“Continuous Processing of Black Powder”

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Abstract

The formulation and processing technology of black powder has changed little since its discovery by the Chinese over a thousand years ago. This paper outlines various tasks involved in the development of a new formulation along with a novel continuous processing technology for the state-of-the-art manufacture of black powder. These tasks included Thermo Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) analysis, and the characterization of various material functions including temperature, wall shear stress dependent shear viscosity, extrudate swell, flow instability and wall slip behavior of the black powder formulation, the simulation of the coupled flow and heat transfer occurring in the twin screw extruder, the design of the die employing FEM calculations, and validation experiments using a thermal imaging camera and a well-instrumented twin screw extruders. Using these characterization and simulation capabilities, the new manufacturing process for the live reformulated black powder formulation was successfully demonstrated over a relatively short duration of time.
**Introduction:**

The main ingredients of the black powder formulation are charcoal, sulfur, and potassium nitrate, KNO₃. The formulation and processing technology for black powder are dated and have changed little over the last millennium. Here we have targeted the development of both a new formulation and processing methodology for the black powder. The conventional processing methodologies that are currently utilized are precarious and prone to incidents and have given rise to significant loss of life and property over the years. The basic steps of the project involved characterization of the existing black powder formulation, development of a modified black powder formulation, characterization of the rheological and thermal behavior of the conventional and live reformulated black powder formulations, development of a processing simulant for the live reformulated black powder suspension, mathematical modeling of the processes using both the simulant and the live reformulated black powder formulations, and finally the processing of both live reformulated black powder and simulant formulations using twin screw mixing/extrusion. The overall thrust is to demonstrate the new manufacturing technology base for black powder.

**Materials and Formulation**

The particle size distributions of the ingredients of the black powder formulation are of interest. These distributions need to be studied carefully since the flow and deformation behavior of the live reformulated black powder formulation will depend on the size distributions of the particles. A Scanning Electron Microscope (SEM) is used to determine the size distributions of the all ingredients.
Particle Size Distribution of the Individual Ingredients:

An SEM examination was made of the three black powder ingredients listed below. The samples examined were:

- Charcoal unsieved A-A-59138 Class D
- Charcoal sieved A-A-59138 Class D
- Potassium Nitrate 010 1486 oxidizer S-1 and Sulfur lot # S-3-115 Service Chemical Inc.

A LEO 982 digital scanning electron microscope was used and samples were sputter coated for 10 seconds with gold and examined using a 1 kV electron beam. The SEM images are shown in Figures 1 through 9.

Charcoal: The size of most unsieved charcoal particles was in the range of 2 – 200 microns, as seen in Figures 1-2. Few particles were seen in the 120 – 200 micron size range (Figures 1-2). Many were observed in the 10 – 50 micron size range and few were observed below 5 microns. Larger particles exhibit a characteristic structure consisting of hollow channels running along the generally longer dimension of the particles (see Figure 2). This structure is less evident, but still prevails, when the charcoal is reduced to smaller particle sizes (Figures 3-5). SEM images of sieved charcoal show particles, which range in size from about 2 – 45 microns (Figures 3-5). This material was not sputter coated and images were obtained at 2 kV on the same instrument as described above. The charcoal was sieved through a USA standard testing sieve ASTME-11 specification No. 325 with 45 micrometer opening. In subsequent work only the sieved charcoal was used in our formulations.
**Potassium Nitrate:** As shown in Figures 6-7, most of the potassium nitrate particles were in the 5 – 150 micron size range and the particles appear roughly spherical in shape (low aspect ratio). Many were observed to fall in the size range of 60 – 70 microns. There is some agglomeration evident, since at higher magnification their structure was seen to consist of one or more attached globules of material.

**Sulfur:** As seen in Figures 8-9, particles were observed to be in the size range of <1 – 60 microns. Particles are roughly spherical or equiaxed in shape and distributed throughout the size range indicated above.

**Behavior of Traditional Black Powder:**

The small amplitude oscillatory shear behavior of the typical currently commercially available conventional live black powder formulation was characterized first. The typical currently-available conventional black powder formulation appears to exhibit relatively high elasticity as revealed by the relatively high values of the storage modulus, G’ (Figures 10-11). Time scans were continuously necessary to follow the changes in the moisture content of the black powder. The non-Newtonian character of the slurry is shown by the decreasing magnitude of the complex viscosity with increasing deformation rate (Figure 12). Overall, it was determined that the currently available conventional live black powder remained as slurry, which led to almost immediate segregation of the water phase from the conventional live black powder upon pressurization. This behavior was clearly demonstrated with capillary flows and persisted even at the lowest length over the diameter ratio dies that were used in capillary flow (L/D=1). Thus, the conclusion that the black powder formulation as it
currently exists cannot be twin screw extruded without modification of the formulation. Upon reformulation the black powder formulation behaved as a viscoelastic suspension, which is able to sustain its shape upon exiting from a die. The rheological behavior of the live reformulated black powder was next evaluated.

