

# Silver Coordination Chemistry in Thermally Developed Imaging Systems, V: The Role of Phthalazine in Photothermographic Imaging

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## Abstract

Photothermographic imaging materials, based on the thermally induced reduction of silver soaps to metallic silver, continue to be an important commercial product used in medical diagnostic applications. Multiple research groups have probed the silver coordination chemistry that is involved with the extraction, transport, and reduction to form a black-and-white image, yet much remains unknown regarding these image-forming reactions. Understanding the silver chemistry of this system, in particular the functions of the phthalazine component of the toner package, is important to improving the development response of these materials. The specific role of phthalazine in this development process, introduced in various forms of silver complexes into the system, and how it can participate at the different stages of development, will be the focus of this talk.

## Introduction

The first silver carboxylate complex containing phthalazine (PHZ) in the coordination sphere was reported in 1995 [1]. This complex, abbreviated as  $[\{Ag(O_2CCH_3)PHZ\}_2]_n$ , is a polymeric species built of carboxylate-linked  $[AgPHZ]_2^{2+}$  dimers, and easily forms at room temperature simply by dissolving silver acetate and PHZ in water. Initially, it was thought that this complex might be a good model of a thermally generated behenate analogue formed during imaging in a film, however, a mixture of this complex in MEK containing any typical photothermographic developer rapidly reduces at room temperature to metallic silver. Therefore, the formation of that type of complex would seem far too reactive to be able to enable image/nonimage discrimination in a coated film, that is,  $D_{min}$  should be  $D_{max}$  even during the coating process.

Because phthalic acid has been reported as an extractant for the silver ion from silver soaps [2,3] it was thought that the phthalate version of  $[\{Ag(O_2CCH_3)PHZ\}_2]_n$  might be a more relevant and more likely intermediate in the thermal development process. The  $[Ag_2PHZ_2PA \cdot H_2O]$  complex was obtained and characterized by normal analytical techniques including crystal structure determination [4]. Despite its poor solvent solubility, this complex also reduces to metallic silver relatively rapidly with photothermographic developers when suspended in organic solvents, analogous to the acetate version.

Recently, the extraction role of phthalic acid was proposed to specifically involve the formation of  $Ag_2PA$  (the 1:1 complex is explicitly excluded in this mechanism) [3], although this complex is less organic-soluble than the starting  $AgBe$  [5]. If the intermediate silver-containing was of the type  $[(AgPHZ)_2 \cdot PA]$ , then intentionally adding it to a photothermographic formulation

should result in quantifiable imaging properties. It is this proposal, to prepare and evaluate silver complexes thought to be most likely intermediates or their direct precursors, in the transport component of the development chemistry, that forms the basis of the investigation described below.

## Experimental

### Preparation of Silver Complexes

All silver complexes were initially prepared following the procedure established for the known complex  $[Ag_2PHZ_2PA \cdot H_2O]_n$  [4], and are abbreviated here as silver-phthalazine-carboxylate (APC) derivatives.

Table 1. Phthalic Acid Derivatives.

1	4MPA		5	F-PA	
2	Sal		6	HPA	
3	mPA		7	PAm	
4	Cl <sub>2</sub> PA		8	AcBA	

### Screening in a Model AgBe Formulation

Samples were evaluated in a model film formulation in the following manner: to 9 g of a 24.7% silver behenate (from pure HBe) dispersion was added 0.6 g B79, followed by 0.45 g Lowinox. The silver complex, 0.1 g, was added, coated 3.3 mil wet, and air-dried. Thermal sensitivity was assessed by holding a  $1 \times 15$  cm strip on a gradient temperature bar (Hotbench™) for 15 s; the thermal onset temperature,  $T_{onset}$  (a visual estimation of the intersection of the baseline with the tangent of the slope), was noted as a measure of reactivity in addition to image color.

