

# Autocatalytic Formation of Silver Particles During Photographic Development

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## Abstract

The kinetics of silver particles formation during development of black and white images was analyzed in terms of several mechanisms. Published kinetic data was employed to test kinetic models derived from the electrochemical mechanism, the mechanism for autocatalytic formation of Ag colloids, and a modified version of the latter mechanism that includes a growth step of Ag clusters yielding metal particle catalysts. In this mechanism Ag particles form an ohmic contact with the silver halide grains and delocalize electrons from the developer into the semiconductor. The delocalized electrons reduce silver ions present either in the AgX lattice or on the semiconductor surface. Development curves corresponding to physical and direct Ag amplification as well as of thermally developable photographic materials were used in the tests, in all cases the data were found to be consistent with the modified autocatalytic mechanism for formation of Ag crystallites.

## Introduction

Photographic imaging is a mature technology involving ingenious light-initiated and catalytic processes.<sup>1</sup> However, a thorough understanding of photographic development has not been achieved due to the complexity of practical systems.<sup>2</sup> In this important chemical amplification step the metallic phase formed on the surface of the AgBr semiconductor assists the reduction of Ag<sup>+</sup> ions by the developer. Both physical and direct development are possible for developers containing complexing agents able to induce partial semiconductor dissolution. The fact that Ag particles form during physical development whereas filaments result from direct development has been usually interpreted as indicative of two different mechanisms.<sup>2</sup> Interestingly, kinetic plots of either mass or optical density of the generated metal yield s-shaped curves, suggesting that Ag deposition is autocatalytic for both development processes.

These data has been rationalized invoking an electrochemical mechanism in which light-generated Ag clusters act as electrodes.<sup>3</sup> Lattice Ag<sup>+</sup> ions are reduced at the metal-semiconductor interface and the reductant is oxidized at a different place on the metal surface. Autocatalysis arises from increases in metal surface area as Ag deposition proceeds; the initial particles evolve into filamentary structures when electron transfer to the electrode is faster than Ag<sup>+</sup> reduction.<sup>2,3</sup> Low resolution TEM results have been interpreted as supporting the electrochemical mechanism.<sup>4</sup> However, results inconsistent with this model are found upon close inspection of the data. Recent TEM studies have provided a different picture of direct development since the initially generated nanometer-sized Ag crystallites aggregate first producing particle networks, which then agglomerate to yield filaments.<sup>5</sup> This evidence suggests that the mechanisms controlling formation and aggregation of Ag particles during photographic chemical amplification are very similar to those governing crystallite formation in metal colloids.

Alternative kinetic models for development based on autocatalytic formation mechanisms of Ag colloids are presented here. Crystallite formation from the latent image clusters was assumed to be the rate-determining step, while filament generation was considered as a secondary agglomeration process. The models were tested using published kinetic results corresponding to development of black and white images. Models derived from the electrochemical mechanism for the early development stages were tested first.<sup>6</sup> Included in the tests was a model used to rationalize the kinetic features of the spontaneous reduction of Ag<sup>+</sup> ions in alcohols containing OH<sup>-</sup> ions.<sup>7</sup> In the proposed mechanism Ag particles act as catalysts for the reduction Ag<sup>+</sup> and autoaccelerated metal deposition is a consequence of continuous increases in the number of the Ag crystallites present on the AgX surface. A modified version of this mechanism was also examined since it is questionable that the latent image clusters, believed to consist of about 4 metal atoms, can act as catalysts for

the reduction of  $\text{Ag}^+$  ions. The reason is that the physical and chemical properties of Ag clusters are significantly different from those of larger particles.<sup>8</sup> Only clusters forming an ohmic contact with the semiconductor grow fast to larger catalytically active particles, whereas those not electronically connected to AgX grow via a slower first-order process. The modified kinetic model included a first-order transformation of the latent image into larger Ag particles; it was found that this is the only model that is consistent with the development data.

