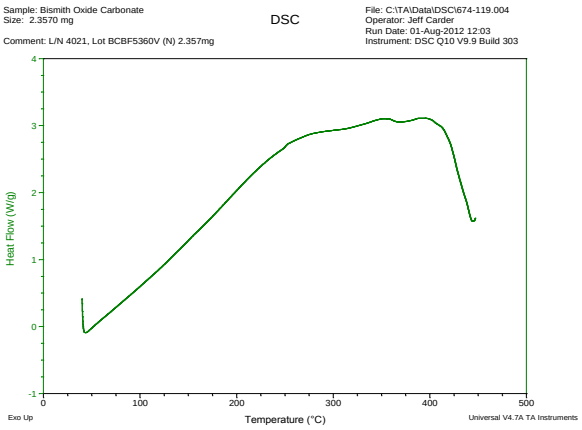


Figure 15) DSC of Bismuth Carbonate Oxide

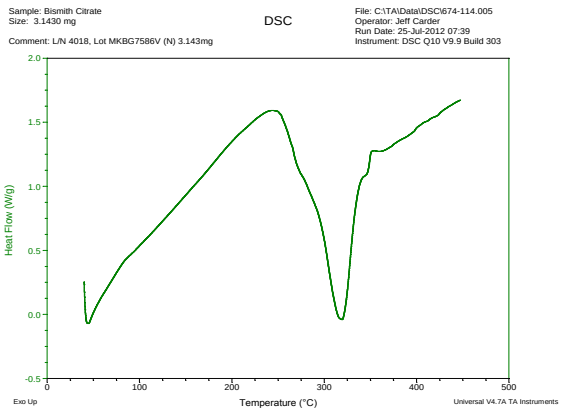


Figure 16) DSC of Bismuth Citrate

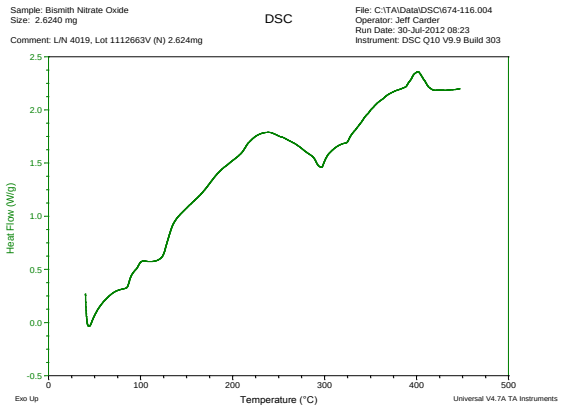


Figure 17) DSC of Bismuth Nitrate Oxide

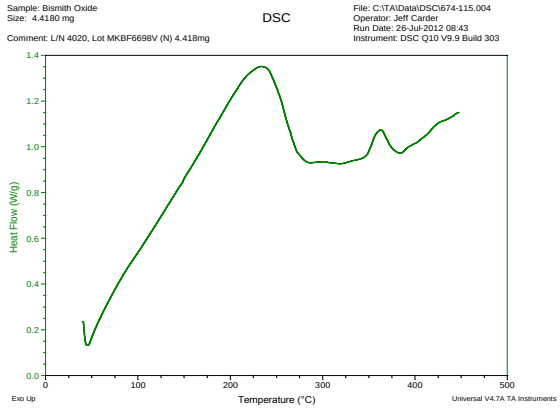


Figure 18) DSC of Bismuth Oxide

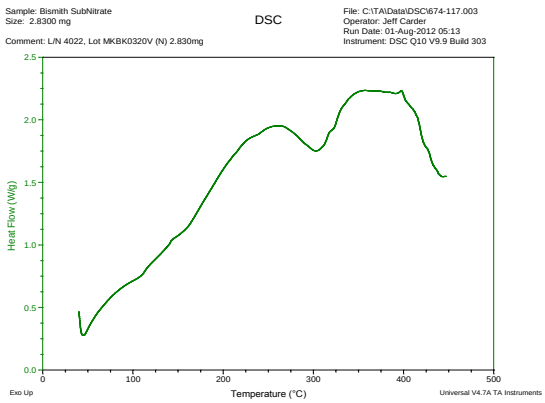


Figure 19) DSC of Bismuth Subnitrate

No observable exotherms or endotherms were detected below 395°F (200°C) in CuPc, CoPc, PbPc or AgPc. Iron displayed a single endotherm at 179°C, see Figure 6, while Magnesium phthalocyanine displayed two endotherms at 238°C and 373°C, see Figure 9. Manganese displayed one above 400°C see Figure 10 and Nickel phthalocyanine displayed two endotherms one at 60°C and the other at 188°C, see Figure 11. Zinc phthalocyanine also showed two endotherms at 90°C and 250°C, see Figure 12. Based on these results, NiPc was a potential candidate for removal. The two porphyrin compounds in Figures 13 and 14 do not show any significant exo or endotherms below 200°C. The same can be said for all of the bismuth salt compounds.

5.3. Compatibility

All selected compounds that passed thermal stability were initially tested for compatibility first with a nitrate ester based lacquer and second with ammonium nitrate (AN). Samples had to pass the test with lacquer before they were investigated for stability with AN. Samples when combined with lacquer were tested by modified Taliani while samples tested with AN were tested on a Differential Scanning Calorimeter (DSC).

The modified Taliani tests consists of combining aliquots of nitrate ester lacquer and the ballistic modifier and heating them to 200°F (~93°C) for 23 hours. The system pressure was observed and recorded. The test is a failure if the combination of the two materials generated a pressure of over 200 mmHg in less than 23 hours. It can be seen from the results of the modified Taliani Tests, see Table 5, that Iron and Manganese phthalocyanines are not compatible with nitrate ester based lacquers; they therefore were excluded from further testing. All other samples continued to DSC compatibility testing with AN.

Table 5) Modified Taliani Test Results on Lacquer and Ballistic Modifiers

Ballistic Modifier	Time at Max Pressure (Hrs)	Delta Pressure (mmHg)	Pass/Fail
Phthalocyanine	1Hr	24	Pass
Silver Phthalocyanine (AgPc)	1Hr	10	Pass
Cobalt Phthalocyanine (CoPc)	1Hr	1	Pass
Copper Phthalocyanine (CuPc)	1Hr	1	Pass
Iron Phthalocyanine (FePc)	1Hr	254	FAIL
Lead Phthalocyanine (PbPc)	1Hr	1	Pass
Magnesium Phthalocyanine (MgPc)	23HR	114	Pass
Manganese Phthalocyanine (MnPc)	5Hr	>200	FAIL
Nickel Phthalocyanine (NiPc)	22	31	Pass
Zinc Phthalocyanine (ZnPc)	23	59	Pass
Cobalt (II) meso-Tetraphenylporphyrin	23	5	Pass
Copper (II) meso-Tetra (4-carboxyphenyl) porphyrin	33	5	Pass
Bismuth Oxide Carbonate	1	<1	Pass
Bismuth Citrate	1	22	Pass
Bismuth Nitrate Oxide	3	8	Pass
Bismuth Oxide	5	10	Pass
Bismuth Subnitrate	2	4	Pass

