JOURNAL OF PROPULSION AND POWER
Vol. 21, No. 3, May–June 2005

Technical Notes

TECHNICAL NOTES are short manuscripts describing new developments or important results of a preliminary nature. These Notes should not exceed 2500 words (where a figure or table counts as 200 words). Following informal review by the Editors, they may be published within a few months of the date of receipt. Style requirements are the same as for regular contributions (see inside back cover).

Nebulizing Spray Technique for Deposition of Propellant Thin Films

Aaron Orland* and Rik Blumenthal†
Auburn University, Auburn, Alabama 36847

I. Introduction

THE difficulties of working with RDX and HMX propellant grains include the inherent safety risks, difficulty in obtaining samples, and the regulatory issues associated with the transportation, storage and handling of these materials.[1] The combination of these obstacles make the study of propellant ignition less appealing to many academic researchers than the study of most other scientific questions. The development of a procedure to prepare useful samples, safely and easily may help overcome many of these barriers and open the arena of propellant research to a wider range of investigators. In this work, we describe a new novel spay deposition technique that can safely be used to prepare thin films of RDX and HMX from readily available sources of analytical samples.

Commercially available analytical reference samples, typically 1 μg/ml, are a readily available source of propellant materials that do not require explosive licensing and that may be shipped inexpensively using commercial shippers. Preparation of thin films from the evaporation of the solvent from propellant solutions results in very uneven films. The unevenness of the films is the result of the limited solubility of propellants in acetonitrile that serves as the solvent for analytic samples. As the solvent evaporates, cycles of supersaturation and spontaneous crystallization then follow that result in the periodic deposition of oddly shaped rings at the edges of receding liquid solution and virtually no deposition on other parts of the sample holder.

The nebulizing spray system that has been designed was based on the design of a typical nebulizing spray found in an electrospray mass spectrometer (Fison VG Trios 2000). In this design, a solution is slowly driven through a capillary tube that is run down the center of a larger-diameter tube that carries much faster moving sheath gas. As the solution emerges from the small tube, the faster moving sheath gas breaks it down into small droplets. The droplets are then carried to the sample in the flow of the sheath gas. During transit, a significant fraction, if not all, of the solvent evaporates into the dry sheath gas, with the remaining solvent evaporatively cooled below room temperature. Under the deposition conditions described hereafter, the RDX and HMX deposit as almost completely dry films. We interpret this observation to indicate that crystallization may begin as the droplet is carried to the sample in the sheath gas and that any remaining solvent rapidly evaporates on contact with the room-temperature sample holder.

Received 28 June 2004; accepted for publication 25 January 2005.

*Graduate Student, Department of Chemistry; currently Senior Process Engineer, Intel Corporation.
†Associate Professor, Department of Chemistry.

II. Experiment

A nebulizing sprayer was constructed from a standard 1/8-in. Swagelock Male Run Tee normal pipe thread (NPT) adaptingtee (Fig. 1). The noncollinear swagelock connection is attached to a source of nitrogen and is used to provide the gas sheath. A rubber septum is attached to the 1/8-in. NPT connector and is secured with wire. A 1.5-in. piece of 1/16-in. tubing is epoxied into one end of a 1.5 in. length of 1/8-in. steel tubing, such that ~1/8 in. sticks out, and the other end is attached to the collinear swagelock connector. One end of a 1-ft length of 32-gauge (0.009-in. o.d., 0.004-in. i.d.) tubing is inserted into a 26-gauge syringe needle with epoxy, and the other end is inserted through the septum using a second syringe needle that is withdrawn back onto the tubing after the tubing has been fed ~1/8 in. out of the end of the 1/8–1/16 in. tube on the other end of the adapter.

A syringe is filled with the 1-μg/ml analytical standard solution purchased from Cerrilant, and the syringe is inserted into a standard syringe pump. The solution is driven through the 32-gauge tubing at a rate of 1.5 ml/h as the N_2 sheath gas is flowed from a pressure of 40 psi. The resulting propellant deposition rate is 4.17×10^{-4} μg/s, or 0.1 μg every 4 min. A platen sample holder (MDC Vacuum Products Corporation SAM-2) is placed downstream of the sprayer and is rotated at a rate of 1–5 Hz. Rotation results in the deposition of propellant rings (Fig. 2) and also provides additional drying time before additional material is added to the same spot on the sample.

