

Pyrotechnic Particle Morphology— Low Melting Point Oxidizers

K. L. and B. J. Kosanke* and Richard C. Dujay†

*PyroLabs, Inc., 1775 Blair Rd., Whitewater, CO 81527, USA

†Mesa State College, Electron Microscopy Facility, Grand Junction, CO 81501, USA

ABSTRACT

The morphology (size, shape and surface features) of the constituent particles in a pyrotechnic composition affects its performance. While this is particularly true for high melting point fuels and oxidizers in the composition, to a lesser extent it is also true for those with low melting points. Particle morphology also constitutes an important part of establishing the likelihood of a forensic match between evidence and materials of known origin. This article catalogs and briefly discusses some morphologic features often associated with some of the most commonly used low melting point oxidizers in pyrotechnic compositions.

Keywords: morphology, oxidizer, forensics, pyrotechnics, potassium nitrate

Introduction

The term morphology is one borrowed from biology, where it is used to describe the appearance of organisms. In pyrotechnics and forensics, the term is often used to denote information about the size, shape, and surface features of particles, where knowledge of these attributes is often important. In pyrotechnics, particle morphology generally influences such things as the ease of ignition and the burn rate of a composition.^[1] Large particle size, rounded shape, and smooth surface features all tend to make ignition more difficult and burn rates lower. While this is especially true for those compo-

nents with high melting points (e.g., metal fuels and high melting point oxidizers), to a lesser extent it is also true for those components with low melting points (e.g., organic fuels and low melting point oxidizers). It is less important for these particles because of their tendency to have begun to melt (or decompose) below the ignition temperature of the composition. See Table 1 for melting points of some common pyrotechnic oxidizers and metal fuels.

An important aspect of forensic science is the identification of materials, often for the purpose of determining their source. Typically this would be accomplished by attempting to “match” one material (or its components) with other material(s). In attempting to determine whether two materials match, various attributes of the two are compared. The degree of certainty of the match is a function of the number of attributes compared and the degree to which they are identical.^[4] For pyrotechnic compositions, one important part of the matching process should be a comparison of the morphologies of the materials. Probably the best known and most complete work on this subject are the writings of McCrone and Delly.^[5] This multi-volume treatise provides extensive overall information. However, of necessity for chemicals, it tends to only include a few of the most common chemicals, and then in only one form (e.g., individually grown crystals). Their atlas emphasizes the identification of the nature of the chemical. This is valuable information but it falls short of what is needed to determine whether a firm match exists between known and evidentiary materials.

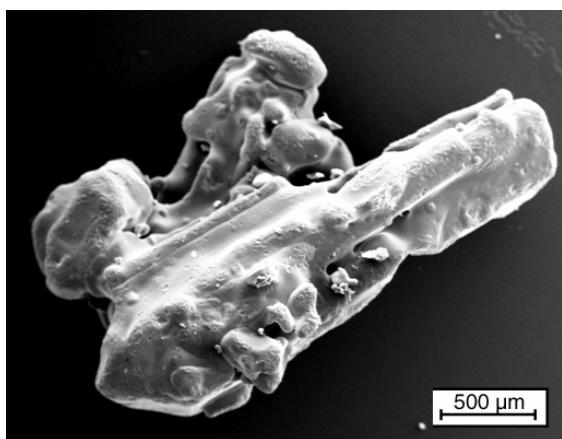


Figure 1. Micrograph of a somewhat typical initial particle of analytical reagent (AR) grade potassium nitrate (35 × magnification).

This article is the second in a series on the subject of pyrotechnic particle morphology.^[6] Whereas the initial article examined a number of different chemicals (metal particles), the current article considers only one. This was done for brevity and to emphasize the wide range of possible oxidizer particle morphologies for a single chemical. Potassium nitrate, the oxidizer in Black Powder (gun powder) and used extensively in fireworks, was chosen because it is probably the most frequently used pyrotechnic oxidizer. However, the information presented for potassium nitrate is generally applicable to other members of that much wider class of common oxidizers, alkali-metal and alkaline-earth nitrates, perchlorates and chlorates.

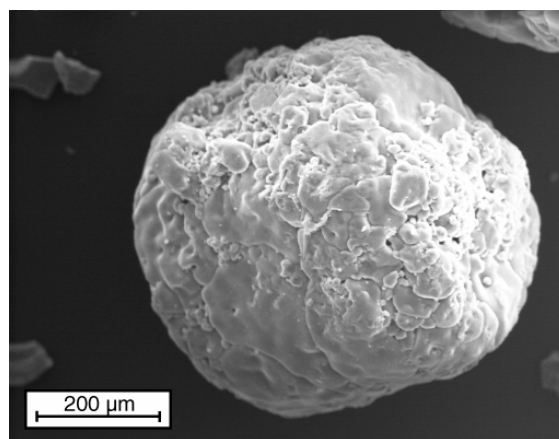


Figure 2. Micrograph of a somewhat typical initial prill of agricultural (AgP) grade potassium nitrate (100 × magnification).

Two sources of potassium nitrate were used in this study. One source was analytical reagent (AR) grade^[7] with an initial average particle size of approximately 6 to 60 mesh (3400 down to 250 microns), see Figure 1 for a somewhat typical example of its initial morphology. The other source was an agricultural prill^[8] (AgP) with an initial average particle size ranging from approximately 18 to 150 mesh (1000 down to 100 microns), see Figure 2 for a somewhat typical example of its initial morphology.

Particle Size

For low-temperature oxidizers, ones that have melting points (or have begun to decompose) at

Table 1. Examples of Melting Points (in °C) for Some Common Pyrotechnic Components of Forensic Interest.

