Novel Particulate Production Processes to Create Unique Security Materials

Mark-Hampden-Smith, Toivo Kodas, Scott Haubrich, Miki Oljaca, Rich Einhorn, Darryl Williams
Cabot Corporation-Albuquerque, New Mexico 87113 USA

ABSTRACT

Particles are frequently used to impart security features to high value items. These particles are typically produced by traditional methods, and therefore the security must be derived from the chemical composition of the particles rather than the particle production process. Here, we present new and difficult-to-reproduce particle production processes based on spray pyrolysis that can produce unique particles and features that are dependent on the use of these new-to-the-world processes and process trade secrets. This process has been utilized to make security materials ranging from spherical up-convertors to ink-jettable phosphors to unique composition infrared phosphors. Specifically a number of luminescent materials are described that exhibit unique luminescent characteristics that can be incorporated into security applications using machine-readable spectroscopic detection systems.

Keywords: phosphors, luminescence, up-convertors

INTRODUCTION

Many anti-counterfeiting features are achieved by incorporating ultra fine particles into paper or a coating. These features include luminescent materials, magnetic, optically variable pigments, thermochromics, amongst others. Most of these particles are produced by well-known and broadly practiced processes. The counterfeit deterrence of particles made by these well-established processes is therefore limited to compositional secrecy, process trade secrets, capital intensity, access limitations, security document integration and reliance on electronic detection methods. Each of these deterrents is constantly under pressure.

In this paper we describe a new powder manufacturing process, spray pyrolysis, that, to our knowledge, has not been employed previously for the production of materials for security applications, and which extends the security of the powder from traditional compositions to new compositions, microstructures and combinations of materials. Furthermore, as a result of the ability to create unique compositions and combinations of compositions resulting from the processing conditions, particles with unique performance characteristics can be produced.

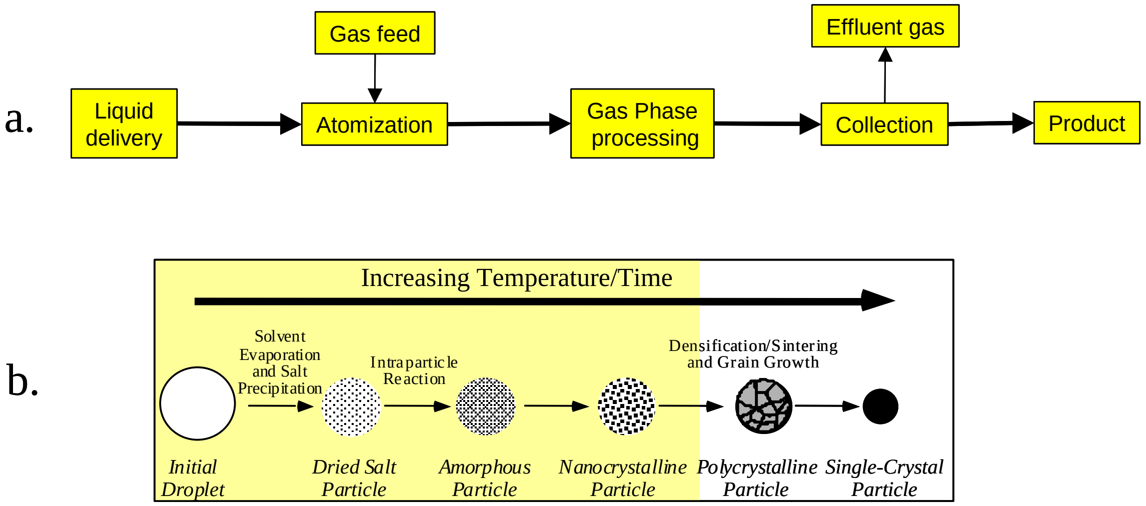
There are several other additional benefits to the powders produced by the spray pyrolysis process that arise because the particles can be produced in the micron size range (typically d_{50} can be tailored between 1 – 2 microns), with controlled spread of the size distribution and with spherical morphology. This leads to improved performance of the inks and pastes derived from these powders through reduced settling, improved handling and more uniform coating of the target substrate.

