

# On the mechanism of phthalazine toner chemistry in controlling silver nanoparticle growth in photothermographic imaging films

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## Abstract

*A combination of normal Raman spectroscopy, SERS, and TEM has been used to demonstrate that phthalazine is the predominant species on the surface of the metallic silver nanoparticles in the image at the final stage of imaging in photothermographic films. Evidence for a small amount of 4-methylphthalic acid, as  $\text{Ag}_2(4\text{-MPA})$ , has also been found. In addition, the organics around the developed  $\text{Ag}^0$  nanoparticles have been directly observed by transmission electron microscopy using  $\text{RuO}_4$  staining techniques. Based on these results, phthalazine adsorption is proposed to play a major role, and the phthalic acid component a lesser role, in controlling metallic silver formation of the preferred metallic silver dendritic morphology.*

## Introduction

Thermally developed imaging materials based on silver carboxylates have been commercially available for over 40 years [1]. The initial success of the “dry silver” products can be directly attributed to the simplicity of development, the absence of wet processing, and a simple heating step (to  $\sim 120^\circ\text{C}$  for 10–20 s) for image formation. Consequently, the introduction of dry technology to the medical X-ray film market in 1995 (now named the Kodak DryView laser imager) was extraordinarily well received, and over 35,000 imagers for that product were sold. Considering this success and the inevitable competition it provoked, it is somewhat surprising how little the fundamental understanding of the imaging processes, which are critical to this technology, has been published. In addition to a few review articles [1,2], only a handful of publications address the important mechanisms that form the basis of this imaging technology [3,4]. Only recently, for example, the most preferred size and shape of the metallic silver in the image was demonstrated to be the “dendritic” form [5,6]. In this case, the dendrites consist of 10–30 extremely fine (5–30 nm diameter), but poly-dispersed nanoparticles of metallic silver in the 50–200 nm diameter range. Filaments, on the other hand, are an inefficient use of silver for optimum optical density and tone. Now that the optimum metallic silver morphology has been established, the next step in understanding the development process is to determine how the optimum morphology can be produced in preference to other morphologies (such as filaments).

The “toner” component of the typical photothermographic (PTG) formulation is usually a pair of compounds based on phthalazine (PHZ) and phthalic acid (PA), and their derivatives,

such as 4-methyl-phthalic acid (4MPA), Figure 1. This co-toner pair has been generally considered to produce the desired tone by affecting metallic silver morphology [1,2,7]. However, there is currently no published report that has provided evidence of any compound of any type located on the metallic silver surface at any time in the development process. The objective of this work is to determine exactly what organic compounds are on the growing metallic silver nanoparticle surface in order to determine which ones contribute most to the morphology of that particle. With this knowledge, rational design of these compounds should be possible for improved properties, such as improved silver efficiency.

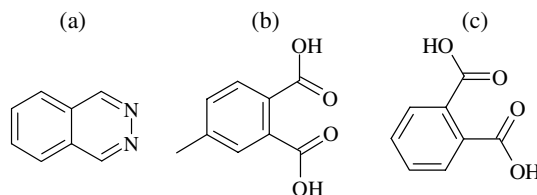


Figure 1. (a) Phthalazine, (b) phthalic acid, and (c) 4-methylphthalic acid

Using a combination of normal Raman spectroscopy, SERS, and TEM, we have now been able to demonstrate that phthalazine is the predominant species on the surface of the metallic silver nanoparticles in the image at the final stage of imaging in photothermographic films. At this stage of the imaging process, even though phthalic acid is part of the “toner package,” phthalazine is the primary component observed on the silver nanoparticle surface. The organics around the developed  $\text{Ag}^0$  nanoparticles have also been directly detected by transmission electron microscopy using  $\text{RuO}_4$  stain. Based on these results, phthalazine adsorption is proposed to play a major role in controlling the formation of dendritic silver.