**Rheological Behavior of Reformulated Black Powder and its Processing Simulant:**

The typical frequency sweep of the reformulated live black powder formulation is shown in Figure 13. The formulation remains in the linear region up to a strain of about .3%. The evaporation of the moisture was a significant issue and required that the moisture content of the live reformulated black powder formulation be determined periodically using thermo gravimetric means. The formulation appears to exhibit relatively high elasticity as revealed by the relatively high values of the storage modulus, G’ (Figure 13). The non-Newtonian character of the slurry is further indicated by the decreasing magnitude of the complex viscosity values with increasing deformation rate. The black powder formulation behaved as a viscoelastic suspension, which is able to sustain its shape upon exiting from a die (Figure 14). This is an important finding and indicated that the black powder formulation can likely be processed using a continuous processing technology.
Processing Simulant Development:

Simulants are necessary to test the mathematical models of the process, and the processing equipment and procedures prior to the use of the live formulations. We identified two powders as inert simulants for KNO₃. These are the sodium chloride, NaCl and ammonium chloride, NH₄Cl. Among these NaCl provided a better density match and NH₄Cl provided a better solubility match. During the mulling operation when water is added to the formulation the temperature of the material is suggested to be in the range of 16 °C to 49 °C. Both KNO₃ and NaCl can be crushed under similar conditions. We decided that NaCl be used as the simulant for KNO₃. A commercial grade of salt, which is about 30 microns in size, was procured. Figures 15 and 16 compare the small amplitude oscillatory shear behavior of the processing simulant versus the live reformulated black powder formulation. The dynamic properties of the simulant with the live reformulated black powder formulation could be matched upon the use of slightly different levels of water in the simulant formulation (Figure 16). Figure 17 shows the thermo gravimetric analysis of the simulant versus the live reformulated black powder formulations. The results indicate that the water loss characteristics of the simulant match the behavior of the live reformulated black powder formulation also.
Twin Screw Mixing/Extrusion Runs with the Simulant:

The simulant formulation was run first with a 50.8 mm Baker Perkins fully-intermeshing co-rotating twin screw extruder (Figure 18-20). The screw configuration involved multiple mixing zones, devolatilization and pressurization sections. Typical pressure traces collected during different runs are shown in Figure 21. The ability to twin screw extrude the formulation validated the formulation and manufacturing methodology development efforts. The temperature distributions of the strands emerging out of the twin screw extrusion process were determined using an Inframetrics thermal imaging camera (Figure 22) to facilitate the comparisons of the experimental results within the simulation results. Coming to dead stops with the twin screw extruder allowed the characterization of the degree of fill in the extruder (Figures 23 and 24).

Rheological Behavior of the Live Reformulated Black Powder Formulation and its Extrudability:

The capillary flow behavior of the simulant and live reformulated black powder formulation is shown in Figures 25-28. The strands of the live reformulated black powder formulation could indeed be formed under various shear rate at the wall conditions, as shown in the inserts of Figure 27. There were some pressure oscillations associated with changes in the water content of the formulation as a function of time during extrusion, as demonstrated for the simulant of the black powder in Figures 25 and 26. However, relatively stable extrusion of the strands for both the simulant as well as the live reformulated formulations was possible.
Figure 28 indicates that the live reformulated black powder formulation exhibits significant wall slip, as indicated by the dependence of the flow curves on the surface to volume ratio of the capillary used. The smaller the surface to volume ratio (the greater is the diameter at constant length over the diameter ratio) the greater is the wall shear stress necessary to extrude the black powder formulation at a given flow rate, as shown in Figure 28. The wall slip behavior of the live reformulated black powder formulation is again demonstrated in Figure 29 using the steady torsional flow. Here a straight-line marker is drawn on the edges of the two disks used in steady torsional flow and the free surface of the suspension sandwiched in between the two disks. One of the discs is stationary and the other is rotated at constant angular speed. As shown in Figure 29 under the applied shear stress condition there is no deformation of the black powder formulation and the suspension moves like a plug. The wall slip velocity versus the wall shear stress behavior of the black powder suspension was characterized as shown in Figure 30 employing two different techniques involving the Mooney procedure and the solution of the inverse problem in capillary flow for the determination of the parameters of the wall slip behavior.