In this paper we provide an overview of the spray pyrolysis process and the characteristics of the particles derived from this process; several examples of luminescent materials where spray pyrolysis is used to make unique materials and the attributes of the layer characteristics derived from the characteristics of the powders.

Overview of Spray Pyrolysis Powder Manufacturing

A schematic representation of the spray pyrolysis process is illustrated in Figure 1a and has been described elsewhere in detail.[1] It starts with the formulation of a liquid that contains either dissolved or suspended reagents, which act as precursors to the final product. The liquid, together with a gas, is then fed to an atomization unit where the liquid is converted into an aerosol. The size and size distribution of the droplets that comprise the aerosol are carefully controlled because each droplet becomes a particle (or aggregate in the case of supported electrocatalyst powders) after gas phase processing.[2]

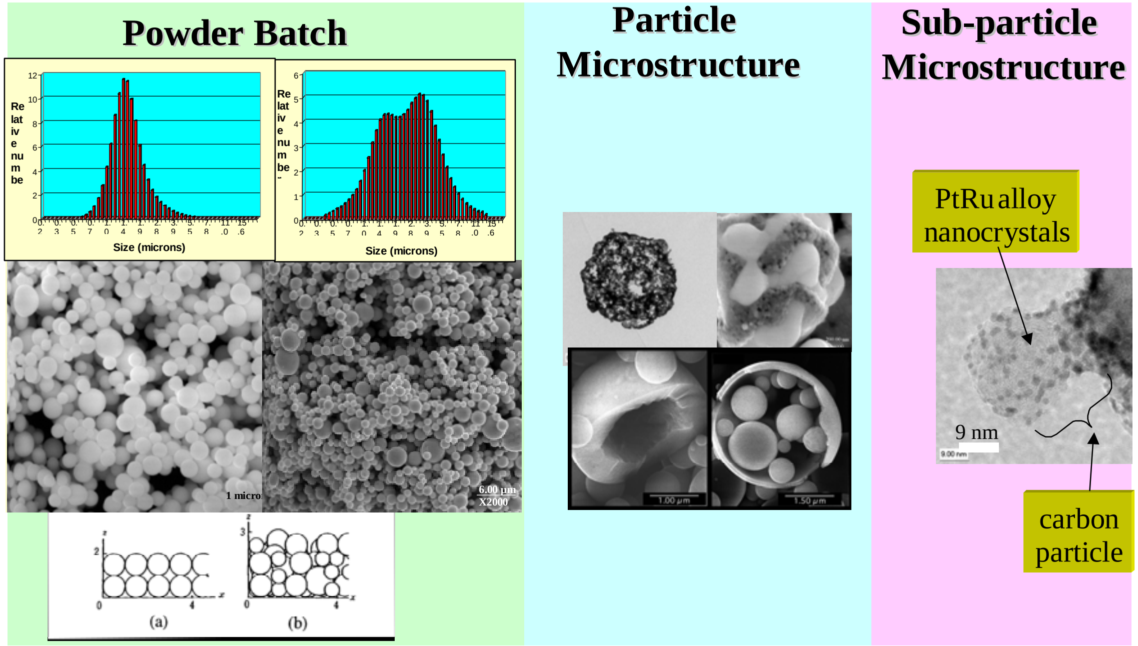
Figure 1. a. Schematic representation of spray-pyrolysis process flow: b, Schematic representation of processes occurring during a spray-based production of unsupported materials:



Many methods of droplet formation exist providing a broad spectrum of droplet sizes, atomization rates (measured by the amount of liquid phase atomized per unit time) and droplet size and size distribution. The gas stream containing the aerosol is then heated in a gas phase processing unit to effect the physical and chemical conversion of the droplets to the final powder. The final powder is separated from the gas stream using conventional powder collection methods, leaving only a gaseous effluent (no liquid effluent to be disposed of). The final powder microstructure and composition depends on the residence time, temperature, the reactive nature of droplet components and the composition of the gas. A schematic representation of these processes is provided in Figure 1b above and typically involves solvent evaporation, thermally or chemically induced reactions, crystal nucleation and crystal growth. Therefore this process can be used to produce a wide variety of materials compositions combined with uncommon microstructures and morphologies. A key feature of the process is that the physical and/or chemical evolution of the particles can be arrested at any stage by quenching of the reaction media.

