Industry Best Practices & Lessons Learned
CAD/PAD Propellant Manufacturing

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PAD Propellant History

- Since the late 1950's the principal method for the formulation and manufacture of composite Propellant has been to use liquid polymer resin crosslinked to become a filled viscoelastic solid.
- There has been an evolution of propellant binders which have included, and have evolved from: PBAN, PBAA, polyester, polyurethane, Butarez CTPB, among others.
- Each of these binder systems brought with it benefits that made it attractive, and manufacturing process issues that had to be resolved.
- HTPB is the latest polymer in this evolution of and it is the current primary choice for production solid propulsion applications.
- HTPB also brings with it issues that must be addressed.

Butarez CTPB Replacement

- Butarez CTPB has been qualified for use in PAD applications since the 1960's.
- The production of Butarez CTPB ceased in the late 1990's.
- Alternatives to the Phillips Butarez CTPB have not been as successful, nor as widely adopted, i.e., HC-434.
- Efforts to replace the Phillips Butarez CTPB with another polymer have focused on HTPB.
- The HTPB is not a direct substitute for CTPB:
  - It requires a bonding agent to improve adhesion to the solid AP crystals
  - It requires a different approach to ingredient introduction in the mix
  - It is often not as forgiving of process variations

CTPB and HTPB Composites

- While CTPB and HTPB are both polybutadienes they have some fundamental differences that preclude using them interchangeably.
- The CTPB is generally cured with a trifunctional epoxy, sometimes in conjunction with BITA (HX-868).
- The HTPB is generally cured using an isocyanate, but unlike the CTPB, it has a low affinity for the solid Ammonium Perchlorate oxidizer particles and thus requires a bonding agent for the AP oxidizer, to reinforce the material.
- The main reason that HTPB has supplanted other binders is that its lower viscosity allows for higher solids loading and greater I_{SP}, along with its general commercial availability.

Best Practices: Processing PAD Propellants

- The purpose of this presentation is to provide extensive lessons learned information to the energetics community for what are considered industry best practices in order to achieve reproducible, predictable composite propellant, with low variance in both mechanical and ballistic properties, particularly for HTPB-based PAD propellant formulations.

- It should be noted that a number of these process optimization steps are applicable to generating good and reproducible propellant regardless of the type of binder being used.

Best Practices: Process Control

- Whether you are involved with production of an existing rocket motor, or you are developing a new propellant for a new rocket motor application, or a replacement propellant for an old rocket motor design, good process control and proper manufacturing documentation are critical to achieving a reproducible product with low process variation.

- Key elements of propellant manufacturing process control are:
  - Temperature and Humidity Control
  - Propellant Ingredient Control
  - Mix Addition Cycles Optimization
  - Propellant Cure Cycle Optimization

Best Practices: Process Control

- Temperature and humidity control in the propellant processing area is essential in order to achieve consistent results.

- Lack of proper temperature and humidity control can adversely affect propellant viscosity, cure, strength, and process predictability.

Best Practices: Process Control

- Liquid ingredient containers should be purged with dry nitrogen or argon and be securely sealed after use.

- Air in the head space of the container can cause the polymer to homopolymerize.

- This can result in incomplete mixing, X-ray indication of foreign material or voids, and potential stress risers.