Metal Fuels	$T_m^{(a)}$	High T_m Oxidizers	$T_m^{(a)}$	Low T_m Oxidizers	$T_m^{(a)}$
Aluminum	660	Barium sulfate	1580	Ammonium perchlorate	d ~ 150 ^(b)
Boron ^(c)	2300	Copper(II) oxide	1326	Barium peroxide	450
Iron	2535	Iron(II) oxide	1565	Potassium chlorate	356
Magnesium	649	Lead chromate	844	Potassium nitrate	334
Silicon ^(c)	1410	Lead(II) oxide	886	Potassium perchlorate	d ~ 400 ^(b)
Titanium	1660	Potassium sulfate	1069	Sodium nitrate	307

Notes: (a) The symbol T_m is the melting point in degrees Celsius (°C); values are taken from references 2 and 3.

(b) The symbol d indicates that the oxidizer decomposes before melting and is followed by the approximate decomposition temperature.

(c) These are metalloids and not strictly metals.

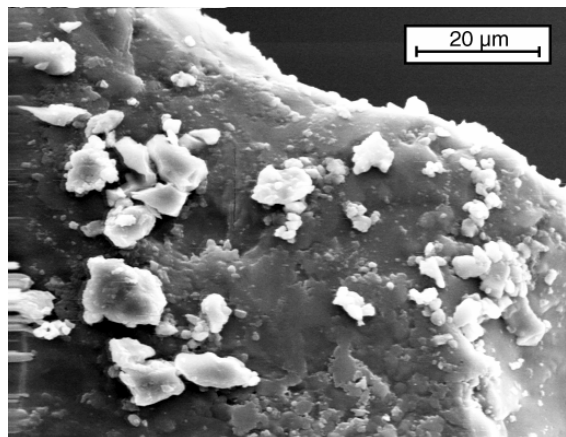
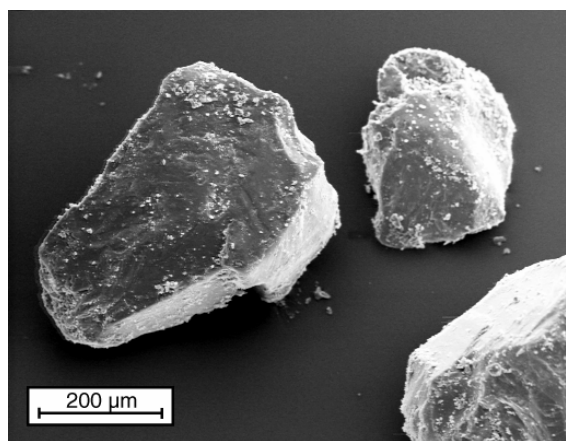


Figure 3. Two images of potassium nitrate, 60 to 100-mesh (150 to 250-micron) particles produced using a rotating disk mill. This documents the presence of many tiny particles adhering to the surface of larger particles. Upper, 100 × magnification; lower, 1000 × magnification.

temperatures below approximately 700 °C, particle size is of less importance than it is for higher melting point components. Nonetheless, relatively small particle size remains important to achieve an intimate mixing of the components of a pyrotechnic composition, and the degree of mixing plays an important role in determining burn rate and other properties of pyrotechnic compositions. Accordingly, even for low temperature oxidizers, it is common for their particle size to mostly fall in the range of 60 to 200 mesh, corresponding to particles ranging from about 250 down to 74 microns. (Of course, for high temperature oxidizers, such as some of those listed in Table 1, small particle size is even more important.^[1])

Table 2. Mesh Fractions of AR Grade Potassium Nitrate Produced by Grinding.

Mesh Range ^(a)	Particle Size (microns)	Fraction (percent)
+60	> 250	1
-60 to +100	250 to 150	16
-100 to +200	150 to 74	31
-200 to +400	74 to 37	28
-400	< 37	24

(a) Mesh numbers are for US Standard sieves. Mesh number is the number of standard diameter wires per inch of wire mesh. A plus sign (+) means *larger than* or *fails to pass through* the specified sieve. A minus sign (-) means *smaller than* or *passes through* the sieve.

Two competing processes act to significantly widen the 60 to 200-mesh range of particle size. One is the diminution process, where most commonly some type of crushing or grinding is used to reduce the particle size to smaller than 60 mesh. In this process, as the large oxidizer crystals are broken, in addition to producing particles in the range of 60 to 200 mesh, many much smaller particles are also produced that range down to a few microns and below. For example, when a portion of AR grade potassium nitrate was processed to produce -60 mesh particles by grinding in a rotating disk mill, many particles in the 0 to 20 micron range were also produced, see Figure 3. (Note: The mill was a 4-inch (102-mm) diameter stone mill, similar to a flourmill.) The upper micrograph is at a magnification of 100 ×, and the lower micrograph is a portion of one of the same particles viewed at a magnification of 1000 ×. Notice that adhering to the surface of the larger particle are some of the very tiny particles that were produced. Table 2 presents the results of a sieve analysis of this ground material. Note that while 99 percent of the larger particles were reduced to smaller than 60 mesh (250 microns), 52 percent of those particles were reduced to smaller than 200 mesh (74 microns).