## Results and Discussion

While there are numerous techniques for probing the chemical nature of surfaces, it is difficult to probe within a coated film with these methods. In addition, most can only be used on surfaces significantly larger than the nano-sized particles that comprise the metallic silver in PTG imaging materials. However, surface-enhanced Raman spectroscopy (SERS) is ideally suited to this task. SERS is surface selective, highly sensitive, and is not limited to powder samples

The SERS phenomenon is a consequence of the coupling between the surface resonance plasmon on nanoparticulate metals with the Raman-active vibrational modes of an adsorbed or adjacent molecule [8,9]. This unique coupling, most commonly observed on copper, silver, and gold, may enhance the vibrational intensities by factors exceeding  $10^6$ . Consequently, this technique should be directly applicable to the study of organic compounds, such as toners, on nanoparticulate silver that is generated in the thermal development reaction of PTG, imaging materials.

Using a commercially available Kodak DryView laser imaging film, processed at Dmax, and 122°C for 15 s, its Raman response demonstrates that PHZ is the predominant organic species on the surface of the imaged silver, Figure 2(a). The data demonstrate that this technique is directly applicable to *in situ* investigation of actual imaging films. Trace A is a SERS spectrum of the DryView film and Trace B is the normal Raman spectrum of PHZ powder. All of the Raman bands in Trace A can be attributed to PHZ, even though the concentration of PHZ in the DryView film is several orders of magnitude lower than PHZ in the bulk powder form.

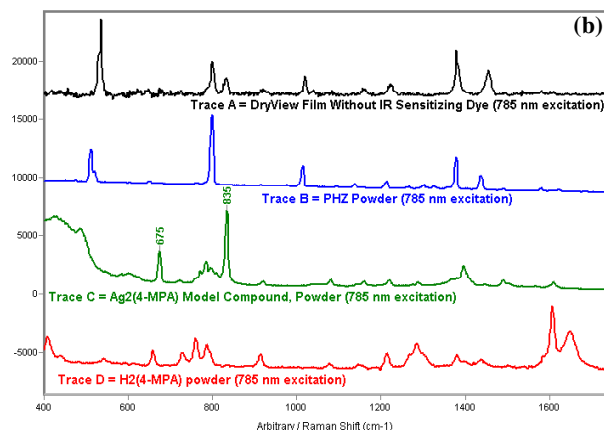
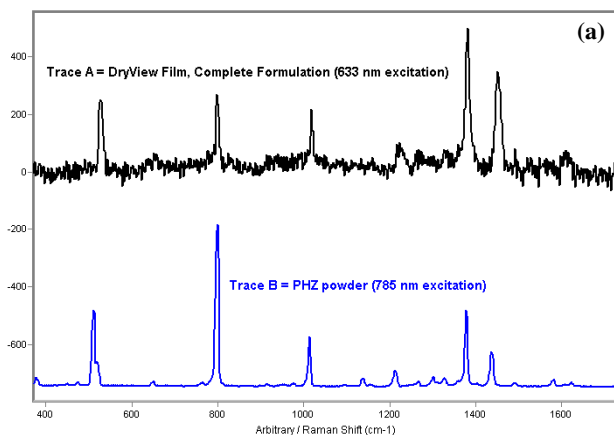


Figure 2. (a). Raman spectral data for a full-formulation DryView film. Trace A is a SERS response from the Dmax region of the PTG media developed at 122°C, 15 s. (b) Raman spectra for a DryView film without the IR sensitizing dye, together with PHZ, Ag<sub>2</sub>(4-MPA), and H<sub>2</sub>(4-MPA) reference spectra.

It has been reported in the literature that PHZ adsorbed onto a silver SERS substrate decomposes, although minimally at the relatively longer wavelength of 633 nm laser excitation [10]. Given that the full DryView formulation imaging layer contains an infrared adsorbing dye ( $\lambda_{\text{max}} = 810$  nm in the film), Raman spectrum of the film cannot be collected using the commonly available 785 nm laser excitation, where PHZ decomposition would be less. Hence, Trace A represents the best spectrum possible of the complete DryView film formulation using readily available instrumentation.

From the SERS data, PHZ is clearly the dominant species in the imaged film. However, it is important to attempt the observation of other organic formulation components present at lower concentrations than PHZ (or slightly farther away from the silver surface). Therefore, longer wavelength laser excitation is necessary in order to minimize the degradation of any silver:organic adducts formed at the surface of the imaged silver. A slightly modified DryView formulation, containing all of the components except the infrared dye, was prepared and imaged under the same time-temperature conditions as that used above. Trace A in Figure 3(b) represents the SERS spectrum (785 nm excitation) of the imaged (Xe white light) IR dye-free film at Dmax (processed at 122°C, 15 s).