Table 6) DSC Results: Ballistic Modifier with AN

Ballistic Modifier	AN Exotherm Temp (C°)	Test Material Exotherm Temp (C°)	Combination Exotherm Temp (C°)	Decrease in Temperature (15% Max)	Pass/ Fail
Phthalocyanine	No Exotherm	234°C	198°C	NA	Pass
Silver Phthalocyanine (AgPc)	No Exotherm	No Exotherm	234°C	NA	Pass
Cobalt Phthalocyanine (CoPc)	No Exotherm	No Exotherm	219°C	NA	Pass
Copper Phthalocyanine (CuPc)	No Exotherm	No Exotherm	243°C	NA	Pass
Iron Phthalocyanine (FePc)	Failed Taliani and so was not further tested				
Lead Phthalocyanine (PbPc)	No Exotherm	No Exotherm	302°C	NA	Pass
Magnesium Phthalocyanine (MgPc)	No Exotherm	No Exotherm	314°C	NA	Pass
Manganese Phthalocyanine (MnPc)	Failed Taliani and so was not further tested				
Nickel Phthalocyanine (NiPc)	No Exotherm	No Exotherm	220°C	NA	Pass
Zinc Phthalocyanine (ZnPc)	No Exotherm	No Exotherm	294°C	NA	Pass
Copper (II) meso-Tetra (4-carboxyphenyl) porphyrin	No Exotherm	No Exotherm	238°C	NA	Pass
Bismuth Oxide Carbonate	No Exotherm	No Exotherm	283°C	NA	Pass
Bismuth Citrate	No Exotherm	No Exotherm	284°C	NA	Pass
Bismuth Nitrate Oxide	No Exotherm	No Exotherm	290°C	NA	Pass
Bismuth Oxide	No Exotherm	No Exotherm	305°C	NA	Pass
Bismuth Subnitrate	No Exotherm	No Exotherm	316°C	NA	Pass

A standard DSC compatibility test required approximately 3mg of ballistic modifier and 3mg of AN. These were placed in a test pan which, along with a control pan was heated to 400°C at a rate of 10°C/minute. The difference in temperature between the sample and the empty pan was recorded as either exothermic or endothermic. AN was analyzed by itself and found to have an endotherm starting at 275°C. The pass/fail criterion for a combination of AN and a ballistic modifier is if the combined exotherm temperature is less that that at which Nitroglycerin self detonates, 162°C.

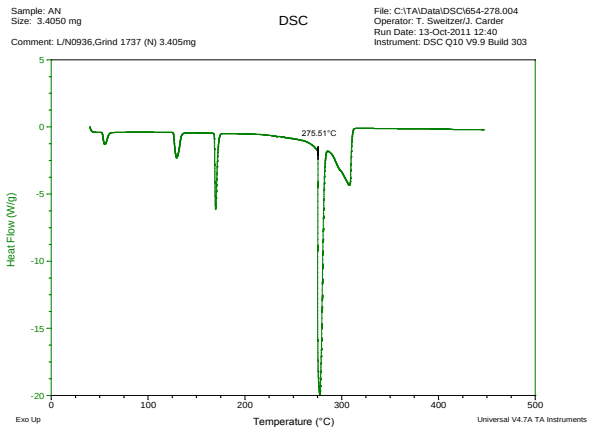


Figure 20) DSC of Ammonium Nitrate (AN)