The other process affecting the range of particle size is agglomeration, the adhering of smaller particles to form larger particles. This process is aided by the presence of moisture and the passage of time. (In pyrotechnics this

process is often referred to as “caking”.) An example of this was observed when a portion of AR grade potassium nitrate was ball milled for 12 hours, without first drying the material; eventually most of the smallest particles agglomerated into a few large masses inside the mill. (Note: the milling media consisted of ceramic cylinders, 0.5 inch (12 mm) diameter by 0.5 inch long, weighing 5.5 grams. Because of the relatively low density of this milling media, milling is described as being “mild”.) At that time, the particles had not yet clumped solidly together, and they still could be fairly easily broken apart when minimal finger pressure was applied to the lumps during sieving. See Figure 4 for examples of the appearance of the agglomerated particles (upper and middle micrographs) and the smaller particles from which they were formed (lower micrograph). When viewed with a visible light microscope, these large agglomerated particles have an opaque white appearance much like that of a snowball.

From a pyrotechnic performance standpoint, compositions prepared using solidly agglomerated particles of low melting point oxidizers are expected to behave somewhat differently than those made using individual solid particles. This is because the increased permeability and porosity of the agglomerated particles should affect their ignition and burning characteristics, as well as their physical properties, such as when being compacted (rammed).

Forensically, while oxidizer particle size distribution can provide potentially useful information, care must be exercised because of the possibility that agglomeration has occurred to differing extents for known and suspect materials. Accordingly, for materials such as low melting point oxidizers, a sieve analysis should be augmented with a microscopic inspection.

Particle Shape

Particle shapes tend to fall into two basic categories, rounded particles and sharp angular particles. Rounded particles may have been formed that way, such as the agricultural prill shown in Figure 2. (Prill is formed by spraying a hot concentrated solution of the chemical species into the top of a tower, where the droplets

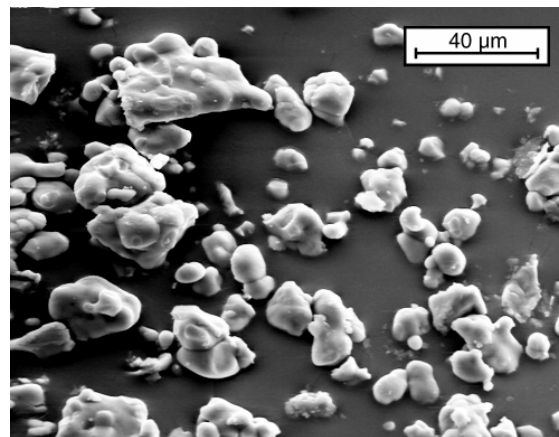
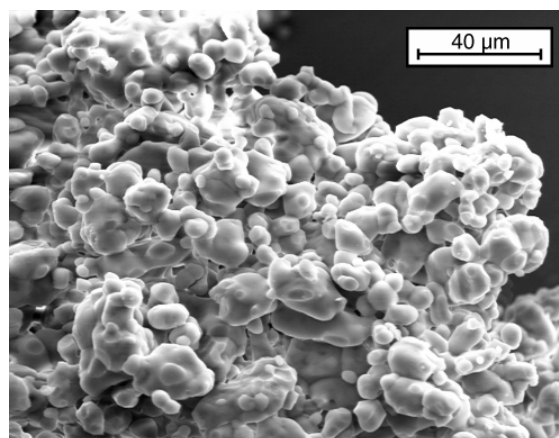
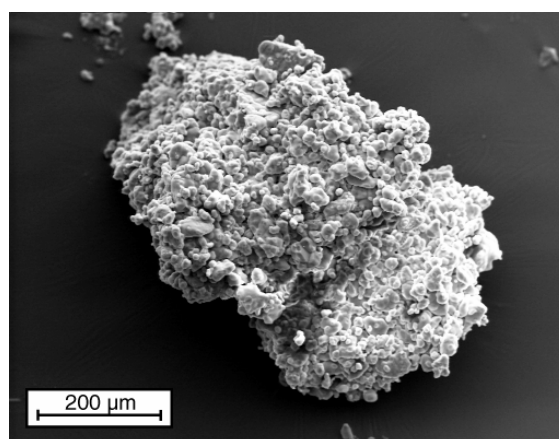


Figure 4. Two mesh fractions of undried AR grade potassium nitrate produced by mild ball milling for 12 hours. Upper, a particle in the range of 60 to 100 mesh (205 to 150 micron) at 100 × magnification; middle, the same particle at 500 × magnification; and lower, < 400 mesh (< 37 micron) particles at 500 × magnification.

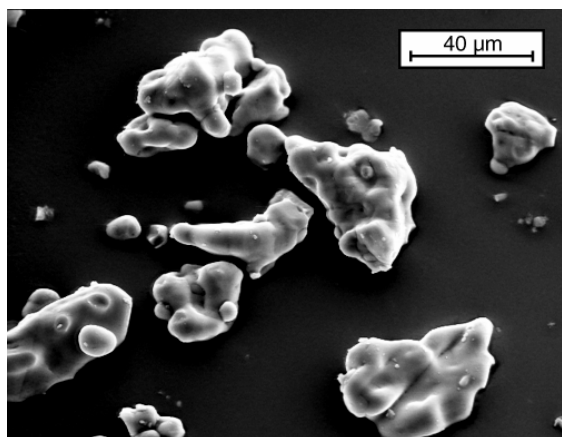


Figure 5. AR grade potassium nitrate particles from the -400 mesh (< 37 micron) fraction produced by mild ball milling for two hours (500 × magnification).

assume a fairly spherical shape when they cool and solidify as they fall.) Particles that are less spherical, but still quite rounded, can be produced during ball milling. In this case, even though the milling media chips-off and crushes particles that must initially be relatively sharp and angular, they quickly lose those features during the milling process as the particles abrade against each other. Figure 5 demonstrates the effect of even a fairly short duration (two hours) mild ball milling. Note that while these -400 mesh (< 37 micron) particles are not as small or rounded on average as those shown in the lower frame of Figure 4, where the milling continued for several more hours, they are already fairly small and quite rounded.