## Results and Discussion

From all of the work reported in the literature to date, the most likely silver intermediate is considered to be some form of  $[\text{Ag}_2\text{PHZ}_2\text{PA}]_n$  or a mixed (asymmetric) carboxylate version (possibly without PHZ in the structure). Consequently, silver phthalazine carboxylate (APC) complexes were selected as a starting point. It is clear simply from reference coatings that the individual components, PHZ, PA, or Lowinox, by themselves provide little or no contribution to an image other than yellow, which is likely Carey Lea Silver [6]. Interestingly, when incorporating the APC complex into the formulations the expected  $\text{Ag}^0$  formation reaction was observed, similar to a simple dispersion with developer, but on drying, the coating remains stable until heated. Under these conditions, the first APC1 sample (containing PHZ and PA in the silver coordination sphere) is indistinguishable from the control containing PHZ and PA added separately, and the higher level of APC1 results in a more reactive formulation ( $T_{\text{onset}}$  is about  $10^\circ\text{C}$  lower). This suggests that the APC complex could be an intermediate in the thermal development reaction.

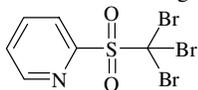
A selection of other APC complexes were prepared and tested in the model system (Table 2).

**Table 2. Summary of  $T_{\text{onset}}$  and Color for APC Complexes in the Model Film Formulation**

APC	$T_{\text{onset}}, ^\circ\text{C}$	Color
1	120	Black
2	130	Yellow
3	125	Light purple
4	140	Light maroon
5	125	Red-black
6	125	Yellow
7	112	Black
8	110	Red-brown

Using a typical complete PTG formulation containing no PHZ or 4MPA (other than that introduced from the complexes), however, showed striking differences between reactivities. Under normal processing conditions, APC1 and APC7 showed good reactivity (and color) at the 10 mole % (relative to AgBe), while APC5 and APC6 showed no reactivity. These results do not correlate to the Hotbench evaluation.

The main difference between the simple model formulations and the full PTG formulation was the absence of AgBr (the latent image-forming component) and antifoggants in the model formulation. The inorganic chemistry of the various components of the formulation should not directly depend on the presence of the latent image, but Strijckers has proposed that development inhibitors, such as the tribromomethyl-antifoggants, are required for a photothermographic response [7]. That is, he proposed that the antifoggants remaining within the sphere-of-influence must be removed by the latent image before the thermal development reaction can occur. In the case of oxidizing antifoggants such as tribromomethyl compounds, TBM (Figure 1), this means oxidation of the  $\text{Ag}^0$  in the latent image and conversion of the TBM to oxidation products and the formation of AgBr.



**Figure 1. TMB compound.**

A simple test of the model formulation, this time containing AgBr with APC1, was carried out and thermally tested on the Hotbench both red and white (UV) light-exposed. In this case, one vertical half of the film was exposed to white lab light (1 min) while the other half only saw red light. Thermal development on the Hotbench produces two different onset temperatures depending on the sensitivity of the film. With this antifoggant, a clear  $10^\circ\text{C}$  temperature differential was observed, starting at  $105^\circ\text{C}$ . Other antifoggants produced similar effects.

These results are consistent with these antifoggant compounds acting as development inhibitors, which apparently function by eliminating  $\text{Ag}^0$  nucleation sites (fog centers). In this case, the antifoggant might not be required to be eliminated prior to development, as proposed by Strijckers [7], but the nucleation sites must be removed in order to provide a thermal differential that allows for exposed vs nonexposed image discrimination when the overall film is developed at a uniform temperature. A simple model of silver soap, developer, and toners is not sufficient to provide accurate insight into the development chemistry of the PTG system, but a model PTG formulation is possible with an antifoggant included in the simple model formulation.