It can be seen that PHZ still dominates the SER spectrum, indicating that this toner is the predominant species present on the silver surface. In addition to the bands attributed to PHZ, there are two bands (675  $\text{cm}^{-1}$  and 835  $\text{cm}^{-1}$ ), which may be attributed to Ag<sub>2</sub>(4-MPA).

Previously, it has been shown that the reduction of Ag carboxylate in DryView media resulted in the formation of a unique combination of metallic silver forms, which are the fundamental imaging elements in a PTG film [5]. It consists of a combination of filamentary and dendritic Ag, with the former usually attached to a AgBr grain upon which the latent image was originally formed during the exposure process, Figure 3(a).

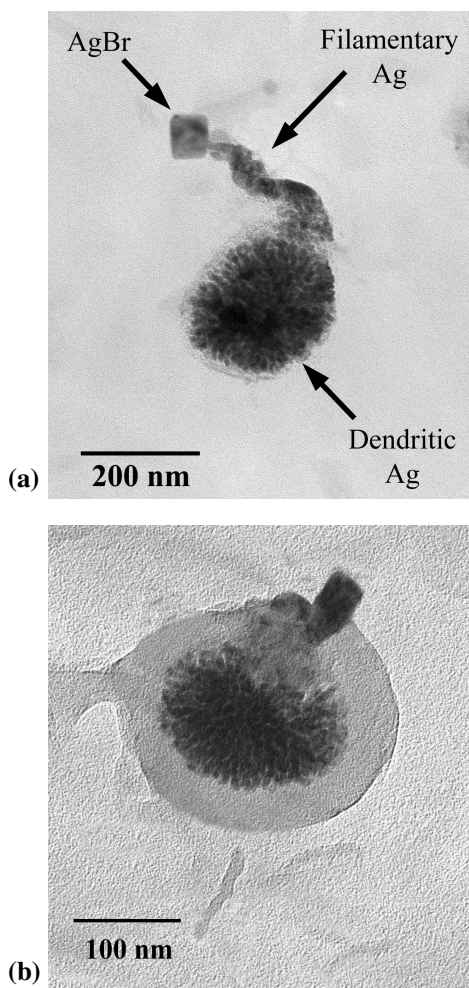


Figure 3. (a) TEM image of developed Ag in DryView media, and (b) lightly stained developed Ag in DryView media, showing both the organic passivation shell and the broccoli-like dendritic Ag core. Note the combination of filamentary and dendritic Ag that develops out from the AgBr grain.

After exposing a thin microtomed cross-section of the media for 5 s to RuO<sub>4</sub> vapor, TEM investigation of stained components identified the presence of an organic shell around the developed Ag but not dense enough to obscure the unique “broccoli-like” morphology of the dendritic Ag, Figure 3(b). Focusing in on these lightly stained features, higher magnification images revealed both the organic shell as well as the known morphology of the dendritic Ag, thereby directly showing the core-shell relationship between the internal dendritic Ag and the external passivation shell. The thickness of this shell was ~40 nm, i.e., significantly more than a monolayer deposit of the organic species. Again, no clear evidence of a detectably thick layer around the filamentary Ag or the AgBr grain was found. Therefore, taken together, this staining data, coupled to the SERS information, suggests that the PHZ toner plays a major role in passivating the dendritic form of the metallic silver in the DryView image.

Four roles have been identified for the compounds typically described as toners: 1) silver ion extraction, 2) silver

ion transport, 3) silver redox potential modification, and 4) adsorption and control of metallic silver growth. Literature discussion of the chemical role of the toners PA and PHZ in metallic silver formation in PTG materials is very limited. Other than general comments regarding the presumed role in crystal growth [1,3] or particle aggregation, the chemistry related to this question remains generally unexplored. The current consensus regarding the role of the PA component is that it is involved with Ag<sup>+</sup> extraction and possibly the transport from the silver soap to the development site (roles 1 and 2), although the structure of the silver phthalate complex intermediate is claimed to be either an asymmetric silver carboxylate dimer or Ag<sub>2</sub>PA (but not the mono-silver phthalate).