Particles reduced in size by grinding predominantly have sharp angular features. Whether the grinding was accomplished using a motorized disk grinder or by hand using a mortar and pestle, the result is essentially the same. The similarity in particle size distribution and angular features of the -400 mesh (< 37 micron) particles can be seen in Figure 6, in which the upper micrograph is of particles produced using the rotating disk grinder, and the lower micrograph is of particles produced using a mortar and pestle. These fairly sharp angular particles can be contrasted with those of the same size but with rounded features seen in Figures 4 and 5.

Another process that may be used for particle size reduction is coacervation. (This is purport-

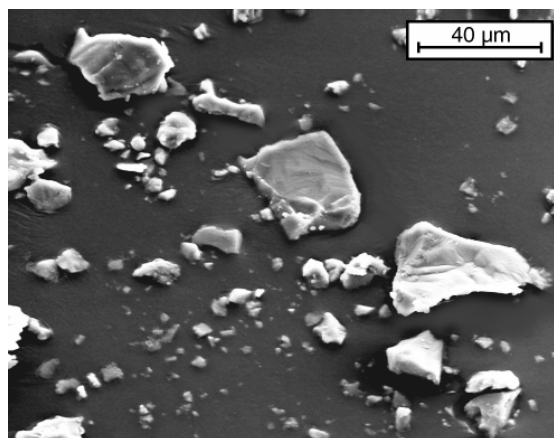
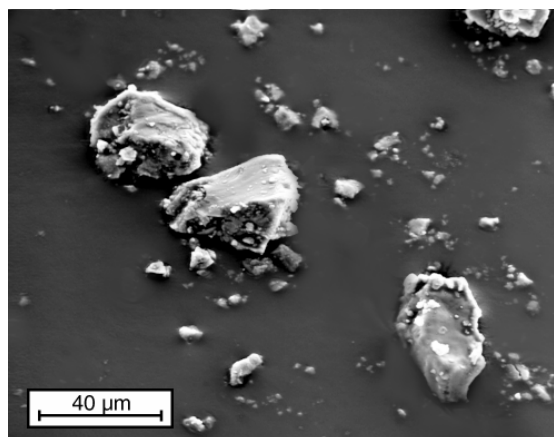


Figure 6. AR grade potassium nitrate particles from the -400 mesh (< 37 micron) fraction produced by grinding (500 × magnification). Upper fraction, produced using a rotating disk grinder; lower fraction, produced using a mortar and pestle.

edly used in the CIA's field expedient method for the manufacture of Black Powder.) In this process, large size particles are dissolved in water to make a nearly saturated solution, usually at an elevated temperature to increase the amount of material that can go into a solution. Then alcohol is added, usually quickly and while stirring vigorously. The alcohol acts to displace the dissolved material from the solution because the alcohol has a much greater solubility, and to some extent also by cooling the solution. In this process, tiny particles are formed, many of which fuse together to form larger particles, especially when not being vigorously stirred. Figure 7 documents the appearance of these particles, where the upper and middle micrographs are views of a particle, in the 60 to 100 mesh (250 to

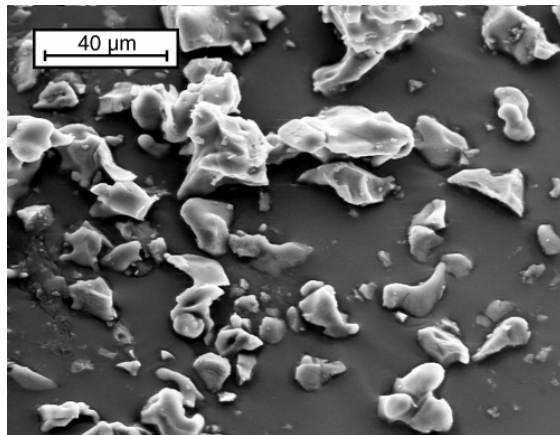
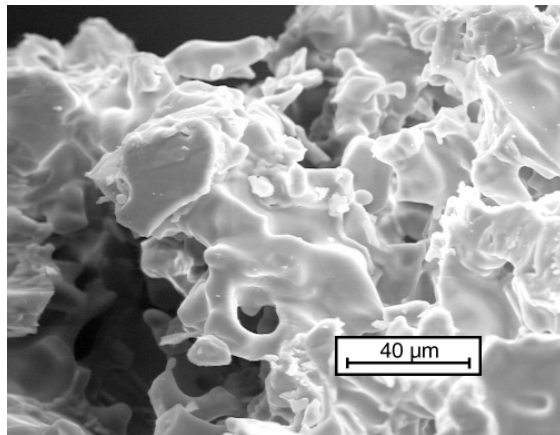
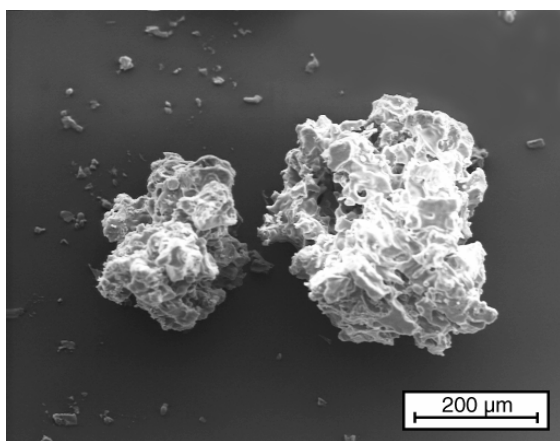


Figure 7. Particles from two mesh fractions of AR grade potassium nitrate produced by hot coacervation with rapid stirring. Upper, 60 to 100 mesh (250 to 150 micron) particles at 100 × magnification; middle, a portion of one particle at 500 × magnification; lower, -400 mesh (< 37 micron) particles at 500 × magnification.