Results of Homopolymerized R-45M

Gel spot found in AP/HTPB Propellant Grain

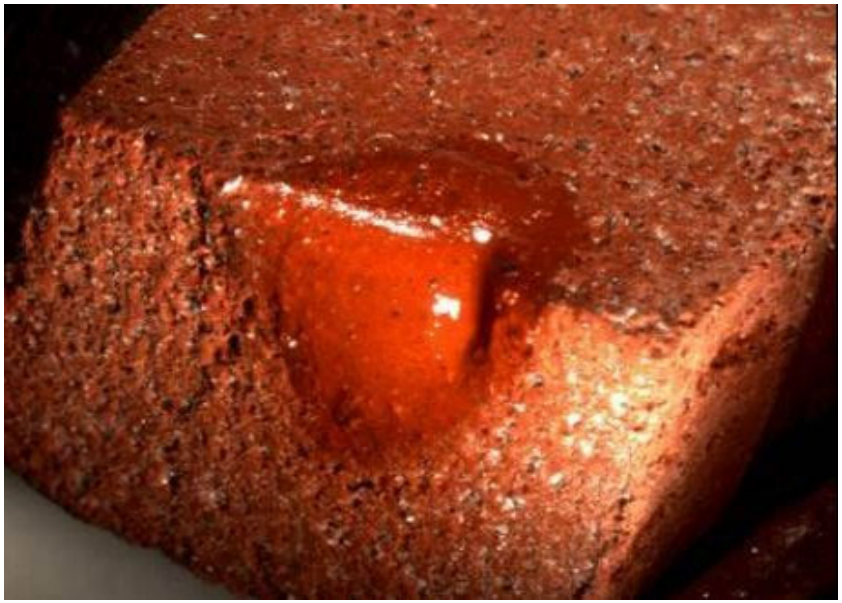


Photo Credit: NSWC IHD, Dept. E

Homopolymerized Droplet of R45M

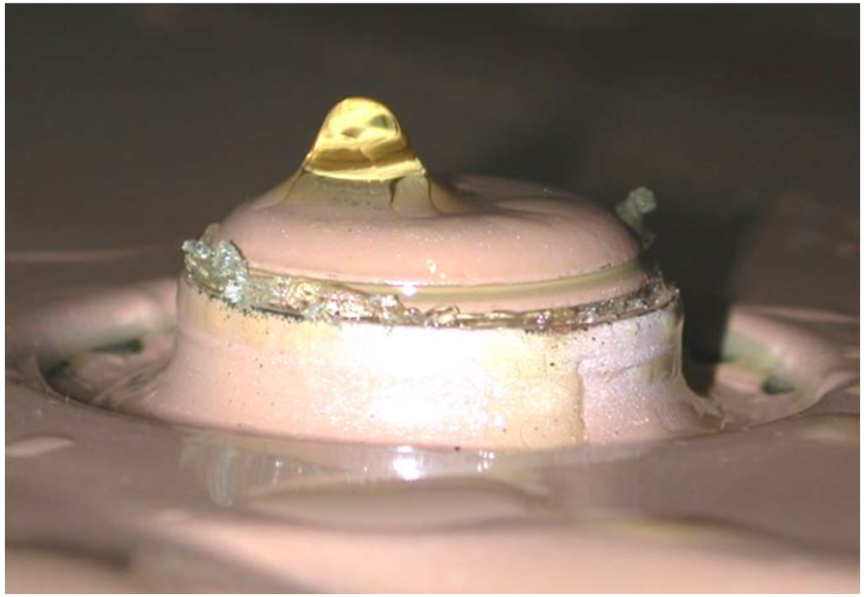


Photo Credit: NSWC IHD, Dept. E

Propellant Ingredient Control

- Use only ingredients of known pedigree purchased from approved vendors.
- Ingredients must meet their individual specification requirements.
- Ensure ingredients have been stored and handled properly.
- Ensure that ingredients have been re-tested as necessary, within a specified time frame.

Propellant Mix Cycles

- In our collective experience, the "best" mix cycle(s) are not necessarily the ones that result in the shortest mix time.
- We have found that the "best" mix cycle(s) are those that yield the best and most consistent propellant properties.
- Optimizing the Takt time (reducing the mix time to a minimum) for the propellant manufacturing process can often result in a false economy from a systems level perspective.
- The entire propellant mixing process must be looked at in terms of overall process/system optimization.