A wide variety of materials can be made by this method in which not only the composition but also the microstructure can be varied. It is the combination of these attributes, control over microstructure at a number of different length scales (as described in the next section) and composition, simultaneously, that is extremely important to applications in Security. We view spray-based methods as a platform to achieve the necessary combination of microstructure and composition for each individual end use application as illustrated in Figure 2. Figure 2 describes how the spray-based manufacturing approach can be used to independently vary three main characteristics of the powder batch: a) the particle size (from below 1 micron to tens of microns average size – in the case of electrocatalyst powders this is the aggregate size – see below) with mono- bi- or tri- modal distributions), b) different particle microstructure (porous hollow, dense, composite with various compositional distributions), c) nanosized active phases can be deposited within the structure of each particle (aggregate, see below) and the composition of this nano-dispersed phase can be varied form single element to multi-component composition.

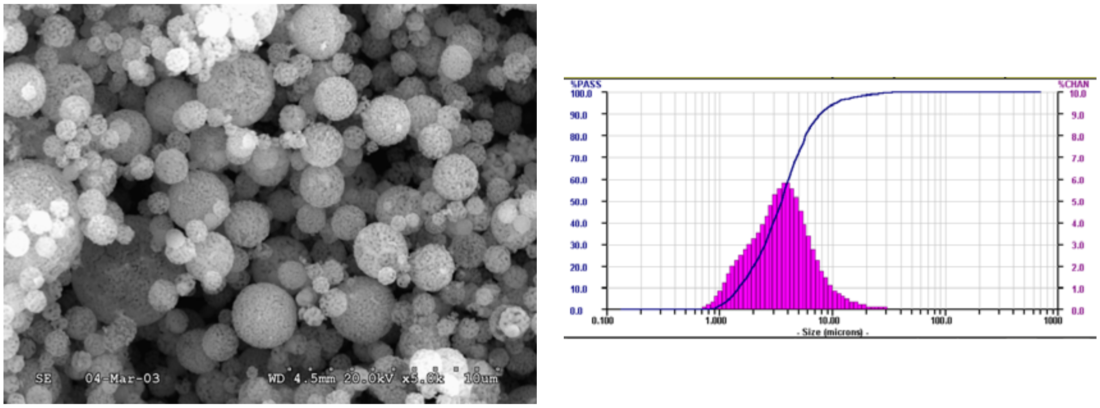
Figure 2. Microstructural features of materials produced by spray-based production categorized at different length scales. Powder Batch: The characteristics of the powder batch can be adjusted by controlling the particle (aggregate in the case of supported catalysts) size and size distribution to influence the flow and packing characteristics of the particles. Particle Microstructure: The individual particles (or aggregates) can be dense, hollow, porous or composite. Sub-particle Microstructure: The particles (aggregates) can be comprised of nano-dispersed phases distributed over the surface of a support.



Luminescent Security Particles

A wide variety of luminescent security materials can be prepared by spray pyrolysis.[4] A typical example of the green emitting phosphor used in security applications Zn_2SiO_4:Mn is shown below in Figure 3..