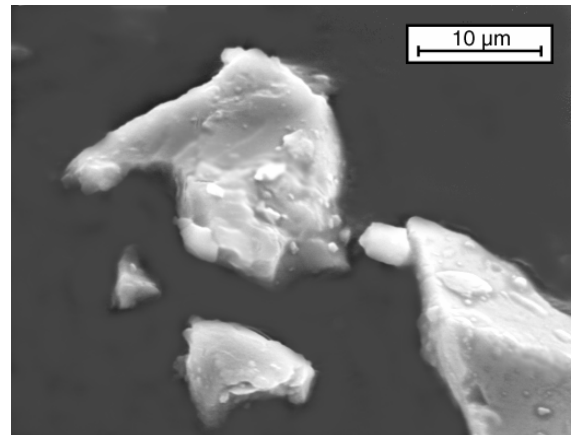
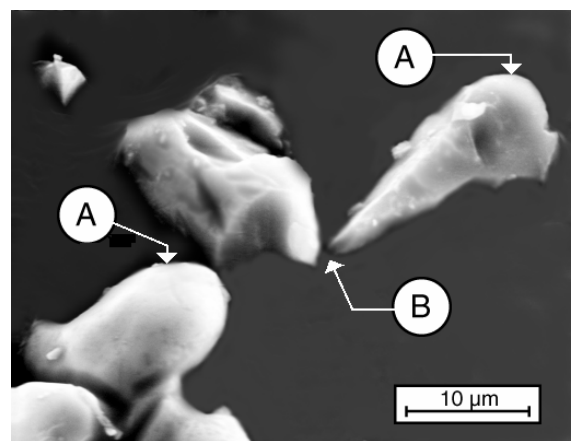


Figure 8. Comparing the sharpness of -400 mesh AR grade potassium nitrate particles. Upper, coacervated particles at 2000 × magnification illustrating features that are sometimes quite rounded (A) and other times fairly sharp and angular (B); lower, mortar and pestle produced particles at 2000 × magnification.

150 micron) fraction, at 100 and 500 × magnifications. The lower micrograph is of the -400 mesh (< 37 micron) particles at 500 × magnification. The larger particles are clearly agglomerations; however, their appearance is substantially different than that seen for the caked particles in Figure 4. The constituent particles are angular as opposed to being rounded and the agglomeration is fairly open as opposed to being relatively tightly packed. Many of the -400 mesh particles are as angular as the ground and crushed particles seen in Figure 6; however, many others are quite rounded. This can be seen more clearly in Figure 8, which compares -400 mesh coacervated particles with

those produced with a mortar and pestle, both at $2000\times$ magnification.

When coacervation is carried out with the rapid addition of the alcohol and vigorous stirring from a near saturated—but cool—solution, the appearance of the particles is substantially similar to those for a hot solution, like those particles seen in Figure 7. However, when the alcohol is added slowly and mostly without stirring, some of the particles produced have a somewhat rod-like shape that is characteristic of potassium nitrate crystals, see Figure 9.

Surface Features

Surface features and texture can significantly affect the reactivity of some pyrotechnic materials (e.g., so called titanium sponge ignites easier than solid titanium particles of the same size). However, for compositions made with low melting point oxidizers, except for particles that are agglomerations of a large number of much smaller particles, surface features are not expected to noticeably affect the ignitability and burn rate of pyrotechnic compositions. However, surface features are an important part of forensic materials comparison.

Some of the possible particle surface features have already been mentioned. For example, particles can be agglomerations of smaller particles that have characteristic shapes, and the agglomerations can be densely packed or have relatively open structures, see Figures 4 and 7. However, there are other characteristic surface features that should be mentioned. When particles are crushed, noticeable fracture patterns can be produced. These particles have concave particle surfaces and deflection fracture marks, sometimes called “whiskers”. (Whiskers are somewhat parallel ridges on the fractured surface). When particle diminution is accomplished by hammer milling, where high speed rotating blades impact and shatter the particles, the number and degree of fracture patterns observed can be significantly greater than those patterns produced by crushing and grinding, see the upper and middle micrographs in Figure 10. The lower micrograph in Figure 10 is a rather extreme example of fracture features formed when this particle was smashed. The degree to