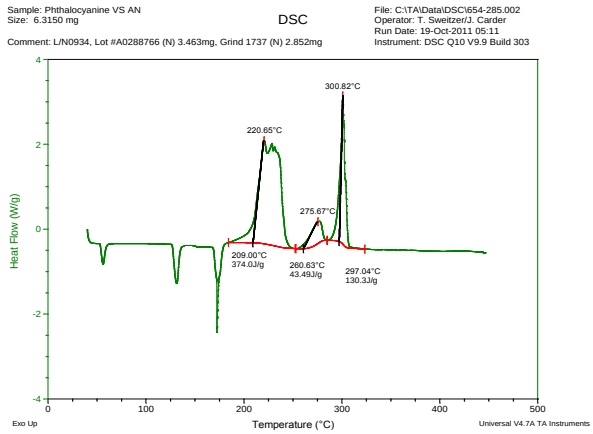


Figure 21) DSC Phthalocyanine and AN

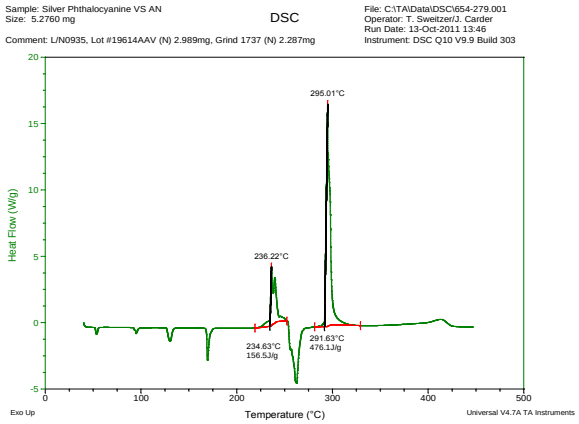


Figure 22) DSC of Silver Pc and AN

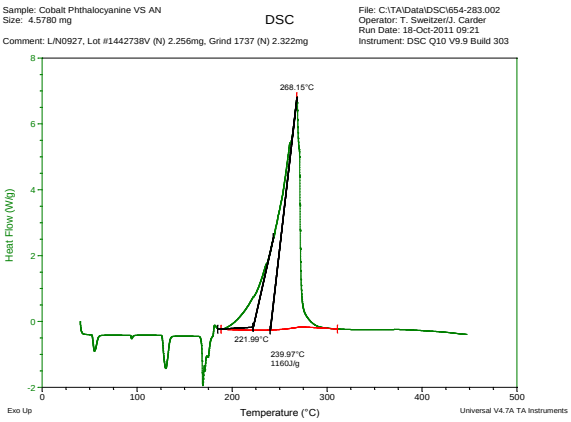


Figure 23) DSC of Cobalt Pc and AN

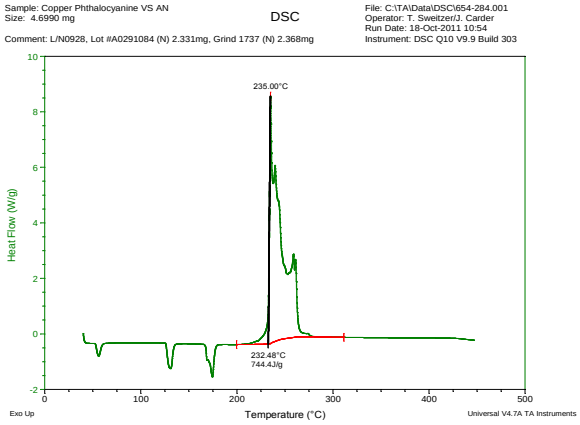


Figure 24) Copper Pc and AN

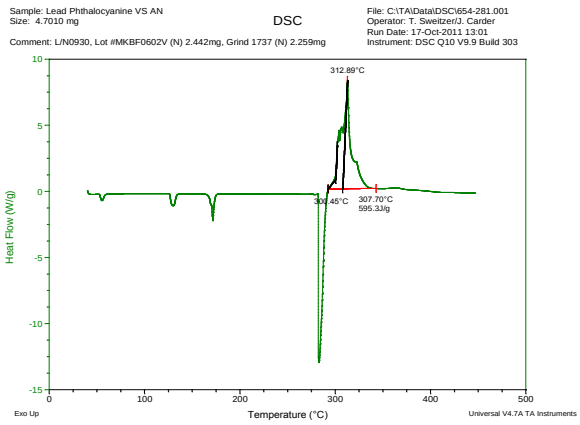


Figure 25) Lead Pc and AN

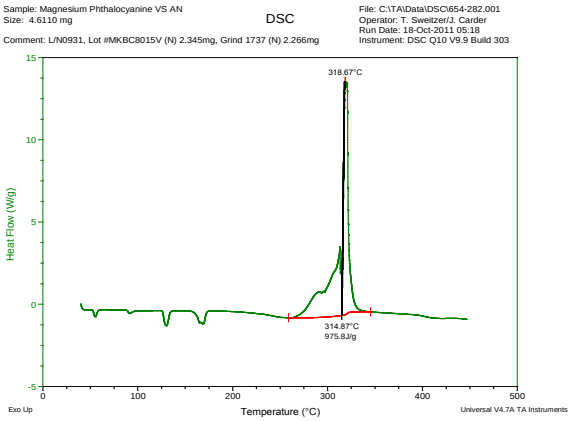


Figure 26) Magnesium Pc and AN

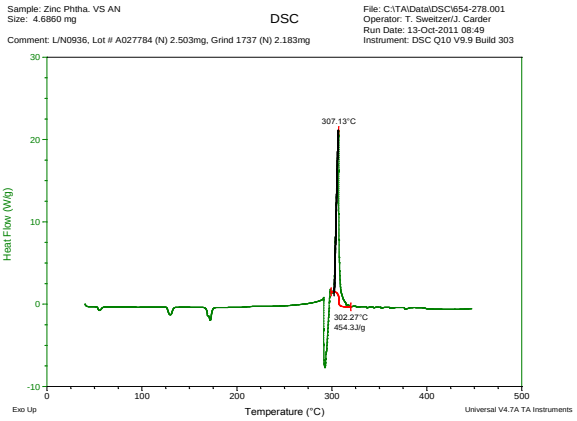


Figure 27) DSC of Zinc Pc and AN

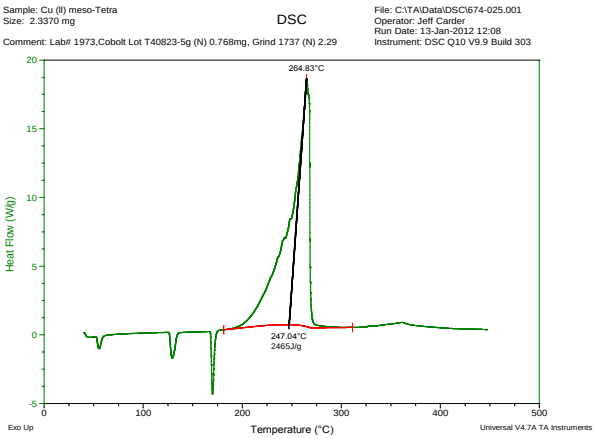


Figure 28) Cobalt (II) meso-Tetraphenylporphryin and AN

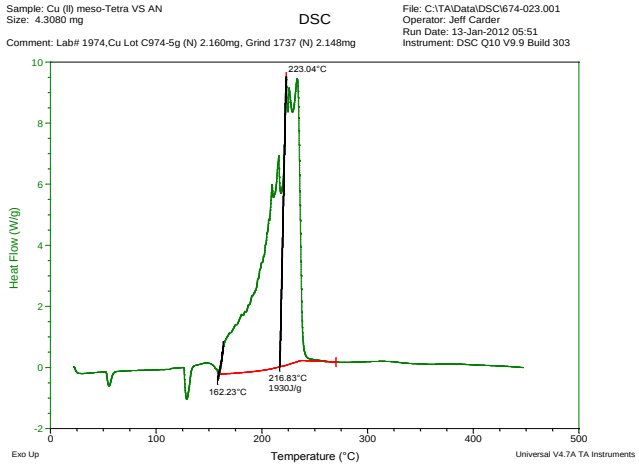


Figure 29) Copper (II) meso-Tetra (4carboxyphenyl) porphyrin and AN

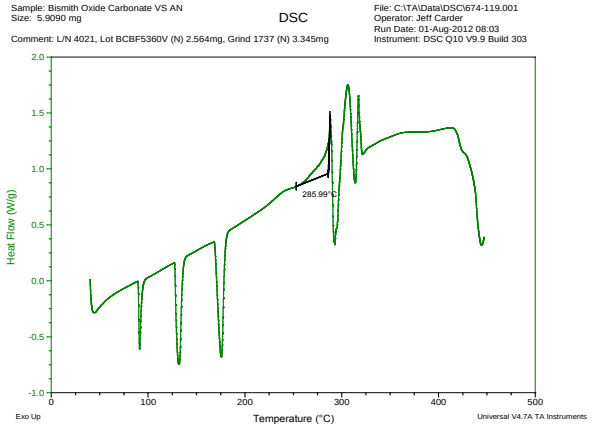


Figure 30) Bismuth Carbonate and AN

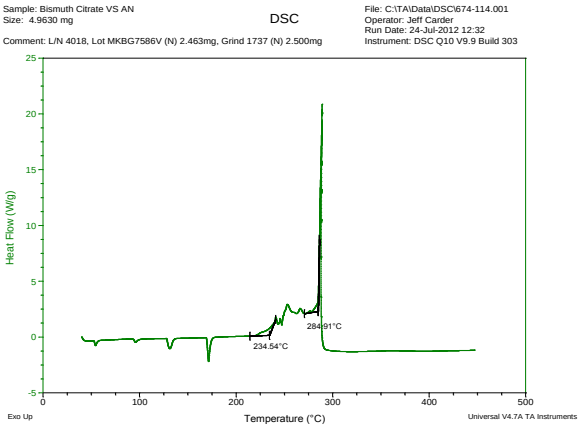


Figure 31) Bismuth Citrate and AN

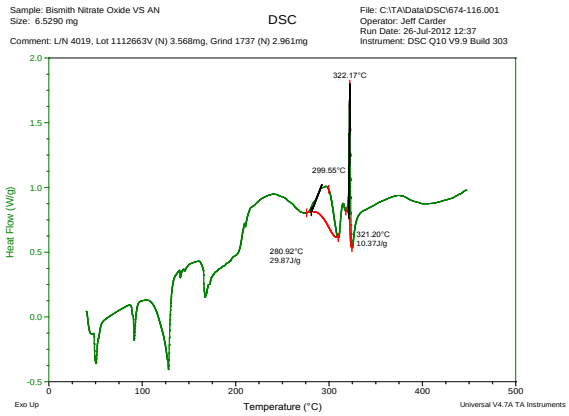


Figure 32) Bismuth Nitrate oxide and AN

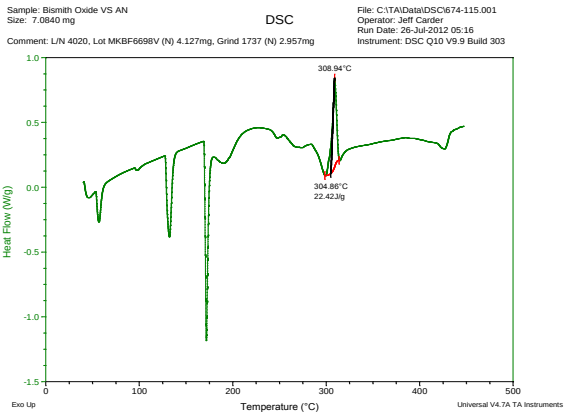


Figure 33) Bismuth Oxide and AN

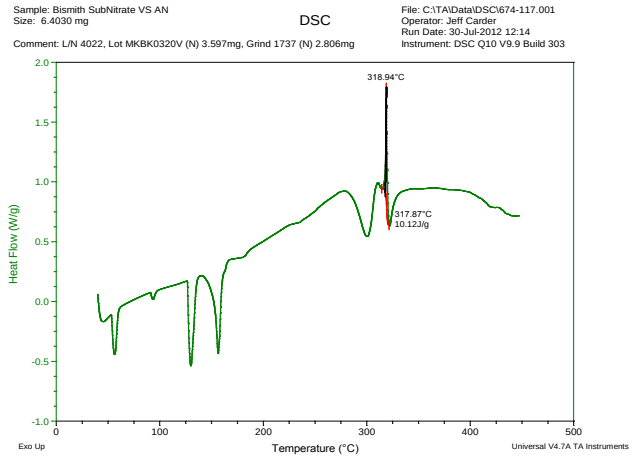


Figure 34) Bismuth Subnitrate and AN

The Thermal Stability and Compatibility Taliani testing resulted in the removal of Iron Phthalocyanine, Manganese phthalocyanine and Nickel phthalocyanine from the list of candidates. The phthalocyanine, without any metal ion chelated to it and lead phthalocyanine were used primarily as a control and for comparison to other species and were not tested further. Silver Phthalocyanine was rejected due to cost ($83/g) and Magnesium phthalocyanine was rejected due to its having a high value in the modified Taliani test. The two porphyrin species, Cobalt (II) meso-Tetraphenylporphyrin and Copper(II) meso-Tetra (4-carboxyphenyl) porphryin) passed compatibility with nitrate esters, but the Copper(II) meso-Tetra (4-carboxyphenyl) porphyrin) failed compatibility with AN. Due to the difficulty in obtaining the porphyrin compounds and their high cost, no further investigations were undertaken with them. Other compounds tested for compatibility that passed included bismuth citrate, bismuth nitrate oxide, bismuth oxide, bismuth oxide carbonate and bismuth subnitrate; all passed both tests.

Cobalt (CoPc), Copper (CuPc), and Zinc(ZnPc) were down selected from the set of available phthalocyanines, as well as all 5 of the bismuth compounds.

5.4. Incorporation of Down Selected Phthalocyanine Candidates into Propellant

5.4.1. Metal Salt Paste Metalo-Phthalocyanine Compounds

The standard practice for incorporating lead salts into minimum smoke rocket propellants is to first grind and dry the material, then mix it with carbon black and a liquid polymer which is one of the propellant binders. This combination of ingredients is traditionally called a metal salt paste (MSP). Initially the down selected phthalocyanines were first incorporated into metal salt pastes with carbon black and polymer at the same weight percent as lead salts are incorporated in the standard propellant formulation. This, due to the mass of the phthalocyanine relative to the mass of metal ion, resulted in a lower level of metal ion concentration than a standard lead paste; approximately 58% that of lead. A second paste was made of each down selected phthalocyanine leaving out carbon black allowing for the addition of more phthalocyanine yielding a metal level in the propellant that was 62% that of lead. These two levels provided a

minimal effect to the energy of the propellant. Pint mixes were made from each of the pastes and tested for viscosity over time, physical properties and burn rate.

5.4.2. Propellant Mixes: End of Mix Viscosity Metalo-Phthalocyanine Compounds