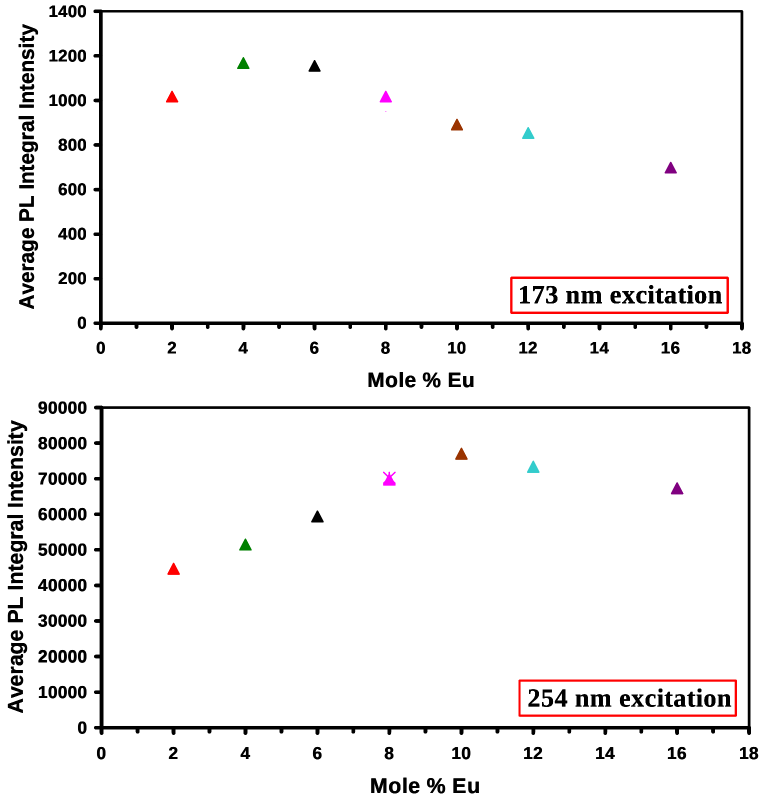
Figure 3: Scanning Electron micrograph (left) and particle size distribution (right) of Zn_2SiO_4:Mn



One interesting aspect of doped materials produced by the spray pyrolysis method is that because the reagents are mixed in solution at the molecular level, the dopant distribution throughout the lattice of the final material appears to be more uniform compared to materials produced by solid state manufacturing methods.[5] This can lead to differences in performance characteristics as a function of dopant levels. Here, we illustrate the security related significance of these attributes in three examples. In the first example, Y_2O_3:Eu, the uniform dopant distribution leads to a non-standard luminescence intensity versus dopant level curve. In the second example, the number and special uniformity of the dopant distribution can be taken advantage of to create unusual emission characteristics than can be incorporated into security documents. In the third example, the emission signature is systematically varied by variation of the <u>host</u> lattice (as apposed to the dopant) in a way that is enabled by the molecular level mixing of the reagents using spray pyrolysis. These features can be used for machine-readable security applications to impart a higher than normal level of security that depends on both the composition <u>*and*</u> the manufacturing method of the phosphor powder. The further benefit of these materials derived from the spherical morphology and small particle size is also described.

In the first example, the photoluminescence characteristics of a prototypical security UV phosphor, red-emitting Y_2O_3:Eu as a function of dopant level and excitation wavelength is shown in Figure 4

Figure 4: Brightness of Cabot Y_2O_3:Eu as a function of Eu dopant concentration.



The dependence of photoluminescence intensity or brightness on the concentration of the europium dopant in Y_2O_3:Eu shows that the behavior of the phosphor is different under VUV (173 nm) and UV (254 nm). The maximum brightness is observed at approximately 5 mol % Eu in the VUV and 10 mol % Eu in the UV.

The second example is a material that shows unique luminescent performance when produced by spray pyrolysis for security applications. Figure 5 shows emission spectra of the standard and selected Cabot phosphors (same host lattice but different dopant levels), obtained using the same excitation wavelength. The spectra from the Cabot powders include blue (400 nm – 450 nm) emission bands not present in the spectrum of the standard. Blue emission resulting from 300 nm excitation was not observed in materials produced by standard methods. The origin of these effects is derived from the addition of certain additives and processing characteristics. Security system designers can take advantage of this unusual spectral band by tuning their detection scheme to look for this blue peak. Phosphors-Composition 2 and 3 can only be made by spray pyrolysis and are the only ones that will give this unique signature.