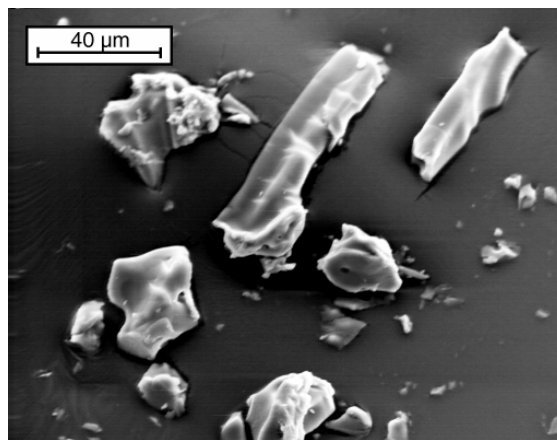
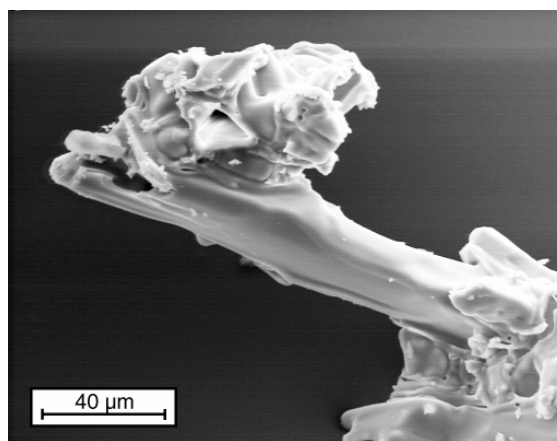
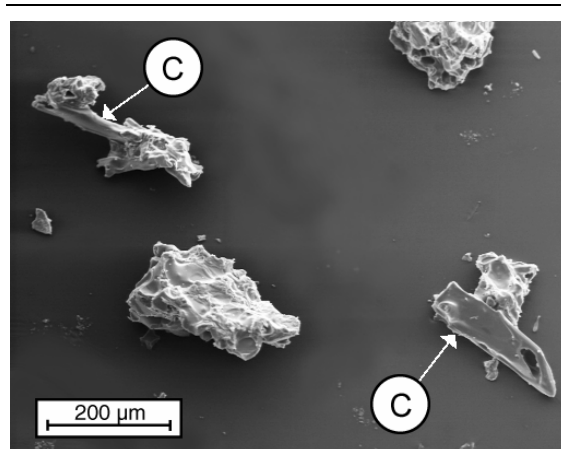


Figure 9. Particles with some rod-like characteristics (C) are produced by slow coacervation. Upper, 60 to 100 mesh (250 to 150 micron) particles at $100\times$ magnification; middle, a portion of one particle at $500\times$ magnification; lower, -400 mesh (< 37 micron) particles at $500\times$ magnification.

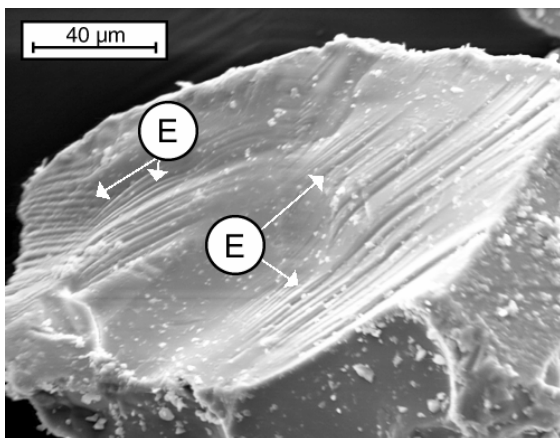
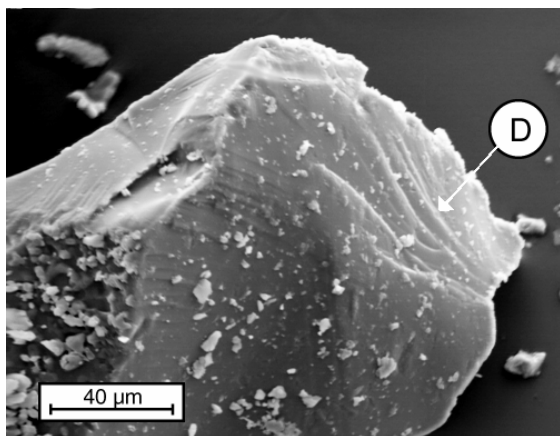
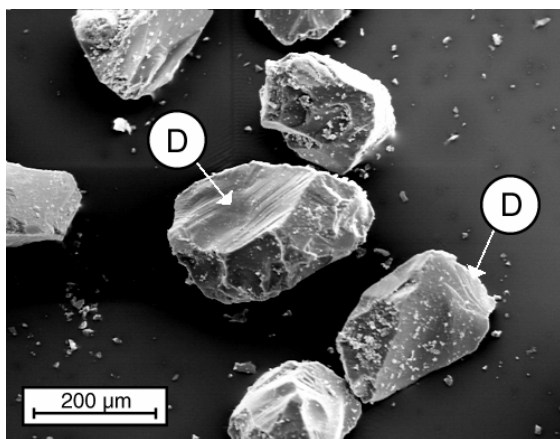


Figure 10. Particles of AR grade potassium nitrate produced by hammer milling. Upper and middle, demonstrating fracture patterns (D) (100 and 500 × magnification, respectively); lower, a rather extreme example of “whiskers” (E) (500 × magnification).

which fracture patterns are produced during milling seems to range from modest (for rotating disk mills) through moderate (for mortar

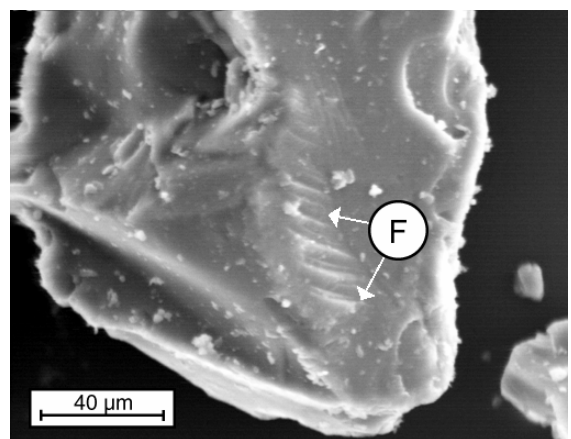


Figure 11. Possible example of tool marks (F) produced during hammer milling AR grade potassium nitrate (500 × magnification).

and pestle) to substantial for hammer milling. Also, on rare occasion, a hammer-milled particle may exhibit what appear to be tool marks (mostly straight parallel grooves) from a blade scraping across the particle, see Figure 11.