Propellant Mix Cycles

- The "best" mix cycle(s) could mean:
  - Mix propellant entirely under vacuum.
  - Polymer, plasticizer, antioxidant, ballistic modifiers, fuels, added early.
  - Coarse particle oxidizer mixed in first.
  - Finer particle oxidizer mixed in incrementally.
  - Mix-to-minimum viscosity.
  - Verify with viscosity reading at different shear rates
  - Curatives added as last addition.

Mechanical Properties

Optimized propellant mechanical properties can be obtained by following these established Best Practices, based upon extensive lessons learned:

- Optimize the solid oxidizer particle packing fraction
- Mix-to-minimum viscosity before curative addition.
- Add curatives at decreased temperatures to preclude premature cure reaction and allow sufficient time for post-mix operations.
- Mix entirely under vacuum.
- Cure to a constant shore A durometer hardness.

Optimizing Oxidizer Particle Size Fit Can Improve Mechanical Properties

Optimizing the oxidizer particle size fit using tapped bulk density testing can aid in improving propellant mechanical strain capability by freeing up more available binder in the propellant matrix, and assuring that there is adequate binder in the interstitial spaces between the solid oxidizer particles

Consider the following:

- 10/1 ratio of particle size coarse/fine is generally optimum.
- 70/30 percentage ratio of coarse/fine is generally optimum.

Packing of Spheres and Its Effect on Viscosity

Do Ik Lee
The Dow Chemical Company

- The idealized packing of binary mixtures of spheres has been constructed as a function of diameter ratio and composition on the basis of experimental data in the literature.

- An analytical method has been developed to calculate the packing of n-component mixtures of spheres using the idealized packing of binary mixtures.

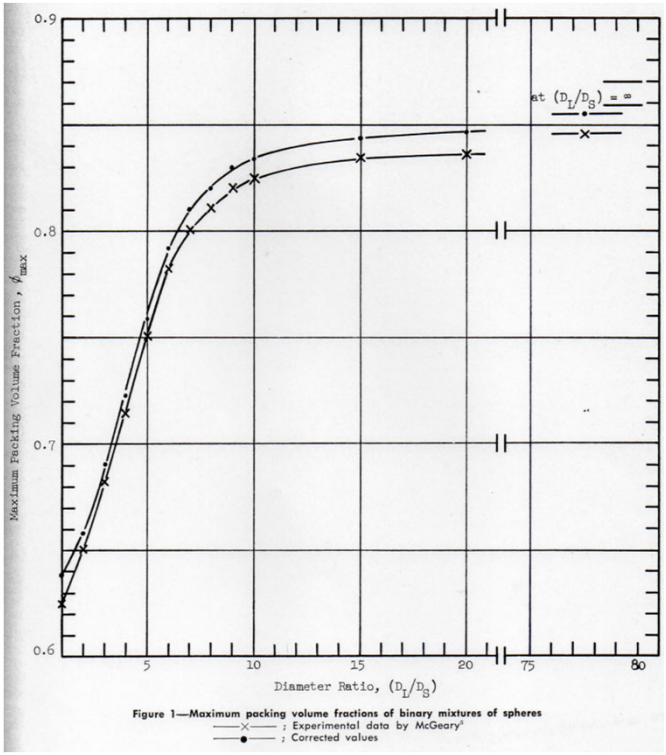


Figure 1—Maximum packing volume fractions of binary mixtures of spheres
—×— ; Experimental data by McGeary[5]
—●— ; Corrected values