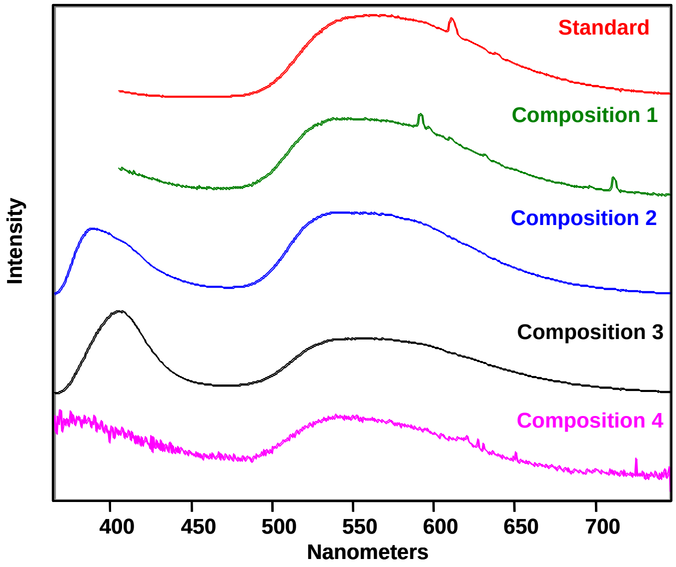
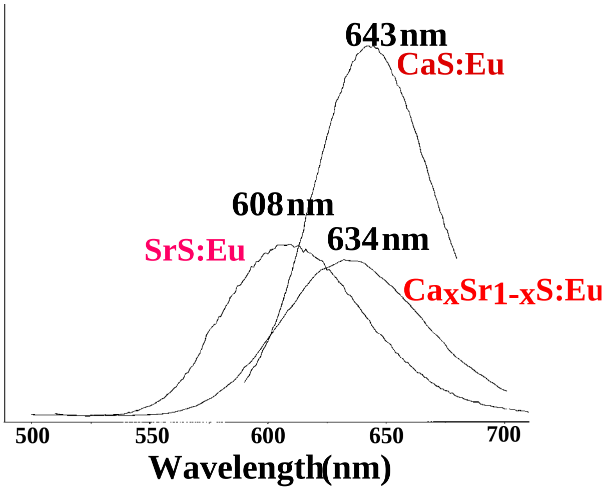


Figure 5: Phosphor emission spectra with excitation at 300nm.

In the third example, adjusting the host lattice rather than the dopant level systematically varies the emission characteristics of the phosphor. In this example, the molecular level homogeneity of the precursors used to produce this phosphor result in a CaS/SrS host lattice solid solution with luminescence characteristics that can be varied anywhere between the extremes of the single phase materials, CaS and SrS, respectively. Only a process like spray pyrolysis can lead to this unique wavelength emission, again making a material like this a unique detectable phosphor.

Figure 6: Emission spectra for several Group 2 metal sulfide compositions (vertical scale is relative emission intensity).



Performance in Layer Structures

A traditionally important aspect of a powder is its performance in a layer structure because most application require powder coatings derived from powder-containing inks and pastes. This is important because the excellent performance observed in a powder can be completely lost if the layer characteristics are poor. In reference to the examples above, printed layers of luminescent powders must be designed to optimize the interaction with light at the appropriate wavelength.

As an example of the benefits of particles produced by spray pyrolysis, Y_2O_3:Eu security phosphor is used here to demonstrate the effect of parameters such as particle morphology, packing, and light scattering in layers. A traditional Y_2O_3:Eu sample made by traditional powder processing methods is shown as a comparative material and screen-printing pastes were prepared with the traditional powder and Cabot proprietary Y_2O_3:Eu powder.