When particles have been ball milled, the large number of impacts can leave the larger particles with a pitted surface texture; see Figure 12. These micrographs illustrate the typical appearance of the 60 to 100 mesh (250 to 150 micron) particles of AR grade potassium nitrate after having been ball milled for 2 hours. At first glance and under minimum magnification, the particle may appear somewhat like the agglomerated particle in Figure 4. However, under higher magnification the difference is obvious. Using the visible light microscope, the difference in appearance between the agglomerated and pitted particles is even more readily apparent. Particles such as those in Figure 12 are translucent and are definitely single particles, appearing much like lightly frosted glass. To the contrary, particles such as those in Figure 4 are opaque white, appearing much like snowballs.

Occlusions or voids, though not uniquely surface features, are sometimes discernable on the surface of particles. This is especially the case for agglomerated particles (see Figure 4), coacervated particles (see Figure 7), and particles produced from prilled chemicals (see Figure 13). However, it should be noted that voids were also occasionally observed in particles

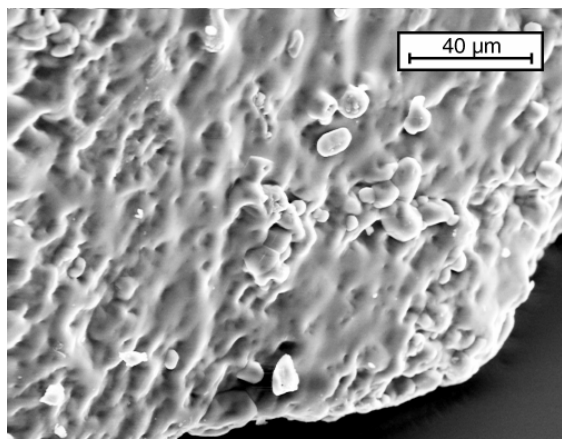
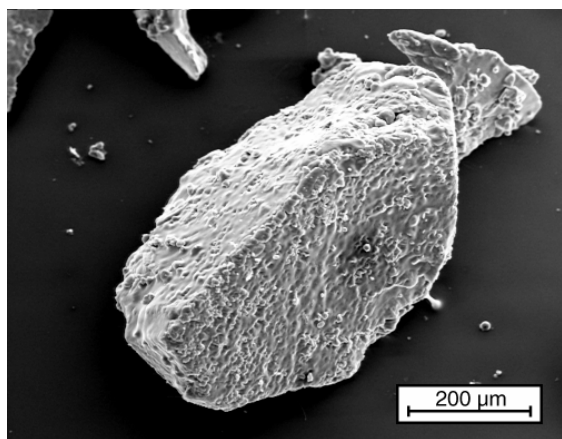


Figure 12. Particle of AR grade potassium nitrate produced by mild ball milling for 2 hours, illustrating the pitted surface of the 60 to 100 mesh particles. Upper, 100 × magnification; lower, 500 × magnification.

produced from potassium nitrate that was slowly recrystallized from an aqueous solution and from potassium nitrate that solidified from high temperature melts.

A definite surface feature, but one that is not characteristic of unexamined potassium nitrate particles, is illustrated in the lower micrographs of Figure 14. The thermal expansion and fissuring of the particle's surface is an artifact introduced during the examination process itself. Specifically this is a result of particle heating when the specimen absorbs the energy of the electron beam of the scanning electron microscope (SEM). (For a more complete discussion of possible causes of thermal expansion and some steps to help limit the problem, see refer-

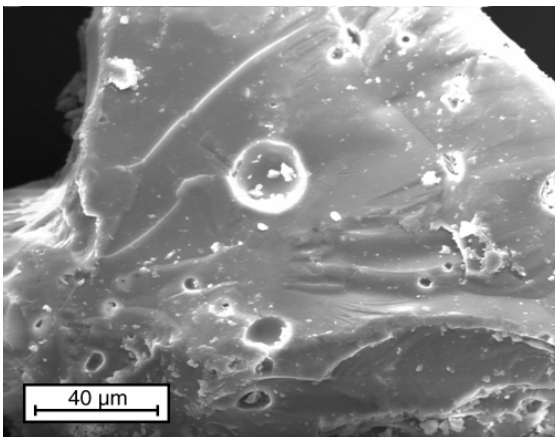
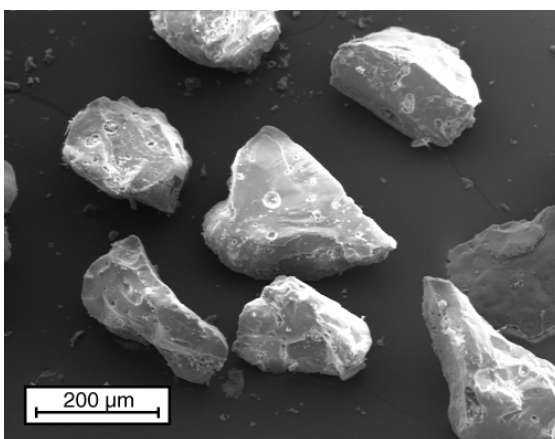


Figure 13. Particle of AgP grade potassium nitrate produced using a mortar and pestle, illustrating the presence of numerous occlusions (voids). Upper, 100 × magnification; lower, 500 × magnification.

ence 9.) The possibility of causing beam-induced artifacts becomes a greater problem at higher magnifications, when the electron beam is more concentrated (the same beam current is spread over a smaller area). The upper micrograph of Figure 14 is the initial image of an uncoated AR grade potassium nitrate particle at 2000 × magnification. The middle and lower micrographs were recorded after approximately one and three minute exposures to the beam of the SEM, and they demonstrate the progressive expansion and development of the fissures in the particle's surface. For these AR grade potassium nitrate particles, essentially no further surface damage was observed after approximately three minutes.