The role of a toner such as PHZ could be to form a silver complex that has lower redox potential than the original silver source and thereby reduce more easily (role 3). The PHZ could also be directly adsorbed to the metallic silver surface and therefore direct the deposit of subsequent silver atoms (role 4). This latter step is crucial to the control of the metallic silver morphology.

The role of organic species related to Ag surface passivation can be probed directly within a coated film with a combination of SERS and TEM. The ultimate goal is to control silver morphology. Chemical identification by SERS and direct imaging of both the Ag and its surface passivant by TEM now opens the door for probing the various roles played by organic species in a dry film formulation at different stages in the formation of the metallic silver image. The DryView film formulation contains several components with the ability to bond to silver, such as PHZ, 4MPA, other carboxylates, and aromatic amine-based compounds. It is significant that only PHZ, and to a lesser extent Ag<sub>2</sub>4MPA, is on the surface—even though Butvar and free fatty acid are in high concentration in the Dmax region.

The discovery of PHZ around the dendritic Ag in the DryView film reveals important features about this toner. First, PHZ is capable of displacing such silver ligand “competitors” as 4MPA (considered a co-toner), fatty acid carboxylates, tetrachlorophthalic acid, and even strong silver ligands such as mercaptobenzimidazole. Most interesting is the apparent strong capability of PHZ to adsorb nearly exclusively onto the dendritic Ag surface, but yet not sufficiently well to completely passivate the nanoparticles, because the nanoparticles still aggregate. However, its passivation property is good enough to prevent the aggregates from coalescing given that the dendritic Ag clusters are now known to be made up of individual Ag nanoparticles and have very large surface areas.

Second, the diameter of the dendritic Ag cluster is ~100–200 nm, Figures 3(a) and (b). The desired Ag aggregate size distribution for the proper cold and neutral tone in commercial PTG media is a size range spread around an average diameter of 100 nm [5,6]. Hence, the microstructure data indicates that PHZ is a toner that has the ability to passivate Ag nanoparticles and induce aggregation, without coalescence, of Ag clusters in this unique aggregate size range. It should also be noted, however, that there is a key feature in the Kodak DryView laser imager film system. Dendritic Ag in this type of film is spherical. This may suggest that other organic species may be present in the (TEM-detected) passivation shell. The possibility that 4MPA (considered as a co-toner) may play a key role to induce the

formation of a spherical morphology to minimize the Ag aggregate surface energy is worth considering. Recent results by Ohzeki et al. have shown that PA and its derivatives have a substantial effect on the Ag aggregate morphology [11]. In this case, a series of experiments were carried out with different derivatives of PA (e.g., NaPA, NH<sub>4</sub>PA, etc.) in order to examine the resulting Ag aggregate shape. It should be kept in mind, however, that these examples are based on a water-coated film formulation.

## Conclusions

For the first time, direct analytical evidence has been obtained that shows the formation of metallic silver nanoparticles within a real PTG construction during the late stage of development is controlled primarily by the surface adsorption of PHZ. These incompletely passivated surfaces are induced to aggregate but not coalesce. While PHZ is the predominant passivant on Ag nanoparticles, the role played by its co-toner, PA, may be to modify the aggregate morphology toward a spherical shape.

Raman spectroscopy and heavy-metal staining in conjunction with TEM investigation have provided the initial evidence for how toners, such as PHZ, affect the developed silver morphology in a photothermographic construction based on Ag carboxylate. We are now in a position to determine what organic compounds are present on various metallic silver morphologies at different stages of thermal development. It is particularly important to establish what is on the first-formed silver filaments in order to understand the filament-to-dendrite transition. Routes to encourage the formation of the dendrites sooner in the development process should provide for improved silver efficiency.

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## Author Biography

*Samuel Chen has contributed to the field of imaging science for over 20 years, concentrating on understanding the relationship between imaging media components and their light absorption properties. He has publications and patents in AgX-based photographic film, Ag based photothermographic and Ag-based thermographic technologies. He is a member of the IS&T, as well as the Materials Research Society.*