Viscosity measurements were taken on the propellant at the end of the mix and for every hour for various lengths of time thereafter to yield information on pot life and therefore how long after completion of the mix the propellant can be effectively in casting. Mixes 1BPS-10494 and 1BPS-10497 made with CuPc were all found to have propellant that thickened beyond usefulness very rapidly. Mixes 1BPS-10493 and 1BPS-10496 were found to be setting up in the viscometer cup at the 5th hour. Measurements for 1BPS-10494 and 1BPS-10497 were stopped after 4 hours because it was observed to rapidly solidify before the next measurement. Only 1BPS-10495 made with ZnPc did not rapidly cure in the sample cup maintaining a low viscosity for 11 hours. Based on this data, an additional 2 pastes were made with ZnPc at levels higher than that of lead in the standard formulation. From these pastes two more mixes were made, 1BPS-10554 and 1BPS-10555. After the initial 6 mixes were made it was decided, based on burn rate data, that two more mixes would be made with higher ZnPc concentrations. Mix 1BPS-10554 had a ZnPc level 1.16 times that of lead in the standard mix and 1BPS-10555 contained sufficient ZnPc to be at a level 1.36 times that of lead. Figure 34 displays the collected viscosity measurements of the metalo-phthalocyanine mixes.

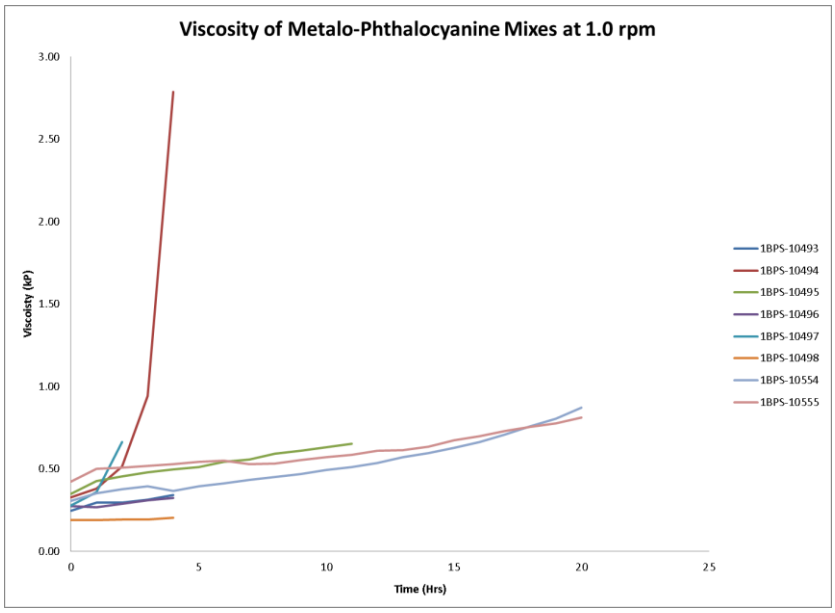


Figure 35) Viscosities of various Metalo-Phthalocyanine mixes taken at 1 sec^{-1}

5.4.3. Mechanical Properties Metalo-Phthalocyanine Compounds

Following propellant cure, tensile specimens were tested by pulling them to failure at a specified rate (2 in/sec) and temperature (77°F) using an Instron Universal Testing Machine. Mixes

1BPS-10493, 1BPS-10494 and 1BPS-10495 which contained the same weight percent metalo-Pc as standard lead salts plus carbon black showed that CoPc produced mechanical properties closest to the standard mix. It also showed that CuPc produced mechanical properties significantly lower stress and modulus than the standard mix. Mixes 1BPS-10496, 1BPS-10497 and 1BPS-10498 where the carbon black was replaced with metalo-phthalocyanine showed the same trend in stress but at lower values. It can also be seen in mixes 1BPS-10554 and 1BPS-10555 that the addition of significantly more amounts of the metalo-phthalocyanine appears to have had a negative effect on mechanical properties, by lowering stress and modulus by non-trivial amounts. It is probable that for these mixes, ZnPc inhibited complete cure of the propellant.

Table 7) Mechanical properties of Metalo-Phthalocyanine Propellant Mixes.

Mix Number	Metal-Pc	Content of Lead in MSP Relative to Pb salts	Stress (psi)	Strain (Max) (%)	Strain (Failure) (%)	Modulus (psi)
Standard Mix	Pb Salt	1	197.62	49.14	49.14	452
1BPS-10493	CoPc	0.58	197.75	48.73	48.77	445
1BPS-10494	CuPc	0.58	168.26	63.57	63.61	317
1BPS-10495	ZnPc	0.58	187.83	51.91	52.00	411
1BPS-10496	CoPc	0.62	192.86	49.32	49.36	442
1BPS-10497	CuPc	0.62	160.08	43.42	43.5	398
1BPS-10498	ZnPc	0.62	173.47	44.16	44.28	431
1BPS-10554	ZnPc	1.16	117.22	51.72	51.84	252
1BPS-10555	ZnPc	1.36	95.52	50.44	50.61	204

5.4.4. Burn Rates Metalo-Phthalocyanine Compounds

Multiple strands of propellant from each of the formulations were fired at various pressures to determine the effects of pressure on burn rate. To measure the propellant burn time, start and stop timer wires were inserted through the propellant strand at a standard distance. The strand was pressurized and ignited from one end. A timer was started and stopped when the respective wires were burnt through; burn rate was calculated as inches/seconds (ips) from the resulting data.