The effect of the wall slip on the development of the flow field in die flows is shown in Figure 31, where the ratio of the volumetric flow rate due to wall slip, i.e., the slip velocity times the cross-sectional area for flow Qs over the total volumetric flow rate, Q is given. This Qs/Q ratio represents the importance of wall slip and indicates that at relatively low wall shear stress values the flow is plug flow and wall slip controls the flow development. On the other hand, as shown again in Figure 31 as one
increases the wall shear stress the effect of wall slip in shaping the flow field decreases as suggested by the decreasing Qs/Q values. The flow curves were corrected for wall slip and Figure 32 shows the fitted shear stress versus the shear rate behavior, i.e., the flow curve of the live reformulated black powder formulation in conjunction with a Hershel-Bulkley type viscoplastic constitutive equation. The wall slip behavior and the temperature-dependent parameters of the Hershel-Bulkley equation (along with the specific heat capacity, density and thermal conductivity) are sufficient for the mathematical modeling of the coupled flow and heat transfer occurring in the twin screw extruder and the die flows.

**Typical Simulation Results: Pressurization Section:**

The live reformulated black powder formulation had to be processed in a Baker Perkins 40 mm twin screw mixer/extruder, located at the US Army, RDECOM-ARDEC, Picatinny Arsenal, NJ. In this twin screw extruder there is a pressurization section prior to the die, which consists of two screws, which are configured side by side to divide the flow into two and provide pressurization with no interchange of materials between the two screw sections. This pressurization section is shown in Figure 33. One of the critical aspects of the twin screw extrusion process development was to assure that these single-screw based pressurization sections could deliver the targeted mass flow rate at the pressure necessary to overcome the pressure drop at the die. The typical FEM mesh used and typical simulation results for the pressurization section of the BP extruder are shown in Figures 34-36. The typical FEM mesh used for the simulation of the flow in the pressurization section is shown in Figure 34, the pressure distribution for 100 rpm with a lead of 0.027m is
shown in Figure 35 and the corresponding shear rate distribution over the cross-sectional area available for flow in the single screw extruder is shown in Figure 36. There is leakage through the flight clearances and the highest shear rates are observed over the clearances between the tip of the flights and the barrel. Figure 37 shows the typical summary of the simulation results that were obtained. Here the mass flow rate through the pressurization section of the extruder is plotted versus the screw rpm for various degrees of fill. The screw lead is the actual screw lead of the single-screw based pressurization section, which is 0.02706 m. The number of leads here indicates the number of leads, which is full with the live reformulated black powder formulation. The results can be summarized as follows:

1. The degree of fill in the extruder decreases with increasing screw rotational speed.

2. The degree of fill in the pressurization section of the extruder increases with increasing mass flow rate. The pressurization rate of the extruder increases with decreasing mass flow rate.

3. These results suggested the conclusion that to minimize the degree of fill in the pressurization section of the extruder one needs to use a relatively low mass flow rate (the smallest possible under the experimental conditions) and a relatively high screw rotational speed. The only problem area in this approach is that the problem is not linear and as one increases the pressurization capability of the pressurization section of the extruder by decreasing the mass flow rate and increasing the screw rotational speed, the same conditions give rise to relatively high rates of viscous energy dissipation and thus increasing the temperature of the black powder
formulation, and decreasing its shear viscosity. The decreased shear viscosity undermines the pressurization capability of the extruder and thus the degree of fill in the extruder would increase again with increasing viscous energy dissipation. Thus, the optimum set of conditions needed to be found.

**Redesign of the Pressurization Section of the Extruder:**

The calculations and the validation experiment revealed that a redesign of the pressurization section was necessary to provide the requisite increased pressurization capability. A number of options were considered. Among these the most practical and easy-to-implement was to decrease the lead of the pressurization section of the screw, which changes the helix angle of the screw (decrease), increasing the helical path distance that the black powder formulation will go through and give rise to a reduced axial distance over which the screw is to be completely full. Typical FEM simulation results with a screw lead that is one half of the current lead of the extruder are shown in Figure 38. Here the axial distance indicates the distance over which the screw is completely full versus the mass flow rate. With increasing mass flow rate the degree of fill in the extruder increases. As expected the degree of fill in the extruder is less with this smaller lead in comparison to the degree of fill in the extruder obtained with the previous lead. Typical mathematical simulation results for the die section of the extruder are shown in Figures 39 and 40. The z-velocity distribution at the die suggests that there is a significant plug flow region associated with the viscoplasticity of the black powder formulation. At shear stress values, which are smaller than the yield stress of the live reformulated black powder suspension, the flow is plug flow with no deformation of
the suspension. The pressure drop through the die agrees with the experimentally observed pressure drop.