## Experimental

Data employed in the simulations was digitized directly from published plots of Ag optical density (OD), or mass, versus development time. With the exception of kinetic results represented by continuous curves, only measured data points were analyzed excluding any lines drawn to connect experimental points. Plots based on relative (or normalized) development time or plots showing discontinuities were not considered; only data sets that allowed testing for autocatalysis were used in the simulations.<sup>9</sup> Kinetic data relevant to physical development were obtained from a study on the reduction of  $\text{Ag}^+$  ions catalyzed by metal particles,<sup>10</sup> and from investigations on thermally developable photographic materials (TDPM).<sup>11</sup> Results representative of direct development were extracted from studies using normal unsensitized motion picture positive type film,<sup>12</sup> emulsions of cubic silver chlorobromide grains,<sup>13</sup> a model system consisting of AgCl particles with gelatin and metal,<sup>2</sup> AgCl and AgBr films as well as liquid emulsions,<sup>14</sup> and a silver bromiodide emulsion.<sup>5</sup> After digitizing the original plots with an Apple OneScanner (Ofoto 2.0 scanner software) the numerical values of the data points were extracted using Data Thief software (version 2.0). These values were then imported into DeltaGraph 4.0, which was used for kinetic evaluations with either Macintosh (II ci) or Pentium-based (Dell Optiplex GX1) computers. Simulations were performed by means of the non-linear square fitting subroutine of DeltaGraph.

## Results and Discussion

Autocatalytic reactions are initially slow but undergo sharp rate increases, followed by decreasing rates as the reactants are been consumed. For these reactions a plot of advance of reaction versus time yields s-shaped curves and the instantaneous rate exhibits a maximum value.<sup>9</sup> All data sets used in this study (50) complied with the classical test for autocatalysis having a maximum when the reaction rate was plotted as a function of time. The accuracy of the scanning and

digitizing methods was tested using published results from the autocatalytic reduction of  $\text{Ag}^+$  ions in 2-propanol solutions of  $\text{OH}^-$  ions.<sup>7</sup> From the data of curve a in Figure 7, and with the corresponding autocatalytic equation (equation 3, see below) a calculated rate constant of  $1.64 \times 10^{-3} \text{ s}^{-1}$  was obtained. The close agreement between this rate constant and the published value,  $k = 1.7 \times 10^{-3} \text{ s}^{-1}$ , indicated that the data extraction methods were reliable.

The first models examined were those that result from the electrochemical mechanism since they are still viewed as realistic representations of the amplification step. It is assumed in these models that the Ag crystallites remain spherical as they grow, and that the growth rate is controlled either by the particle surface area or by diffusion of reactants.<sup>6</sup> Equation 1 is the solution to the growth rate expression in the former case,

$$OD_t^{1/3} - OD_o^{1/3} = k t \quad (1)$$

whereas equation 2 applies to the latter situation,

$$OD_t^{2/3} - OD_o^{2/3} = k t \quad (2)$$

where  $OD_t$  and  $OD_o$  are the optical densities of metallic Ag at time  $t$  and at  $t = 0$ , respectively. Because OD is, in most cases, proportional to the metal mass ( $m$ ) analogous equations can be employed where OD is substituted by  $m$ . Out of the 50 kinetic curves that were analyzed equation 1 gave reasonable fits to the data in 19 cases, and equation 2 in only two cases. However, even in the best cases these equations were able to fit only part of the data, usually results measured at long reaction times. For this reason neither equation was considered to appropriately represent development kinetics. Obviously, the chemical mechanisms used to derive equations 1 and 2 are not a realistic representation of development.

The mechanism that explains the spontaneous formation of Ag crystallites in basic 2-propanol yields a kinetic model represented by the first-order autocatalytic equation:<sup>7</sup>

$$\ln [f / (1 - f)] = k_{obs} t - \ln ([\text{Ag}^+]_o / n [\text{Ag}_n]_o) \quad (3)$$

where  $f = OD_t / OD$  (or  $m_t / m$ ),  $[\text{Ag}^+]_o$  is the initial concentration of silver cations and  $[\text{Ag}_n]_o$  is the concentration of silver particles needed to start the autocatalytic reaction. A plot of  $\ln[a / (1 - a)]$  vs. time yields a straight line with a slope equal to the rate constant  $k_{obs}$ , with  $k_{obs} = k_a [\text{Ag}^+]_o$  where  $k_a$  includes the concentration of 2-propanol (the solvent and reducing agent). This kinetic model has been applied in studies on the photoreduction of  $\text{Ag}^+$  ions by ZnO colloids,<sup>15</sup> and

on TDPM systems.<sup>11</sup> The original autocatalytic mechanism was adapted to describe a possible formation path for silver particles during photographic amplification. It was assumed that the reductant concentration in the developer is much higher than the concentration of silver ions that undergo reduction, meaning that the reductant concentration remains constant throughout the development process. Another assumption was that the nanometer-sized Ag particles existing on the surface of larger AgX grains form an ohmic contact with the semiconductor. Therefore, electron density from the metal is delocalized into the conduction band of AgX. A consequence of this process is that Ag particles become electron deficient, which drives oxidation of the reducing agent on the metal surface. Electrons delocalized in the conduction band initiate the reduction of Ag<sup>+</sup> ions that are located on the surface of the AgX lattice forming additional metal particles. Since the rate of oxidation of the reducing agent (and the rate of Ag<sup>+</sup> reduction) increases with increasing number of Ag particles present on the AgX surface, the net result is an autoaccelerated generation of metal crystallites.