Table 8 displays the burn rate data at 1000psi for all of the mixes made with phthalocyanine based pastes. It can be seen from this data that in comparison to the lead salt standard propellant there is a significant decrease in the burn rates of the phthalocyanine paste propellants at 1000 psi. One can also see that there is very little variation in the burn rates among the various phthalocyanine propellants regardless of the concentration of metal ion in the propellant.

A plot of the burn rates vs pressure for the baseline propellant containing a lead based metal salt paste is presented in Figure 36. It can be seen from Figure 36 that there is a significant change in the slope of the burn rate between about 1000 psi and 2000 psi. This "saddle" is a direct effect of the ballistic modifier and it provides a range where the burn rate displays minimal changes with pressure change.

Table 8) Burn Rate Comparison at 1000psi.

Mix Number	Relative to Pb salts	Metal-Pc	r_{1000} (in/sec)
Standard Mix	1	Lead	0.352
1BPS-10493	0.58	CoPc	0.209
1BPS-10494	0.58	CuPc	0.207
1BPS-10495	0.58	ZnPc	0.191
1BPS-10496	0.62	CoPc	0.220
1BPS-10497	0.62	CuPc	0.211
1BPS-10498	0.62	ZnPc	0.234
1BPS-10554	1.16	ZnPc	0.225
1BPS-10555	1.36	ZnPc	0.223

Figures 37 through 44 display the burn rate data taken from the various pint mixes made with phthalocyanine burn rate modifiers. It can be seen from Figures 37 and 40 that Cobalt phthalocyanine is not an effective burn rate modifier at these levels. Figure 38 for Copper phthalocyanine at 57% of lead loading, is similar to the cobalt mixes, mostly a straight line while Figure 41 appears to have the unusual feature of two saddles, but this is due to data scatter. The two zinc phthalocyanine mixes are also similar to CoPc in that they are also straight lines.

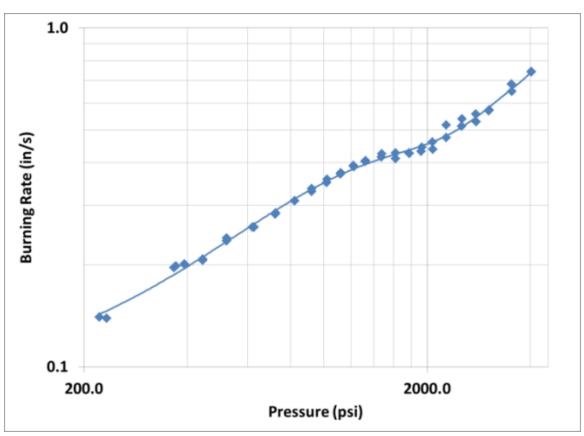
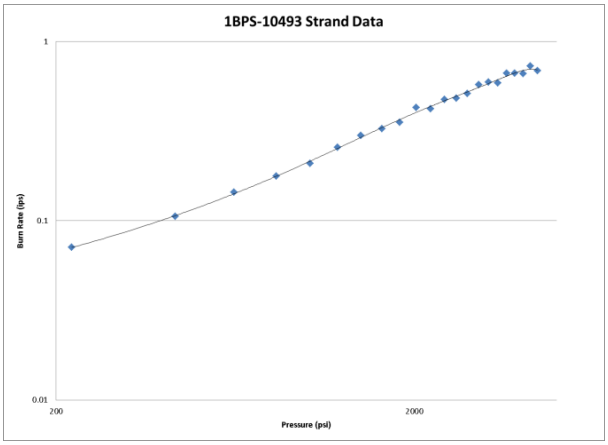


Figure 36) Burn Rate Data for Base Line, Lead Salt Modifier Propellant



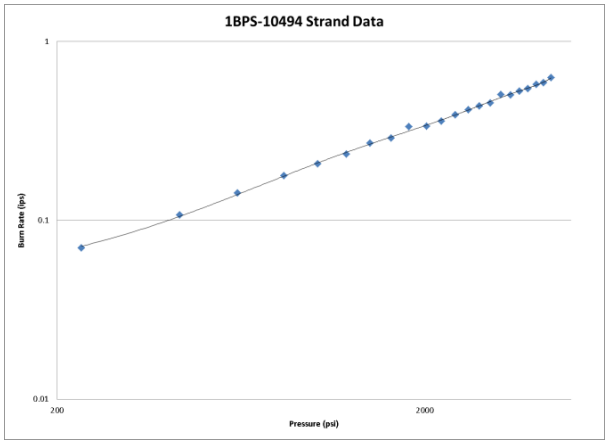
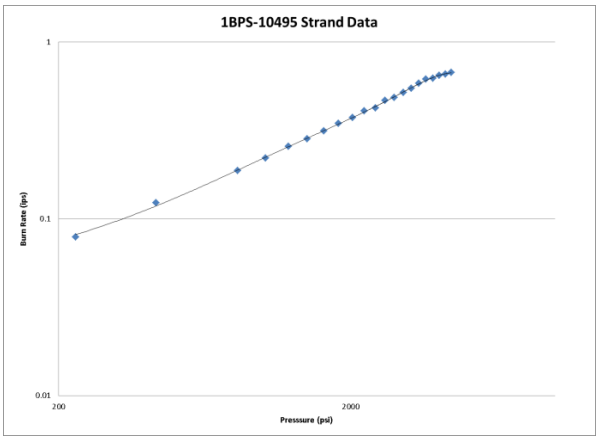


Figure 37) Burn Rate Data, Mix 1BPS-10493 **Figure 38) Burn Rate Data, Mix 1BPS-10494**



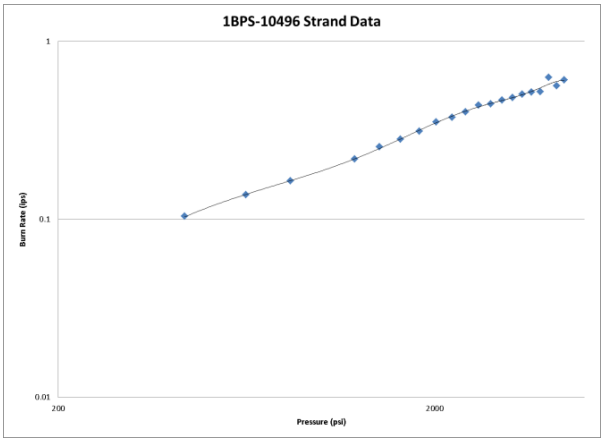
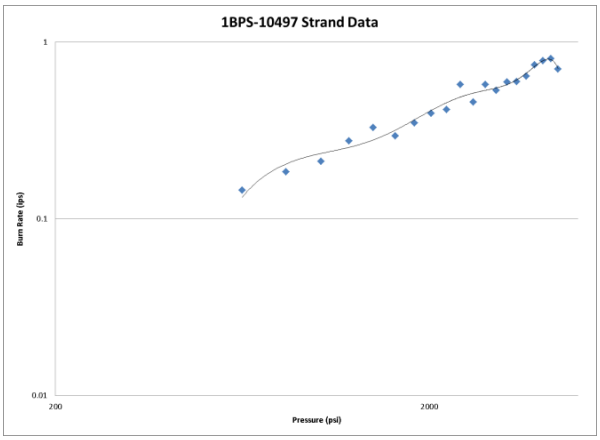


