Silver Coordination Chemistry in Thermally Developed Imaging Systems, VI: Direct Thermal Imaging Materials

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Abstract

Both thermographic and photothermographic imaging materials, based on the thermally induced reduction of silver soaps to metallic silver, are important commercial products used in medical diagnostic applications. Understanding the silver chemistry of these two systems, in particular, the functions of the individual toners and developers, is an important component to improving the development response of these materials. The thermographic toner reactivity is the focus of this talk.

Introduction

Direct thermal imaging constructions based on the reduction of silver are relatively simply formulations: only a silver source, an electron source, and an image "toner" (in a binder) are required [1,2]. Agfa's Drystar, for example, is based on silver behenate, 3,4-di-hydroxybenzoic acid and 2H-1,3-benzoxazine-2,4(3H)-dione (benzoxazine dione, BOD) (Figure 1) [3].

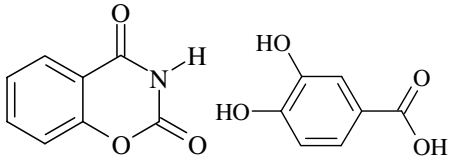

***Figure 1**. 2H-1,3-benzoxazine-2,4(3H)-dione and 3,4-di-hydroxybenzoic acid.*

Common to all imaging materials based on silver soaps is the formation of the metallic silver image, which must be a neutral black. Thermal development of the silver soaps with just the developer typically provides a brownish image, hence the incorporation of materials such as BOD in order to improve the image tone. Because the image color and tone are controlled by the metallic silver nanoparticle morphology and their relative juxtaposition [4,5], it has been assumed that the toners operate by modification of these properties. That is, the toner adsorbs to the metallic silver surface as the particle grows, and influences the nucleation, growth, and aggregation processes. In order to optimize the silver formation in these systems, it is important to better understand the details of how these toners function. We now present new evidence regarding the role of toner reactivity and the formation of AgToner complexes. The solid-state structure of the first pure AgToner complex, $[AgBOD]_2$, is discussed below in its role during thermal development. The thermal behavior of mixtures of silver soaps with these types of toners, and the solid-state structure of the AgToner complex provides good evidence that the toner is involved directly with the initial stage of reaction and formation of developable silver complexes.

Experimental

Crystals of AgBOD suitable for single-crystal X-ray diffraction were obtained by slow ligand exchange of HBOD for phthalazinone in the insoluble AgPAZ complex, as described elsewhere along with the single-crystal X-ray diffraction details [6]. Differential Scanning Calorimetry (DSC) was carried out on a TA Instruments Dual Sample DSC Model 910 by heating (10°C/min) ~10 mg samples under N_2 flow (50 mL/min). Samples were prepared by thoroughly mixing the selected amounts of fine powders.

Results and Discussion

There is very little information in the literature related to the solid-state structures of silver toner complexes, which are thought to be important in all thermographic imaging systems [1,2,7]. Solubility is the main reason that the solid-state structures of AgToner complexes, such as with BOD, have never been reported. These complexes are extremely difficult to crystallize in sizes suitable for conventional X-ray diffraction techniques. We have recently been able to solve the solid-state structure of $[AgBOD]_2$ (Figure 2).

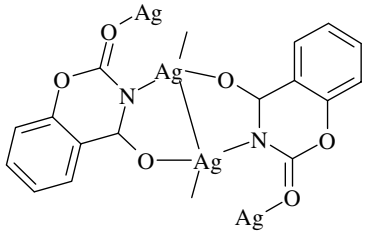

***Figure 2**. Molecular structure of $[AgBOD]_2$.*

The $[AgBOD]_2$ dimer is constructed of an eight-membered ring, much like silver carboxylates. Such a simple low molecular species might be expected to exhibit some organic solubility, but in this case, a long Ag-O bond, 2.712 (5) Å, is observed to connect the carbonyl and the Ag^+ ion in adjacent $[AgBOD]_2$ dimers, which inhibits solubility.

The thermal reactivity of HBOD with the silver soap induces a solid-state reaction to form a new silver complex by ligand exchange from the HBOD ionizable proton (N-H). In this case, phase transitions normally observed in the 120–200°C temperature range for silver stearate [8] are seen to change dramatically on the second heat. In the stoichiometric case of a 2:1 mole ratio mixture of HBOD and $[AgSt]_2$, the reaction would be:

$$[AgSt]_2 + 2HBOD \rightarrow [AgBOD]_2 + 2HSt \quad (1)$$

where a fully exchanged reaction would produce the $[AgBOD]_2$ and free fatty acid. This reaction was readily observed by the

dramatic changes in the thermal phase changes of the silver stearate and the formation of HSt (mp = 68°C) (Figure 3).

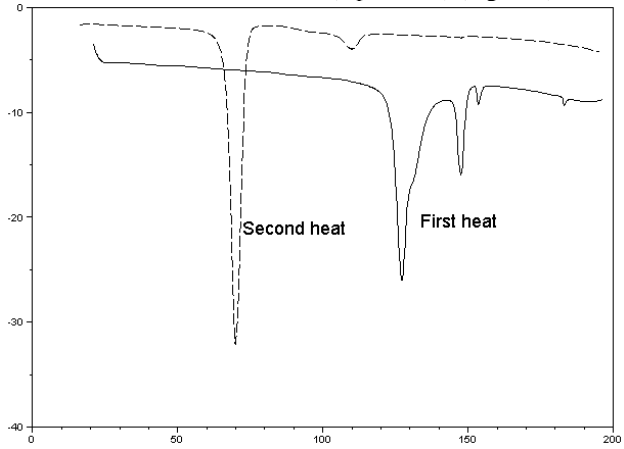

***Figure 3**. DSC of HBOD in silver stearate.*

The DSC-monitored reaction of silver stearate with BOD shows a nearly 100% increase in the free HSt phase, along with the corresponding loss of all the normal $[AgSt]_2$ phase changes in the 100–200°C range, confirming complete conversion of the $[AgSt]_2$ complex. Other toners used in direct thermal imaging formulations, when subjected to the analogous DSC reaction with $[AgSt]_2$, responded similarly. Interestingly, however, addition of the separately prepared $[AgBOD]_2$ complex into a direct thermal imaging formulation, in place of the HBOD, showed decreasing optical density with increasing $[AgBOD]_2$ levels. These results suggest that the $[AgBOD]_2$ complex itself is less reactive with the developer in these formulations than the silver carboxylate.

On the other hand, under the conditions of the image formulation stoichiometry (large excess of silver carboxylate**)** the initial silver complex formed could be expressed as

$$StAgAgSt + HBOD \rightarrow StAgAgBOD + HSt \quad (2).$$

The asymmetric silver dimer implied by (2), and the proclivity of both silver carboxylates and the $[AgBOD]_2$ complex to form ligand-bridged eight-membered rings, is completely consistent with the solid-state thermal reaction, as well as with asymmetric silver carboxylates detected by X-ray diffraction in photothermographic components [9–11].

Conclusions

The first structure of a silver toner complex, $[AgBOD]_2$, a possible product formed in the thermal imaging chemistry of silver carboxylates, has been resolved. Similar to silver carboxylate structures, the structure of this complex is a dimer constructed from eight-membered rings. From this structure and supplemental DSC and NMR experimental data, we conclude that the pure $[AgBOD]_2$ complex is not formed at any time in any significant concentration in the imaging layer of the thermographic imaging formulation. Thermal reactivity generates a new silver complex intermediate in between the starting silver soap and $[AgBOD]_2$, which is likely to be an asymmetric silver dimer.

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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.