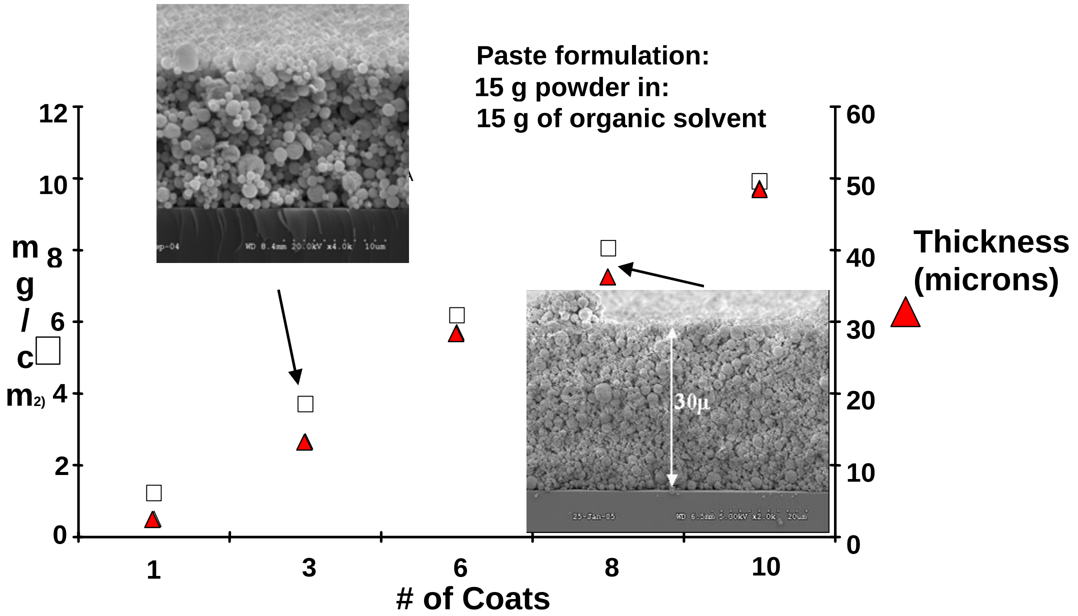
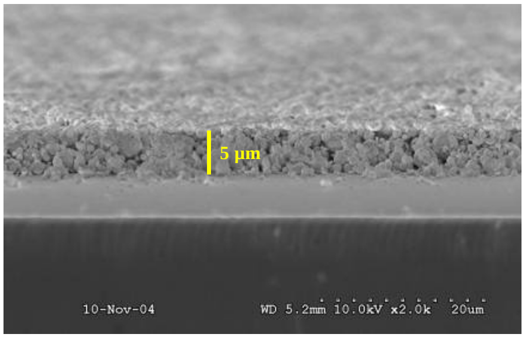


Figure 7: Amount phosphor deposited as a function of the number of layers printed.