Figure 39) Burn Rate Data, Mix 1BPS-10495 **Figure 40) Burn Rate Data, Mix 1BPS-10496**



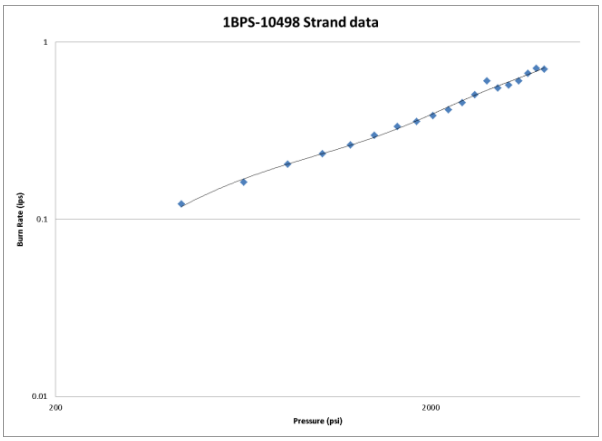
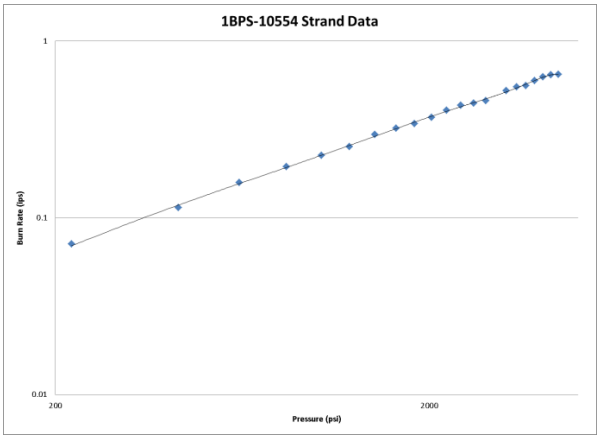


Figure 41) Burn Rate Data, Mix 1BPS-10497 **Figure 42) Burn Rate Data, Mix 1BPS-10498**



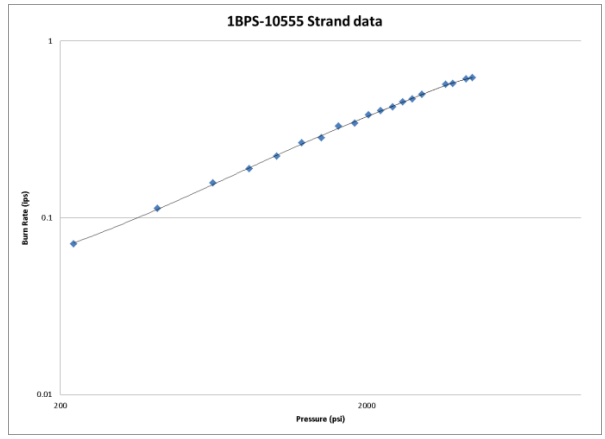


Figure 43) Burn Rate Data, Mix 1BPS-10554 Figure 44) Burn Rate data of 1BPS-1055

The two mixes made with higher levels of ZnPc, 1.16% and 1.36% of the standard lead loading, required a reduction in the AN concentration, which, as expected reduced the impulse of the standard propellant from 225.5 to 222.5 and 220.2 lb_f-sec/lb_m, respectively. Unfortunately, even these higher loadings of ZnPc did not affect any significant changes in the burn rate, see Figures 43 and 44.

5.4.5. Propellant Service Life Metalo-Phthalocyanine Compounds

N-Methyl-p-Nitroanaline (MNA) is a common ingredient in min-smoke propellants which is used to stabilize the propellant over time by chelating NO_2 from decomposed nitroglycerin (NG) and butanetriol trinitrate (BTTN). Without MNA in the propellant, the NO_2 would collect, create pressure spots in the propellant and eventually crack it. Cracks in propellant provide extra surface area for the flame front when the motor is fired. This extra flame front would cause internal pressures that would be higher than the case was designed for; resulting in an explosion of the motor. Typically, the standard loading of MNA in a minimum smoke propellant is sufficient so as to still be present in the propellant at levels higher than 0.2% after 63 days of accelerated aging.

Propellant mixes made with the elevated levels of ZnPc and the standard amount of MNA were tested for propellant service life. Samples of the cured propellant were held at 160°F and were to be tested for MNA depletion at 0, 14, 28, 42 and 63 days after cure. When tested immediately after the propellant was made the MNA level was found to be 0.71% which is normal for this propellant. But when the propellants were tested at 14 days, the MNA level was found to be zero (0). To ensure the safety of the operators and technicians, the samples were immediately collected and destroyed by burning.

The stability data in conjunction with the non-effect of the metal phthalocyanines on ballistic properties indicates that the commercially available metal centered phthalocyanines are not a viable avenue for replacing lead in minimum smoke propellants.

5.5. Incorporation of Down Selected Bismuth Salt Candidates into Propellant

5.5.1. Metal Salt Paste – Bismuth Salts

Metal salt pastes were made of each of the 5 bismuth salt candidates, bismuth oxide carbonate, bismuth citrate, bismuth nitrate oxide, bismuth oxide and bismuth subnitrate since each of them passed thermal stability and compatibility. Initially, all pastes were made with the same weight percent of bismuth salt as in a standard lead salt paste. The chelating molecules used in these salts have less mass than phthalocyanine so, it therefore occurred that more bismuth was put into the paste than metals previously used in these tests. It can be seen from the data in Table 8 that bismuth citrate was the only candidate in this series that had less bismuth in the final propellant than a standard lead salt based propellant mix. It can also be seen that adding the same amount of bismuth oxide carbonate and bismuth oxide yield a significantly higher amount to bismuth in the propellant.

Table 9) Bismuth level Calculations in Propellant

Bismuth Salt	MW (AMU)	# Bi Ions	% Bi as compared to Pb	Mix Number
Bismuth Oxide Carbonate	509.97	2	1.30	1BPS-10612
Bismuth Citrate	398.08	1	0.83	1BPS-10610
Bismuth Nitrate Oxide	286.98	1	1.16	1BPS-10613
Bismuth Oxide	465.96	2	1.42	1BPS-10611
Bismuth Subnitrate	1461.99	5	1.13	1BPS-10614

5.5.2. Mix viscosity

It is noted that the bismuth salt, triphenyl bismuth (TPB) is used in this propellant formulation as a cure catalyst; it is present in very small amounts in this particular formulation for that purpose. Therefore, pot life was of concern with regards to adding non-trivial amounts of bismuth salts to the mix. The standard for pot life at ABL is described as being below 5kp at 1 sec^{-1} for several hours. Viscosity data from the five mixes shows that mixes made with bismuth salts varied with the salt added, see Figure 45. The mix containing bismuth oxide, 1BPS-10611, displayed a rapid increase in viscosity at 2 hours after the end of the mix. Mix 1BPS-10614, containing bismuth subnitrate also showed an increase in viscosity after 5 hours. The other 3 mixes displayed only slight increases over a 6 hour period.

A second set of pastes were made from bismuth nitrate oxide and bismuth subnitrate. Two of the mixes made from these pastes (1BPS-10792 and 1BPS10794) were repeats of 1BPS-10613 and 1BPS-10614 while mixes 1BPS-10793 and 1BPS10795 contained the same amount of their respective pastes but also had a replacement of 5% of the AN with the bismuth nitrate salt that was in the paste for that particular mix. Table 10 contains bismuth levels for each of the mixes. Viscosities of these four mixes are presented in Figure 46. It can be seen from this data that only mix 1BPS-10795 had a viscosity close to that considered acceptable to ABL Operations.