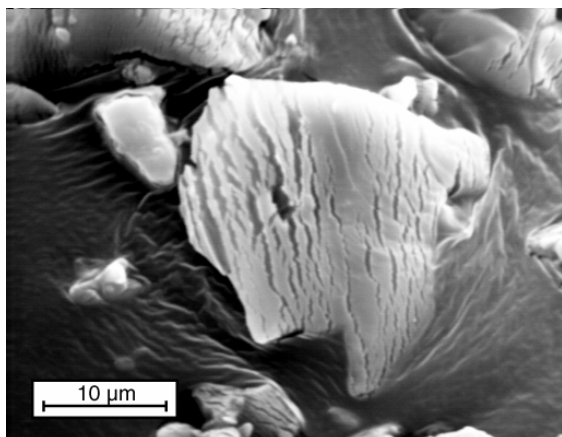
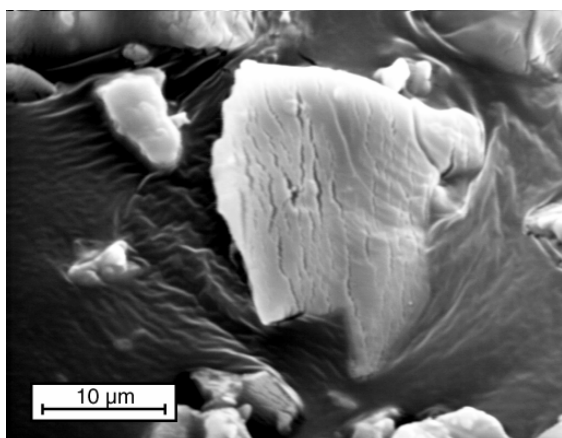
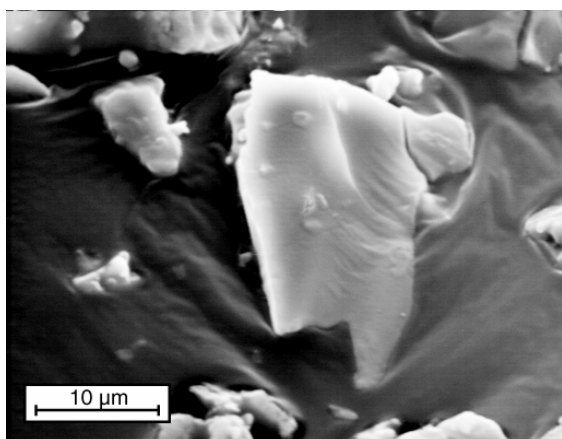


Figure 14. Illustration of SEM beam-induced surface damage (thermal expansion) to AR grade potassium nitrate particles under high magnification (2000 ×) as a function of time. Upper, initial image; middle, image recorded after approximately one minute; lower, image recorded after approximately three minutes.

Conclusion

Particle size, shape and surface features of low melting point oxidizers are not as critically important in determining the ease of ignition and burn rate of pyrotechnic compositions as they are for many other components in these mixtures. Nonetheless, knowledge and control of these attributes is necessary to maintain consistent performance of pyrotechnic devices. Further, from a forensic standpoint, an investigation of these attributes can be an important part of establishing reliable matches between known and evidentiary materials. [Unfortunately, the converse is also true (i.e., failing to consider detailed particle morphology makes any claim of a match less credible.)]

As a note of caution for the forensic analyst, it is important to avoid over-inferences based on a limited investigation of particle morphologies. Specifically, while it is true that the method of particle size reduction plays a major role in determining particle morphology, so do many other things. Accordingly, one should resist the temptation to use particle morphology as the sole basis to infer the method of production of the material. For example, consider the potassium nitrate particles shown in Figure 15. These particles definitely have sharp angular features. Based on the information presented in this article, one might be tempted to conclude that the method of their production was by crushing or grinding, see Figure 6. Similarly, one might be tempted to exclude the possibility that this material was produced by extended ball milling, see the lower micrograph of Figure 4. However, if either conclusion were reached, it would be erroneous. Figure 15 is the -400-mesh (< 37-micron) fraction of AgP potassium nitrate produced by 12 hours of ball milling. The rather extreme difference in particle morphology, when compared with that seen in Figure 4, is simply due to differences in the physical properties of the AR and AgP grades of potassium nitrate.

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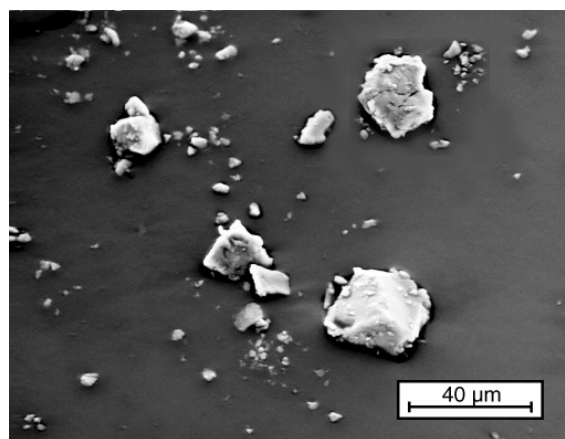


Figure 15. Micrograph of the -400 mesh (< 37 micron) fraction of AgP potassium nitrate produced by ball milling for 12 hours (500 × magnification).

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