Cabot powder



Traditional powder

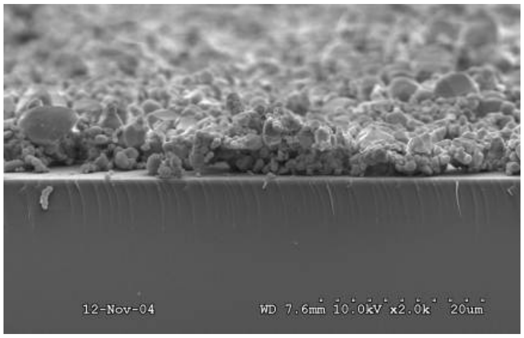
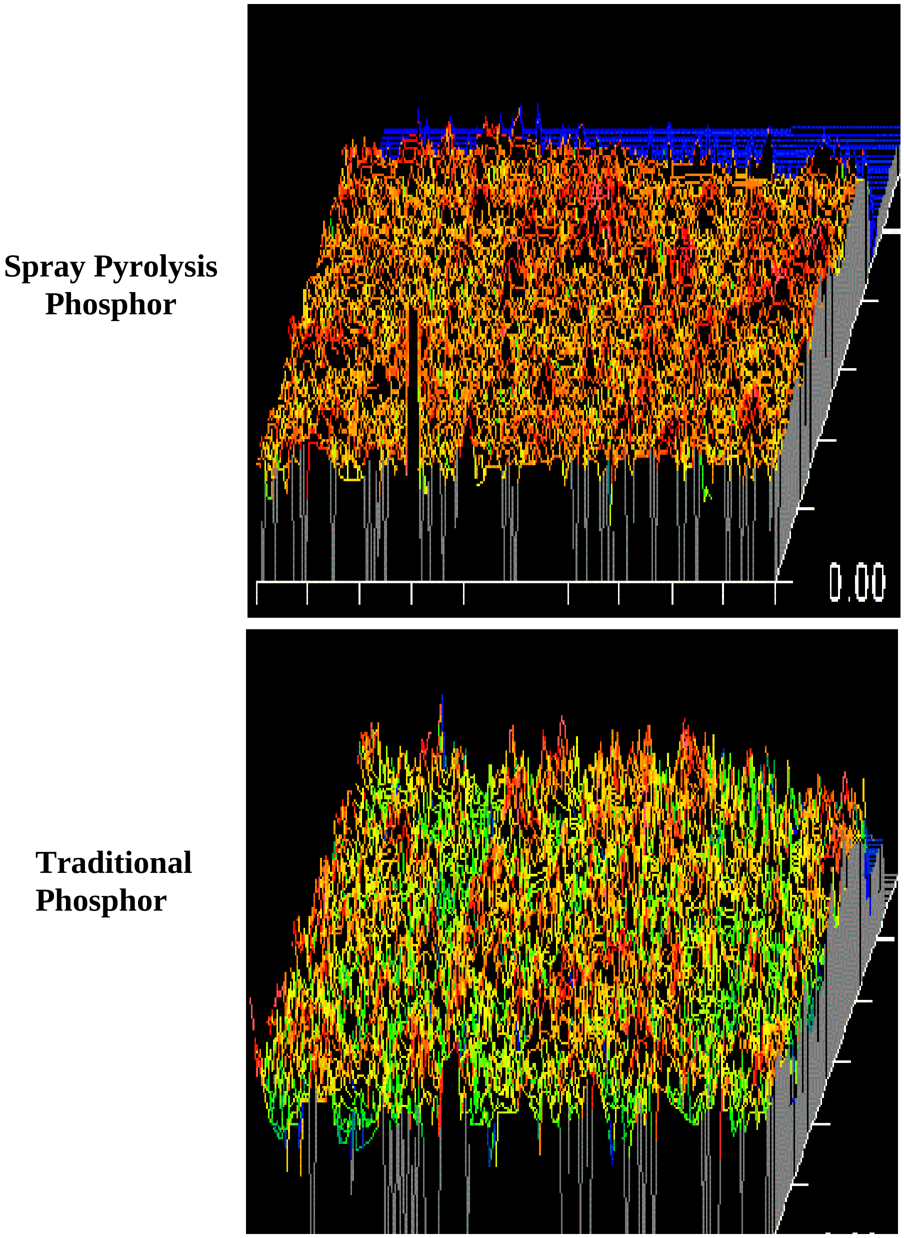


Figure 8: SEM images of ~ 5 micron layers printed using Cabot and traditional powders.

SEM images of thin phosphor layers prepared by screen printing show that the Cabot Y_2O_3:Eu powder forms a more uniform layer with a smoother surface than the traditional powder used for comparison. Surface profilometry measurements in Figure 9 show a significantly rougher surface texture resulting in the layer printed using the traditional sample compared to that using the Cabot powder.