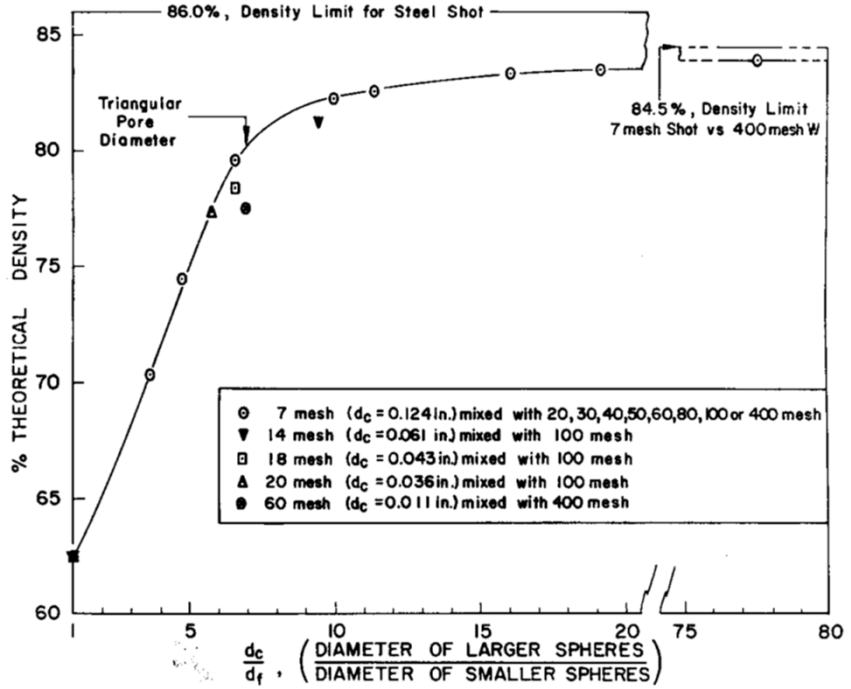
Mechanical Packing of Spherical Particles

R. K. McGeary

Nuclear Materials and Equipment Corporation, Apollo, Pennsylvania

An idealized experimental study of particle packing was made. Spherical metal shot of several discrete, narrow size ranges was efficiently packed in glass containers by mechanical vibration. Packing arrangements and the dynamic process of packing were studied visually. One-size spheres packed in an orthorhombic arrangement with a density of 62.5% of theoretical density. Forming of high-density multicomponent packings was shown to require at least a sevenfold difference between sphere sizes of the individual components. A quaternary packing with a density of 95.1% of theoretical density was formed from spheres with diameter ratios 1:7:38:316 and volume compositions 6.1:10.2: 23.0:60.7% respectively. Such packings could be poured from their glass containers, thus proving that effective mechanical packing is simply an efficient arrangement of spheres of prescribed sizes and proportions. The significance and utility of this work to the ceramic and other industries is discussed.

Maximum observed packing of some binary mechanical mixtures of spheres.



Optimizing Oxidizer Particle Size Fit

Tapped bulk density can be measured by:

- Blending a small amount of each of the solid ingredients in their proper ratios per the proposed formulation.
- Pour a known amount into a test tube (or graduated cylinder).
- Tap or drop/bounce the test tube onto a surface from a known height (1 or 2 inches) several times. Testing must be performed the same way on all samples.

Optimizing Oxidizer Particle Size Fit

Tapped bulk density can be measured by (cont.):

- Measure the column height of the material in the test tube.
- Repeat the test for other coarse/fine ratios planned. The samples with the lowest column height would be the highest bulk density and should yield the lowest viscosity and greatest strain capability.
- A shaker table with appropriate fixturing may also be utilized for testing.

Optimizing Oxidizer Particle Size Fit

Tapped bulk density samples from LabRAM test mixes of a propellant processed to define the optimum lead nitrate particle size. Please note that Sample "C" has the highest bulk density.