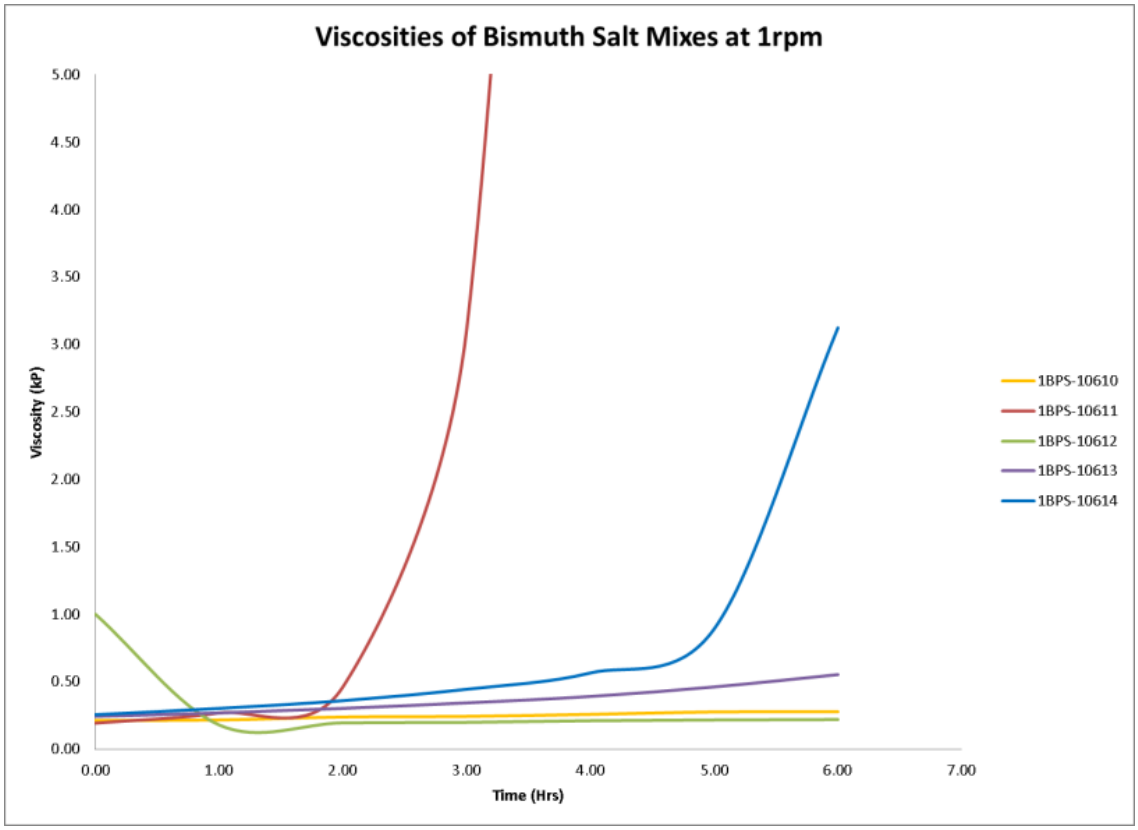


Figure 45) Viscosities of Bismuth Salt Mixes

Table 10) Alternate Bismuth Salt Mixes

Mix Number	Bismuth Salt	Extra Bismuth Salt Addition
1BPS-10792	Bismuth Nitrate Oxide	0
1BPS-10793	Bismuth Nitrate Oxide	+5%
1BPS-10794	Bismuth Subnitrate	0
1BPS-10795	Bismuth Subnitrate	+5%

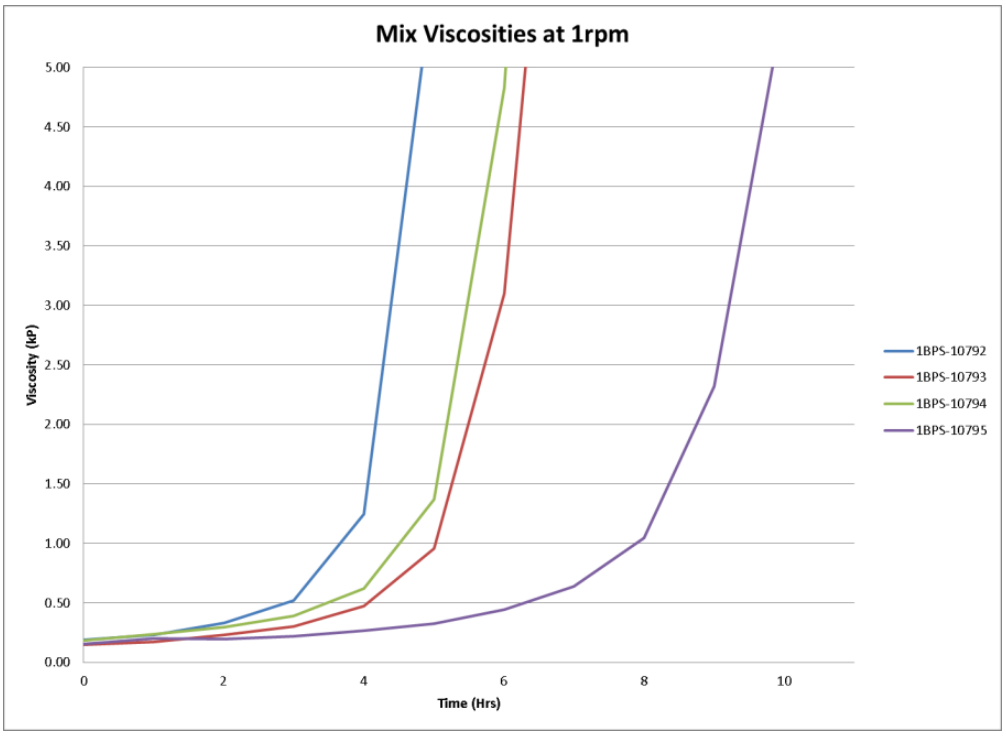


Figure 46) Viscosities of Alternate Bismuth Salt Mixes

5.5.3. Mechanical Properties

Table 11) Mechanical Properties of Various Bismuth Salt Mixes

Mix Number	Metal-Pc	Stress (psi)	Strain (Max) (%)	Strain (Failure) (%)	Modulus (psi)
	Lead Salt	197	49.1	49.1	452
1BPS-10610	Bismuth Citrate	206	61.9	61.9	389
1BPS-10611	Bismuth Oxide	195	55.4	55.4	394
1BPS-10612	Bismuth Oxide Carbonate	202	57.4	57.4	389
1BPS-10613	Bismuth Nitrate Oxide	195	59.6	59.9	380
1BPS-10614	Bismuth Subnitrate	181	55.2	55.2	378
1BPS-10792	Bismuth Nitrate Oxide	174	50.1	50.1	370
1BPS-10793	Bismuth Subnitrate	174	53.1	53.1	337
1BPS-10794	Bismuth Nitrate Oxide	NA	NA	NA	NA
1BPS-10795	Bismuth Subnitrate	NA	NA	NA	NA

Tensile strength specimens were tested in the same manner as propellants previously analyzed in this study. Data for all the bismuth salt mixes and the standard mix with lead salt (1BPS-10518) are presented in Table 11. It can be seen from this data that there is not a significant difference in the mechanical properties of the first five mixes. However there is a non-trivial reduction in modulus and stress in the two mixes made with the bulk paste. No data was available for the two mixes made with the bulk paste and the additional bismuth salt because insufficient propellant was cast. Even though a standard size pint mix was made, not all of the propellant cast out of the mix bowl into the cure container due to rapidly increasing viscosity. Since this is primarily a burn rate study, it was elected to use the available propellant for burn rate testing instead of mechanical properties.