Spray Pyrolysis Phosphor

Traditional Phosphor

Figure 9: Surface profilometry images showing the roughness of a layer prepared using a traditional phosphor compared to the Cabot phosphor. (higher and more peaks indicate more roughness)

Figure 9 illustrates surface profiles obtained by the Zygo instrument for ~15 micron screen-printed phosphor layers with Cabot and the comparative powder. It can be seen that Cabot phosphor layers have less surface roughness compared to the comparative phosphor layer, which may translate to different optical properties for the layers including higher brightness.

CONCLUSIONS

The spray pyrolysis powder manufacturing process has been described and compared to other particle manufacturing processes. This process enables the production of materials with unique particle characteristics that lead to unique performance characteristics such as sphericity, narrow particle size distribution and unique hierarchical structures that are difficult or almost impossible to reproduce using conventional powder manufacturing processes. These characteristics result in unique luminescence spectral phenomena. There are many opportunities to apply this process to the security industry where unique compositions produced on a unique manufacturing process result in unique physical properties that provide a high barrier to counterfeiting. Examples include improved printability for up-convertors, brighter UV phosphors, particles with unique morphologies, and particles with unique hierarchical structure as well as process-dependent luminescence spectra.

REFERENCES

1. See e.g. Kodas, T.T. and M.J. Hampden-Smith, *Aerosol Processing Of Materials*. 1999, New York: Wiley-VCH and references therein.
2. This process and related processes are described in detail in numerous patents, see for example: M.J. Hampden-Smith, T.T. Kodas, Q.P. Powell, D.J. Skamser, J. Caruso, and C.D. Chandler, U.S. Patent No. 6,338,809, 1-15-2002. “Aerosol method and apparatus, particulate products, and electronic devices made therefrom.” T.T. Kodas, M.J. Hampden-Smith, J. Caruso, D.J. Skamser, and Q.P. Powell, U.S. Patent No. 6,106.393, 8-15-2000. “Metal-carbon composite powders, methods for producing powders and devices fabricated from same.”
3. T.T. Kodas, M.J. Hampden-Smith, U.S. Patent Application 20020184969A1, 12-12-2002. “Combinatorial synthesis of particulate materials.” T.T. Kodas, J.J. Hampden-Smith, U.S. Patent Application 20020176927A1, 11/28/2002. “Combinatorial synthesis of material systems.”.
4. M.J. Hampden-Smith, T.T. Kodas, J. Caruso, D.J. Skamser, Q.H. Powell, K. Kunze, U.S. Patent No. 6,210,604, 4-03-2001. “ X-ray phosphor powders, methods for making phosphor powders and devices incorporating same.” M.J. Hampden-Smith, T.T. Kodas, J. Caruso, D.J. Skamser, Q.H. Powell, K. Kunze, U.S. Patent No. 6,197,218, 3-06-2001. “Photoluminescent phosphor powders, methods for making phosphor powders and devices incorporating same. M.J. Hampden-Smith, T.T. Kodas, J. Caruso, D.J. Skamser, Q.H. Powell, K. Kunze, U.S. Patent No. 6,193,908, 2-27-2001. “Electroluminescent phosphor powders, methods for making phosphor powders and devices incorporating same.” M.J. Hampden-Smith, T.T. Kodas, J. Caruso, D.J. Skamser, Q.H. Powell, U.S. Patent No. 6,180,029, 1-30-2001. “Oxygen-containing phosphor powders, methods for making phosphor powders and devices incorporating same.” M.J. Hampden-Smith, T.T. Kodas, J. Caruso, D.J. Skamser, Q.H. Powell, K. Kunze, U.S. Patent No. U.S. 6,168,731, 1-02-2001. “Cathodoluminescent phosphor powders, methods for making phosphor powders and devices incorporating same.”
5. D. R. Tallant, C.H. Seager, and R.L. Simpson, *J. Appl. Phys.*, **Vol. 91**, No. 7, 1 April 2002

*Mark_Hampden-Smith@cabot-corp.com; phone 1(505) 342-1492; fax 1(505) 563-4300; www.cabot-corp.com