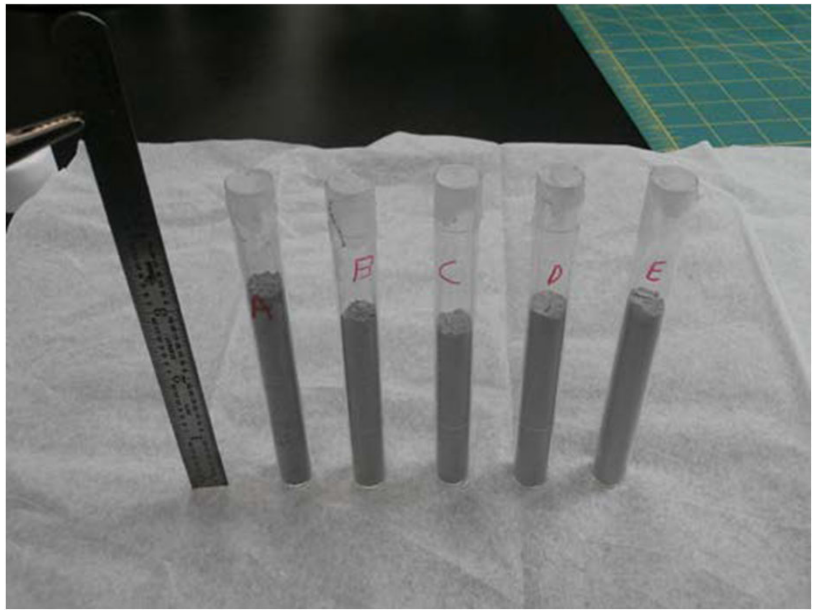


Photo Credit: NSWC IHD, Dept. E

Optimizing Oxidizer Particle Size Fit

Optimized oxidizer packing fraction i.e., the highest bulk density solids loading, yielded the first mix of this propellant formulation demonstrating within specification cold strain mechanical properties in over 10 years.

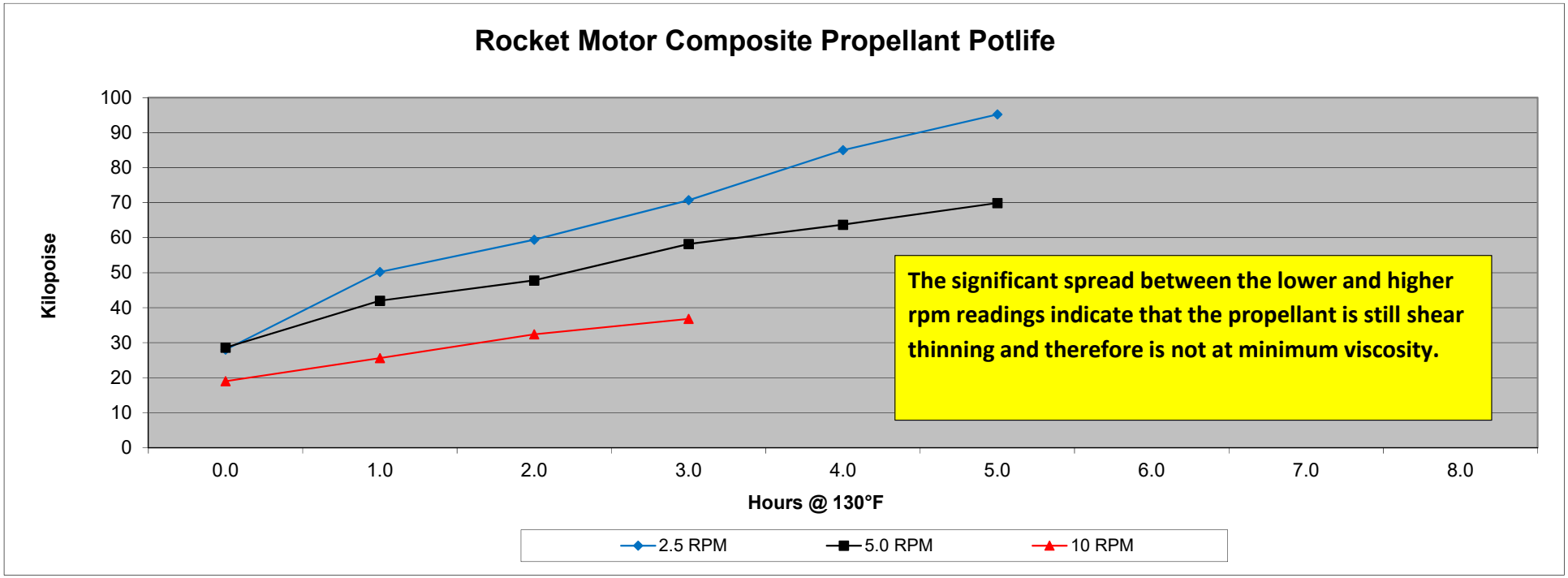
- Accurate particle size measurement is critical, using a defined grind code can often be more accurate than using potentially confounded PSA measurements.
- Any changes in particle size or bulk density to modify the amount of free binder will also likely affect the propellant burning rate.
- There needs to be a trade-off between optimizing the mechanical properties of the propellant, while also maintaining the proper ballistic properties.

