# Advanced Development Accelerators: One End of a Lipidic Scale for Silver-Ion Binding Materials

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## Abstract

Advanced development accelerators (ADAs) are materials that are added to films that enhance development of AgX-containing sublayers. Use of ADAs generates greater photographic speed or enables the downsizing of AgX grains with improved granularity. Mechanistic work shows that ADAs are materials on the high end of a lipidic scale of silver-ion binding compounds. Common inhibitors of development are on the low end of the lipidic scale. Silver-ion binding materials that enhance interlayer inhibition are "in between" with medium lipophilicity. The mechanistic evidence points to an off-the-grain mechanism for ADAs in which their silver salts become novel silver-atom generators in the presence of reducing developers.

## Introduction

In silver halide-based media, silver-ion binding materials are inhibitors of silver development. Phenylmercaptotetrazole and substituted benzotriazoles are premier examples. Such molecules released from DIAR couplers typically give speed losses. These inhibitors are usually low in lipophilicity. In this paper, we show that when the lipophilicity of silver-ion binding materials is increased, speed losses turn into speed gains.

Historically, pyrazolotriazole couplers give greater onto-green interimage effects than pyrazolone couplers. This means that pyrazolotriazoles induce greater interlayer inhibition; and the cause was traced to the greater silver-ion binding ability of pyrazolotriazoles compared to pyrazolones.

Greater interlayer interimage was found by attaching a "free" benzotriazole (N-H not blocked) to a pyrazolone coupler.[1] We found a simple ballast could replace the coupler moiety and the interimage effect was a function of the ballasting on the benzotriazole.[2] High ballasting did not improve the interimage, but at an intermediate ballasting, interimage was increased.

## Discovery

While investigating the lipophilic effects on silver-ion binding materials, we found that at sufficiently high lipophilicity, silver-ion binding materials turned into speed-enhancing compounds.[3] For example, Table 1 shows a series of purines with different levels of ballasting. These were tested in the fast magenta sublayer of a multilayer film.

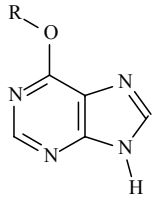


*Figure 1. Ballasted purines.*

**Table 1. Speed and granularity for differently ballasted purines.**

| Compound | Speed | Granularity |
|---|---|---|
| None | (0) | 0.021 |
| C10 | -0.20 | 0.023 |
| C12 | 0.07 | 0.024 |
| C14 | 0.30 | 0.018 |
| C16 | 0.40 | 0.020 |
| C18 | 0.40 | 0.021 |

At sufficiently high lipophilicity, purines give enhanced speed, defined as the stops of exposure needed to give a density of D-min + 0.15. Furthermore, there is a loss, not a gain, of interimage.

These findings led to the hypothesis that there is a lipidic scale of activity for silver-ion binding materials. At low lipophilicity, silver-ion binders are classical inhibitors. At medium lipophilicity, the compounds induce interimage increases. At high lipophilicity, speed increases are seen with loss of interimage.

Furthermore, we found that there are laydown effects. For silver-ion binding materials of medium lipophilicity, we find that 10X lower laydowns give enhanced interimage. Higher lipophilicity analogues require higher laydowns to give speed increases.

A spectacular example is with ballasted mercaptotetrazoles. Phenylmercaptotetrazole (log Kow 3.3) is an inhibitor of development. With ballasting to give a log Kow of 11.6, low levels of film laydown give enhanced

interimage with only a slight loss of speed. At sufficiently high log Kow, 19.4, mercaptotetrazoles give enhanced speed with loss of some interimage.

## Mechanism

Speed enhancement only occurs with dual melts when the speed addenda are kept separate from the emulsion until just prior to coating.[3] Single melts give speed losses.

Ultraballasted speed addenda up to log Kow 16.8 still give speed. Even polymeric addenda give speed.[4]

Speed addenda coated in an interlayer between the slow yellow and fast magenta sublayers give approximately half the speed increase. Even polymeric addenda in the interlayer give speed increases. We found that only 0.1% of a log Kow 7.0 purine coated in the interlayer is found in the fast magenta sublayer after processing. When this same 0.1% of the purine was coated in the fast magenta sublayer, no speed enhancement was observed.

All these results say that the mechanism is "off the grain."

With use of speed addenda, microscopy of silver specs within magenta clouds show both enhancement of the number of silver specs as well as the area of silver per spec. Other measurements confirm enhanced silver formation.

We find that light latensification prior to development eliminates the speed enhancement of silver-binding addenda. We conclude that addenda are chemical latensifiers of subdevelopable latent images. When such subdevelopable latent images are made developable by light, the addenda are inert.

The only chemistry we know regarding the speed enhancing addenda are hydrogen ionization and silver salt formation. Furthermore, we observe silver salt formation in film during Process C-41. Preformed silver salts give speed enhancement. This speed enhancement is independent of the level of sulfite, iodide, bromide, or metal sequesters in the developer. The speed enhancement is also independent of the level of DIARs that release inhibitors.

We speculate that the speed addenda are silver atom generators. Developers reduce the silver salts to silver atoms that transport to the grain and find latent images or decompose to a conduction band election.

To confirm this mechanism, the silver salt of a purine was treated with Process C-41 developer in a film that contained a magenta image coupler (a pyrazolone) but no silver halide. The green density was 0.165 higher than a check without the purine salt, and the silver formed was 0.7-mg/sq ft.

Independent studies showed that the purine accelerators titrate with 1.5 molar equivalents of silver ion. Therefore, we believe that the silver salt in film (Fig. 2) is:

## Conclusion

We believe there is a lipidic scale of performance for silver-ion binders. Low lipophilicity gives a classic inhibitor.

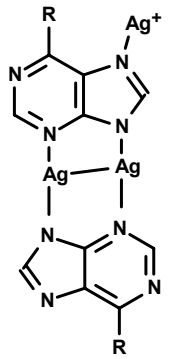


*Figure 2. Proposed 3:2 complex.*

Medium lipophilicity gives materials that improve interimage with low speed losses. High lipophilicity gives speed enhancements.

The mechanism of speed enhancement appears to be off the grain. Molecular orbital calculations and silver-ion titrations point to a 3:2 silver-ligand salt that is reducible in a Process C-41 environment. We have no evidence how these silver-atom clusters transport to subdevelopable latent image sites.

## References

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## Biography

Lou Friedrich is a Research Fellow in the R&D Laboratories of Eastman Kodak Company. His interests are in the modeling and mechanisms of imaging materials by the application of experimental design and chemometrics. Before joining Kodak in 1980, Lou received his education at MIT, Berkeley, and Yale in the field of organic chemistry, and was on the faculty at the University of Rochester for 13 years. Email: louis.friedrich@kodak.com