**Twin Screw Extrusion of the Live Reformulated Black Powder:**

The live reformulated black powder formulation could indeed be processed using the suggested conditions and the geometries. Some typical material distributions in the twin screw extruder obtained upon dead stop of the extruder are shown in Figure 41. Overall, the formulation and the new manufacturing process for the novel black powder formulation could be demonstrated.

**Conclusions**

1. A combination of experimental characterization methods and numerical simulation techniques were applied to develop and demonstrate twin screw mixing/extrusion of a novel black powder formulation.
2. The use of detailed analysis methods prior to the extrusion of the first pound of the live reformulated formulation provided a rigorous assessment of the thermo-mechanical conditions of the energetic material.
3. The continuous process was successfully demonstrated for the new, novel black powder formulation.
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SEM picture of the unsieved charcoal under 500X magnification

Figure 1
SEM picture of the unsieved charcoal under 2000X magnification

Figure 2
SEM picture of the sieved charcoal under 500X magnification
SEM picture of the sieved charcoal under 1000X magnification

Figure 4
SEM picture of the sieved charcoal under 2000X magnification
SEM picture of the KNO₃ under 500X magnification

Figure 6
SEM picture of the KNO$_3$ under 2000X magnification

Figure 7
SEM picture of the Sulfur under 500X magnification

Figure 8
SEM picture of the Sulfur under 2000X magnification

Figure 9
Conventional black powder formulation
Conventional black powder formulation
Figure 12

Conventional black powder formulation
Reformulated live black powder formulation
Frequency Sweep Experiment. Strain=0.1%, T=18°C

Figure 13
The capillary flow of the live reformulated black powder formulation

Figure 14
The reformulated live material exhibits larger magnitude of complex viscosity confirming squeeze flow observations.
Reformulated live black powder versus simulant

Figure 16
Comparison of Thermo-Gravimetric Analyze for Simulant and reformulated live Black powder

Figure 17
Extrusion of Black Powder Simulant

Figure 18
Steady State Pressure Profiles for the various conditions studied

Figure 21
Temperature distribution of the simulant with thermal Imaging camera.
Dead stop

Figure 24
Figure 25

Black Powder simulant
Figure 26

Black Powder simulant
Capillary Data D=0.0984” L/D=20
Modified live black powder formulation, extrudate shape upon exit from the capillary die.
Flow curves of modified live black powder formulation: Effect of the surface to volume ratio of the die.

Figure 28
Live reformulated black powder
Steady Torsional Experiment
Shear Rate 0.5 s$^{-1}$

Figure 29
The wall slip behavior of the live reformulated black powder

The graph shows the relationship between corrected shear stress (Pa) and slip velocity (m/s) for two different formulations of black powder:

1. **Capillary Mooney analysis**
   - Equation: \( U_s = \beta \tau^s \)
   - Slip Velocity: \( s = 3.3321 \)
   - \( \beta = 9.44E-20 \)

2. **Inverse problem**
   - Equation: \( U_s = \beta \tau^s \)
   - Slip Velocity: \( s = 2.19 \)
   - \( \beta = 3.29E-14 \)
Reformulated live black powder formulation
Corrected Shear Stress, Pa

Corrected Shear Rate, s⁻¹

\[ \tau = \tau_o + m \gamma^n \]

\[ \tau_o = 70,000 \]

\[ n = 0.38 \]

\[ m = 6147 \]

Reformulated live black powder formulation

Figure 32
Pressurization Zone

Figure 33
Typical FEM mesh used in the simulations
Pressure distribution in the single screw section (lead of 0.027 m) at 100 RPM

Figure 35
Shear rate distribution in the single screw section (lead of 0.027 m) at 100 RPM
Mass flow rate for the pressurization section versus the screw rotational speed at different degrees of fill of the extruder.

Figure 37
Mass flow rate versus the degree of fill in the pressurization section of the extruder

Figure 38
Black Powder Simulant, $\Delta P_{\text{total}} = 800$ psi and corresponding flow rate of 22 lb/hr at 25°C ($D_{\text{Land}} = 0.2''$ and $L/D = 2.5$)
Black Powder Simulant, $\Delta P_{\text{total}}=800$ psi and corresponding flow rate of 22 lb/hr at 25°C ($D_{\text{Land}}=0.2\text{”}$ and $L/D=2.5$)