Best Practice: Mix-to-Minimum Viscosity

- Lower mix viscosity results in greater propellant strain capability
- Better mix-to-mix reproducibility and lower variance.
- Verify with viscosity measurements before curative addition
  - Measure at 3 speeds (shear rates) to ensure that propellant is not continuing to demonstrate shear thinning and is in fact at minimum viscosity, i.e., additional mixing will not lower the viscosity any further, it is as well mixed as it can be.
  - Curative should be added at reduced temperature to delay onset of cure

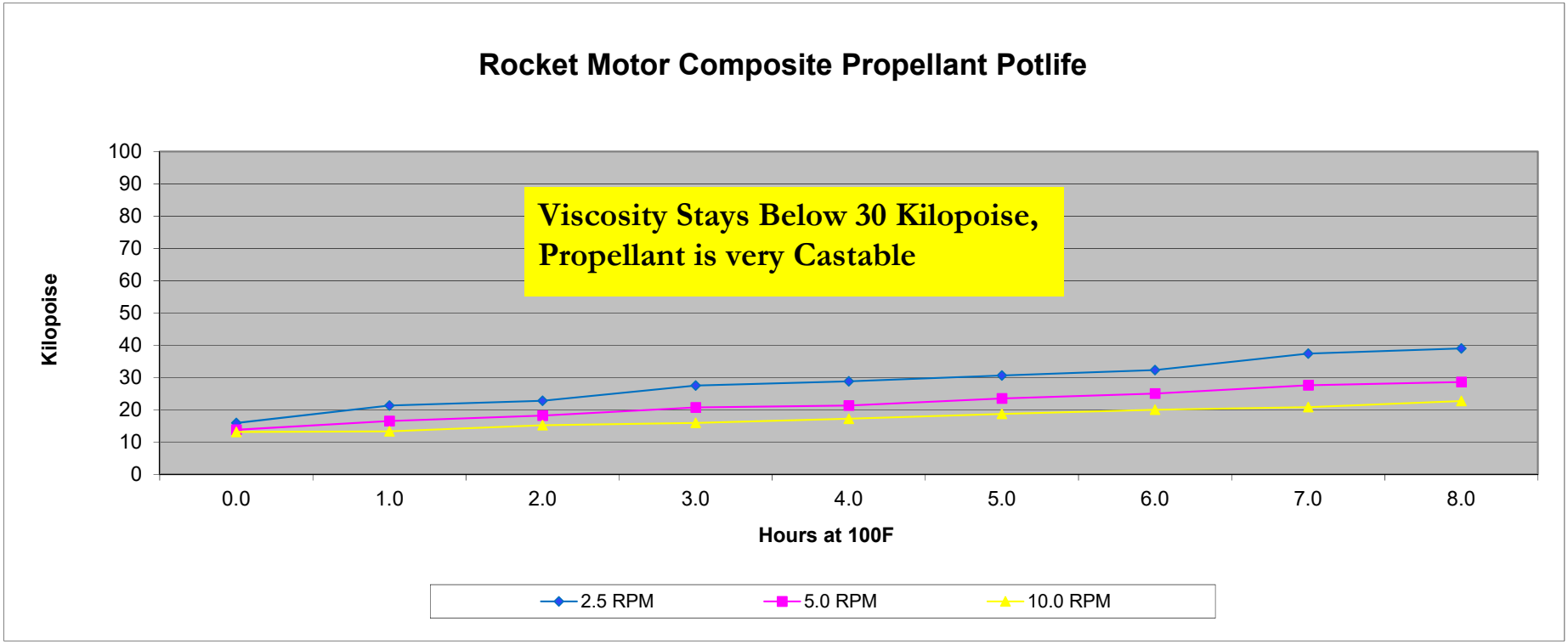
Best Practice: Mix to Minimum Viscosity "Long and Cool"