5.5.4. Burn Rate Properties

Burn rate data on the bismuth salt mixes was taken in the same manner and under the same parameters as previous mixes in this study.

Table 12) Burn Rate Comparison of Bismuth Salt Paste Mixes at 1000 psi

Mix Number	Ballistic Modifier	r_{1000} (in/sec)
	Lead Salt	0.354
1BPS-10610	Bismuth Citrate	0.244
1BPS-10611	Bismuth Oxide	0.244
1BPS-10612	Bismuth Oxide Carbonate	0.246
1BPS-10613	Bismuth Nitrate Oxide	0.240
1BPS-10614	Bismuth Subnitrate	0.243
1BPS-10792	Bismuth Nitrate Oxide	0.243
1BPS-10793	Bismuth Subnitrate	0.246
1BPS-10794	Bismuth Nitrate Oxide	0.265
1BPS-10795	Bismuth Subnitrate	0.254

Table 12 displays the burn rate data at 1000psi for all of the mixes made with bismuth salt based pastes. It can be seen from this data that, as with the phthalocyanine based propellants, there is a decrease in the burn rates of the bismuth salt paste propellants as compared to the standard lead paste propellant at 1000 psi. One can also see that there is very little variation in the burn rates among the various bismuth salt propellants regardless of the concentration of metal ion in the propellant with the exception of 1PBS-10794 and 1BPS-10795. These two mixes displayed a positive correlation between additional bismuth salt and higher burn rate. However, this is a small gain for a non-trivial exchange of bismuth salt, an ingredient which would make smoke, in place of ammonium nitrate which doesn't.

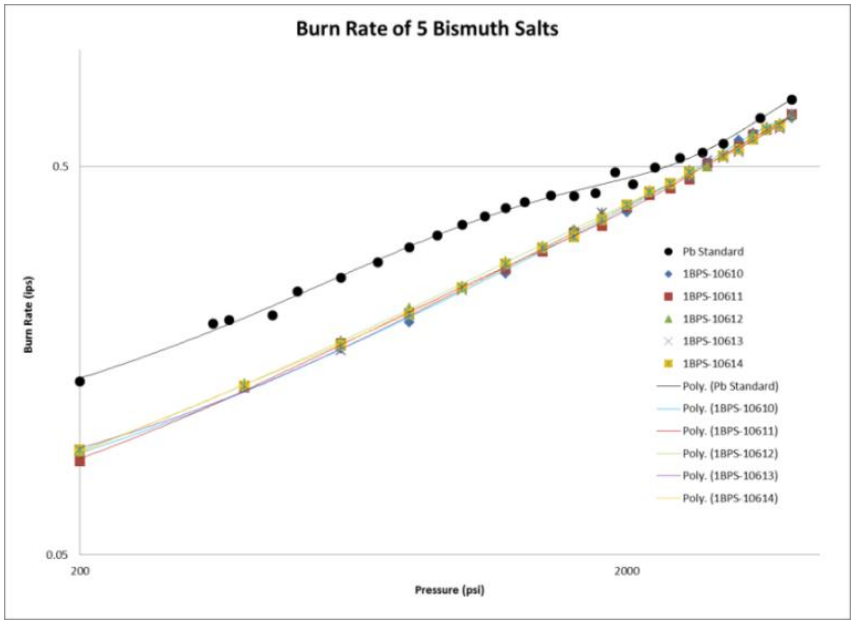


Figure 47) Burn Rate Data of 5 Bismuth Salt Mixes

As compared to the same formulation with lead salt (See Figure 36) all of the burn rates from the 5 bismuth salt mixes displayed a virtual straight line (See Figures 47 and 48). Any evidence of a saddle in these burn rates is insufficient to determine if it is a true saddle or scatter in the data. One effect of the bismuth salts was the lowering of the burn rate from the lead based standard. The amount by which the rate was lowered varied between bismuth salt and pressure. Overall average decrease in burn rate for the 5 bismuth salt mixes was approximately 10%.

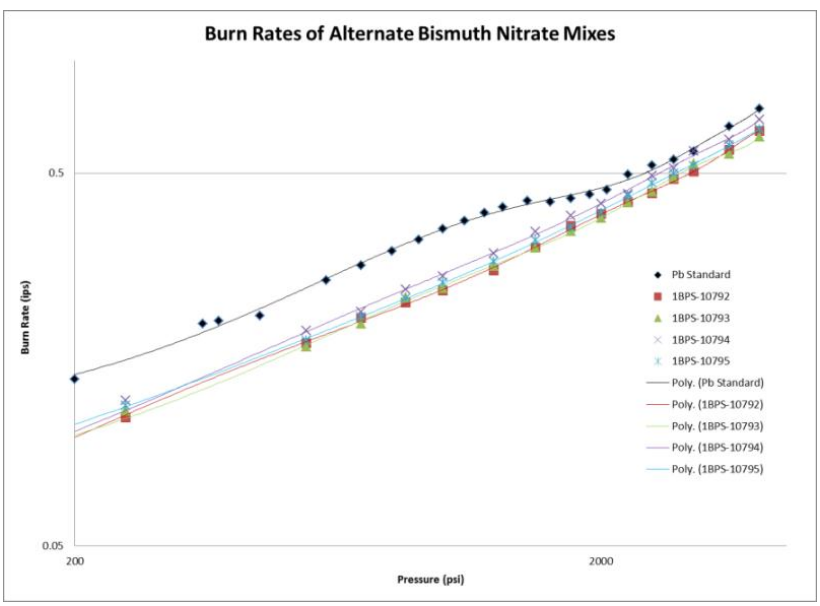


Figure 48) Burn Rate Data of Alternate Bismuth Nitrate Mixes

Burn rates of the final four mixes do not appear to be noticeably different from those of the initial mixes. No significant saddle is detected even in the two mixes which had a replacement of 5% AN with a 5% free replacement of bismuth salts. Due to the absence of ballistic modification with the bismuth containing propellants, no work was performed on service life of these compositions.

6. Conclusion

The purpose of this project was to investigate the possibility that by using an extensive organic chelating molecule, the negative characteristics of certain metals with regards to propellant pot life and service life might be mollified or blocked. The organic chelators chosen for this project were from the prophyrin/porphyrazin family, phthalocyanines. Several of the commercially available metal centered phthalocyanines passed screening tests and were incorporated into a difficult to ballisticly tailor propellant formulation. It was found from these tests on stabilizer depletion, mechanical and burn rate properties that the metalo-phthalocyanine compounds did not perform as expected. As compared to the same formulation containing a lead based ballistic modifier, the metalo-phthalocyanine modified propellants displayed shorter service life, lower burn rates and in some instances reduced tensile properties.

Several bismuth compounds were also investigated for their effects on propellant burn rate. Although all bismuth candidates passed the same screening tests that the phthalocyanine molecules were subjected to, and some bismuth compounds had useable pot lives as well as near equivalent physical properties, they did not have burn rates as high as that of propellant with lead as a ballistic modifier nor did they have the desired saddle at about 1000 psi.

This work demonstrates, that within this scope, that the chelating organic compound does not influence burn rate or other properties relative to propellant processing or characteristics. Future work can be directed to finding a metal ion substitute for lead regardless of its processing or effects on propellant properties and then encase it entirely in an organic structure such that it could not affect the propellant until the pressures and temperatures of combustion released it.