### Functional Model PTG Formulation

As noted above, according to Sahyun and Maekawa, the first silver complex intermediate formed during thermal development is AgHPA or  $\text{Ag}_2\text{PA}$ , respectively. The second complex, according to Maekawa, is  $\text{AgPHZ}^+$  and/or  $\text{AgPHZ}_2^+$  with an unspecified counterion. If these complexes are important components in the development process, then intentionally incorporating them into the formulation (in place of the individual compounds) might be expected to produce a film that exhibits at least similar reactivity. Enhanced reactivity might be expected because the intermediate is already present. We have explored this proposal in both complexes, adding  $\text{Ag}_2\text{PA}$  as a solid dispersion with the corresponding PHZ added separately, and adding  $\text{AgPHZ}_2\text{X}$  complexes with 4MPA added separately (Table 3).

**Table 3. Maekawa Intermediates in the Model System: AgBe, Lowinox, PVB.**

		Hotbench, $^\circ\text{C}$
$\text{AgPHZ}_2\text{NO}_3$		Yellow, 130
$\text{AgPHZ}_2\text{TCPA}$		Yellow, 130
$\text{AgPHZ}_2\text{SO}_4$		Yellow, 130
$\text{AgPHZ}_2\text{CBBA}$		
$\text{Ag}_2\text{PHZ}_2\text{NO}_3$	+ 4MPA	Black, 118
$\text{AgPHZ}_2\text{TCPA}$	+ 4MPA	Red, 130
$\text{AgPHZ}_2\text{SO}_4$	+ 4MPA	Black, 115

The silver complexes containing only the PHZ ligand behave like AgBe without toner, or with PHZ only. Addition of the co-toner, 4MPA, however, facilitates the toning process to form black. Note that the  $\text{AgPHZ}_2\text{TCPA}$  version, with 4MPA, provides a red-toned image. From this model set, it appears that the counterion could be a critical component of the silver phthalazine complex. The strong acid counterion versions do not facilitate thermal development.

Addition of Ag<sub>2</sub>4MPA with increasing amounts of the PHZ co-toner provided a faint image at best. This result implies that Ag<sub>2</sub>4MPA cannot be the intermediate proposed, although one could argue molecular levels, significantly smaller than the submicron particulates added, might still form within the imaging system and have the solubility/mobility that the Maekawa mechanism requires. The high surface area of the particulates in the dispersion used and the temperature at which thermal development occurs make this latter point less likely.

Addition of AgPHZ<sub>2</sub>X with increasing amounts of the 4MPA co-toner yields results similar to the Ag<sub>2</sub>4MPA + PHZ. Very little image with the NO<sub>3</sub><sup>-</sup> counterion and CBBA, an example having a weaker acid counterion, showed the highest optical density at ~0.3.

## Conclusions

We conclude that this model system is a reasonable model for the full formulation, particularly when taking into account the single, narrow development temperature of the latter, which would not be expected to overlap precisely with the formulation containing fewer components. It is this formulation that is expected to provide insight into the development chemistry occurring during development and enable designed changes.

Silver complexes having a composition containing both 4MPA and PHZ, such as Ag<sub>2</sub>PHZ<sub>2</sub>4MPA, can be incorporated within a PTG imaging construction without premature Ag<sup>0</sup> formation only if antifoggants are present to prevent room-temperature reduction. These complexes could be considered as one form of silver containing intermediates generated during thermal development of PTG formulations.

Ag<sub>2</sub>PHZ<sub>2</sub>4MPA complexes in the PTG formulation containing antifoggants are stable even under development conditions in the unexposed regions, which is a key requirement for any silver-containing intermediate formed in the film.

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## Author Biography

*David Whitcomb, B.A., Ph.D., has been investigating the silver chemistry of photothermographic imaging materials since 1989. In 1999, two years after 3M transferred several business units into a new company, the medical imaging business was sold to Eastman Kodak Company. He is currently continuing this silver chemistry research effort, which also includes understanding the optical properties of the metallic silver nanoparticles. He has over 50 technical publications and 19 patents.*