Composite PAD propellant Viscosity versus Time prior to the introduction of "Long and Cool" mix-to-minimum viscosity process



Best Practice: Mix to Minimum Viscosity "Long and Cool"

Composite PAD propellant after introduction of "Long and Cool" mix process.



Best Practice: Mix Process Comparison

Initial Mix Process	Mix-to-Minimum Viscosity "Cool Mix" Process
150 Gallon Mix Procedure:	150 Gallon Mix Procedure:
Total mixing time: 215 minutes	Total mixing time: 320 minutes
Avg. Mix Temperature: 150°F	Avg. Mix Temperature: 119°F
EOM Temperature: 130°F	EOM Temperature: 113°F
End-of-Mix Viscosity: 25 kilopoise	End-of-Mix Viscosity: 10 kilopoise

Mix Comparison Showing the Effect of Cool Mixing to Minimum Viscosity (150-Gallon Mix Scale)

Mix	Total AP, %	Coarse/Fine	Fine AP, Part. Size	EOM Temp	EOM Viscosity	E_M @ -65°F	S_M @ 165°F
Mix A	81.35	31/69	36.9µm	125°F	**25.0 Kps**	**11.8%**	139.9 psi
Mix B	81.35	31/69	35.8µm	113°F	**9.9 Kps**	**16.4%**	120.3 psi
MIL-DTL-32124						8% min.	49 psi min

Note the Benefit of improved cold temperature Strain Capability achieved with cooler, longer mixing

Best Practice: Vacuum Application

- Powders such as ground AP, will not suck up into the vacuum line if not incorporated into the propellant before pulling vacuum, even though it is not mixed.
- For the powder to be sucked up, it needs to be entrained in air entering and exiting the mixer bowl. With the bowl sealed, there is no entrainment.
- A short cycle without vacuum to "wet" powders entrains air into the mix which may or may not be totally removed.
- If air is not completely removed from the propellant, it could accelerate oxidative hardening as it ages.
- At the start of each cycle pull vacuum to 30-40 mm and start mixing action. Full vacuum should be <5mm at the end of each cycle.

Best Practice: Burning Rate Control

For a given formulation, burning rate can be predicted and/or adjusted based upon the specific surface area of the oxidizer and/or the particle size and amount of the smallest oxidizer cut.

However, even minor formulation changes intended to achieve a certain goal will affect other parameters.

- For example, increasing the specific surface area of the oxidizer to increase burning rate may also increase viscosity and decrease strain capability.

Best Practice: Cure to Constant Shore "A"

- Monitor the propellant curing via Shore "A" durometer hardness readings and leave the propellant in the curing oven until constant hardness readings are obtained.
- Cure times at a given temperature may vary from mix to mix with fluctuations in oven temperature as well as with new lot sets of ingredients.
- Cure times could also vary based on other items or material in the oven.

Industry Best Practices Summary

- Maintain good process control of ingredients, processing, and processing area.
- Remove air before incorporating powders
- Document all aspects ingredient preparation, mixing, casting, and curing.
- For development efforts, limit the number of variables in the mix.
  - Multiple variables can produce unexpected results which can lead to incorrect decisions.
- Always mix the propellant to minimum viscosity, at a reduced temperature, to obtain optimized, low-variation propellant mechanical and ballistic properties.
- Cure to a constant Shore "A" durometer hardness.