III. Results and Discussion

Two images of a sample with three 0.1-μg RDX rings deposited at nebulizer-to-sample distances of 1.0, 0.75, and 0.50 in. (outer to inner) are shown in Fig. 2. Figure 2a is an image taken with a random angle of illumination. Figure 2b is the same sample with the light source placed close to the horizontal plane of the sample holder. The difference between the images is a result of the granular microstructure of the film. (See details hereafter.) At more normal angles of illumination, a significant fraction of the incident light is scattered from the metal substrate surface, giving little contrast in the image (Fig. 2a). At shallow angles of illumination, scattering by the metal substrate is minimized, whereas scattering from the granular film is not significantly attenuated, and the contrast is increased (Fig. 2b).

It is apparent that the distance between the nebulizer and the substrate strongly influences the nature of the propellant deposit. The outer and middle deposits appear as continuous rings with maxima in scattered light intensity at the center of the ring, whereas the inner deposit appears as two separate rings with a minimum intensity at the center of the ring. The more uniform outer ring and middle ring structures are the result of simple spreading of the solution droplets

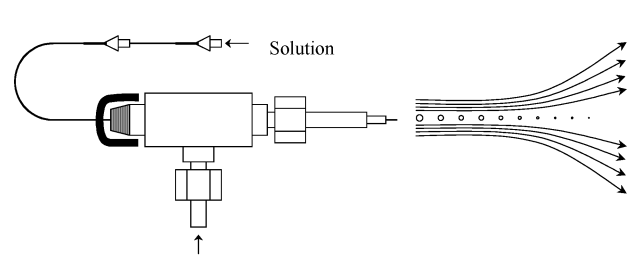
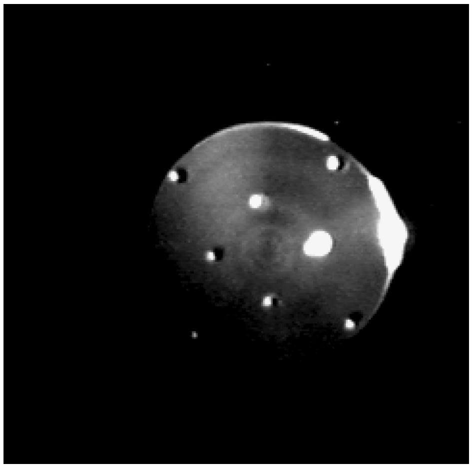
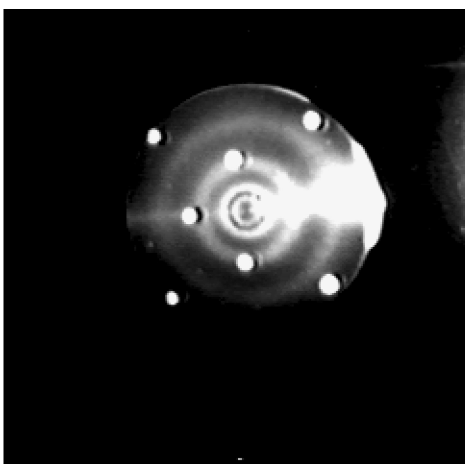


Fig. 1 Schematic of nebulizing sprayer.



a)



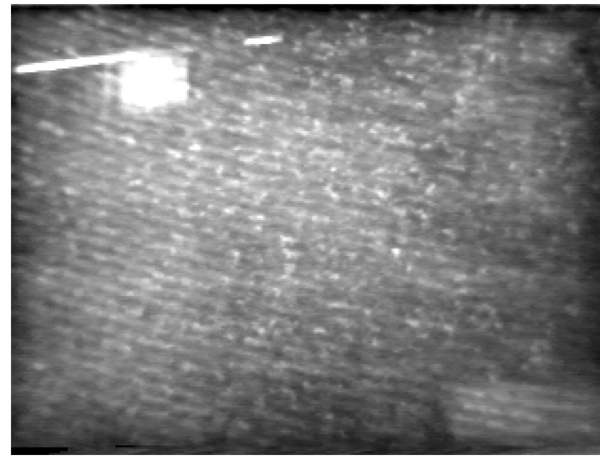
b)

Fig. 2 Sample platen with three 0.1-mg deposits of RDX illuminated at a) a random angle and b) a shallow angle.

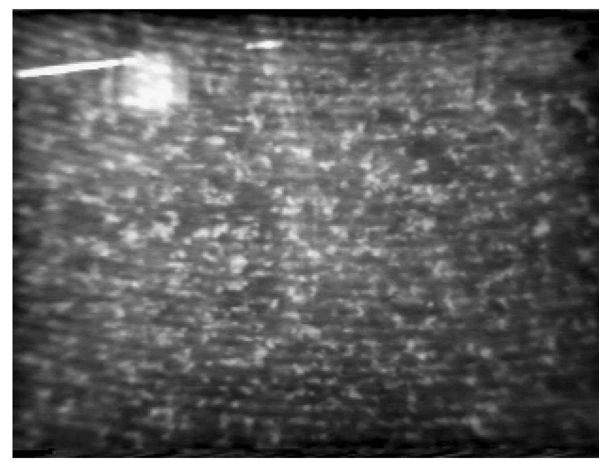
in the sheath gas as they travel to the sample and crystallization of the deposit at the location where the droplet impinged. The outer ring is broader then the middle ring due to the greater distance from the nebulizer to the substrate that allows more time for spreading of the droplets in the sheath gas.

The double-ring structure of the inner deposit is the result of a substrate distance that is too short to allow sufficient time for the desiccation of the solution droplets to the saturation concentration before the droplets reach the surface. Consequently, unsaturated liquid solution is deposited on the surface. If the deposited droplets are sufficiently large, the solvent might not evaporate before the substrate completes a full rotation, and newly deposited droplets may merge with the older droplets to form larger droplets. The unsaturated larger droplets will dissolve some, or all, of the earlier solid deposits, leaving the centerline nearly devoid of solid deposits. As the larger droplets evaporate, the solids deposit in rings at the edges of the evaporating droplet due to the cycles of supersaturation and crystallization described earlier. As this process is repeated, the solids deposited farthest from the centerline are preferentially left intact, and a double-ring structure is formed.

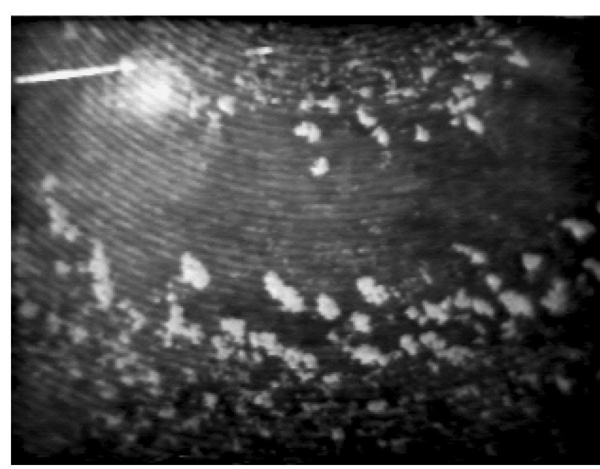
Microscope images of each of the three deposits made are shown in Fig. 3. The common features in the upper left part of the images of Figs. 3 are artifacts of the microscope and camera. The curved lines seen in the background of image are machining grooves in the metal platen substrate. They have increasing curvature going from the outer ring to the inner ring, consistent with the diameter of the ring-shaped deposit. The outer and middle ring deposits, Figs. 3a and 3b, respectively, consist of a sparse coverage of small crystallites that have diameters comparable to the spacing of the machining groove, $\leq 10\ \mu$m. The smaller radius of the middle ring combined



a)



b)



c)

Fig. 3 Microscope images of a) outer ring, b) middle ring, and c) inner ring of three deposits shown in Fig. 2.

with the identical amounts of RDX deposited results in the greater density of particles observed in the image of the middle ring. The image of the inner-ring deposit was taken at a slightly lower magnification than the two other images to allow the image to cover the entire double-ring structure. The large, irregularly shaped deposits appear to be simple agglomerations of the same smaller crystallites that were observed in the outer and middle ring. The observation of agglomerations at the boundary of the open region along the centerline of deposition are consistent with the model of open area generated by the growth of larger droplets from additional droplets growth, described earlier.

IV. Conclusions

A new nebulizing spray method for the deposition of propellant films from analytical samples that do not require special licensing has been described. Deposition at nebulizer to substrate distances of 0.75 in. or greater results in the deposition of uniform distributions of $\sim$10-μm crystallites. At shorter deposition distances a double-ring structure is observed, which can be explained as being the result of placing the substrate too close to the nebulizer. This new method for the preparation of propellant samples for model studies is both simple and inexpensive. More important, it does not require the shipping, handling, and storage of propellant materials; hence, it avoids many of regulatory issues associated with the conventional studies of propellant materials that tend to discourage research in the field.

Acknowledgments

This material is based on work supported in part by the U.S. Army Research Office under Grant DAAD19-01-1-0349. The authors would like to acknowledge our colleague, Andreas Illies, for his observations that electrospray sources produce almost dry sprays, and Rose Pesce-Rodriguez, for the initial suggestion of evaporating the solvent from analytic standards to get solid deposits.

Reference

[1] Title 27, Part 55, Code of Federal Regulations, Burean of Alcohol, Tobacco, Firearms, and Explosives, Dept. of Justice, April 2004.