In general, plots of  $\ln [f / (1 - f)]$  vs. time were linear at intermediate development times but deviations were detected at long or short times. Only 10% of the data sets showed complete agreement with the kinetic model during the induction period, indicating that the simple autocatalytic mechanism is an incomplete representation of the development steps in many systems. Development kinetic curves of TDPM are described fairly well by this model, implying that electron delocalization in the conduction band of the silver carboxylates takes place. Although electron mobility is considered to be low at room temperature,<sup>16</sup> it is probably higher at the high development temperatures of these materials. The simple autocatalytic mechanism assumes that reduction of Ag<sup>+</sup> to form a silver atom is a slower step than growth process of the metal atoms that forms nanometer-sized Ag crystallites.<sup>7</sup> However, during the growth step Ag atoms and clusters are susceptible to attack by the oxidized reducing agent, which is one of the reasons for the dependence of the particle formation rate on the nature of the reductant. This oxidative cluster decay is not considered in the original autocatalytic mechanism, where generation of new Ag clusters is assumed to occur far away from the site involved in the oxidation of the reductant. A further implicit presumption, also found in electrochemical models,<sup>2</sup> is that the Ag clusters, such as the latent image containing only a few Ag atoms, are able to perform redox reactions and electron transfer steps analogous to the known catalytic reactions of larger metal crystallites. However, such notion is questionable in view of current knowledge of properties of clusters since their properties are very different from those of larger silver particles.<sup>8</sup> An

alternative approach is to consider that some clusters grow by aggregation to reach nanometer sizes, at which point they form an ohmic contact with AgX and are able to inject electrons into the conduction band the semiconductor and oxidize the reductant. On the other hand, clusters that fail to aggregate fast form a Schottky barrier with the semiconductor and must grow until the contact becomes ohmic. In this case, the growth process is assumed to involve reduction of Ag<sup>+</sup> bound to the clusters, which is a slower step. Thus, the modified mechanism consists of a non-catalyzed growth step as well as a catalyzed step for the generation of Ag particles, and is formally equivalent to the general mechanism of autoaccelerated reactions.<sup>9</sup> The solution to the rate expression is:

$$\ln (f + p) - \ln [p (1 - f)] = (1 + p) k t \quad (4)$$

with

$$p = k_1 / (k_2 [Ag^+]_0) \quad (5)$$

where  $k_1$  is the rate constant for the uncatalyzed (first-order) reaction,  $k_2$  is the rate constant for the catalyzed (second-order) reaction and  $k = k_2 [Ag^+]_0$ . Since the uncatalyzed reaction is expected to be significant only during the early reaction times, where the latent image grows, it is reasonable to assume that  $p \ll f$  as well as  $p \ll 1$  after the induction period. With this approximation equation 4 transforms into equation 6,

$$\ln [f / (1 - f)] = k t + \ln p \quad (6)$$

which was used to evaluate  $p$  from the intercepts of the straight lines that resulted from the kinetic data at intermediate times. Small values of  $p$  were obtained in all cases ( $k_1 \ll k$ ), these values were then utilized in conjunction with equation 4 to replot the kinetic data. Although this procedure improved the linearity of the plots for 60% of the data sets, the improvement was not entirely satisfactory particularly for longer reaction times. These results indicate that the cluster growth step affects the autocatalytic process even after the induction period. A logical interpretation is that species similar to the latent image clusters are formed by the reduction of Ag<sup>+</sup> with conduction band electrons, and that these species are also unable to participate in the self-accelerating process until their sizes increase to several nanometers.

Simulations of the development curves were performed using equation 4 in conjunction with the non-linear square fitting subroutine of DeltaGraph. Values of  $k$  and  $p$  estimated from equation 6 were introduced as initial rate parameters. In all cases the simulations reproduced accurately the experimental curves, giving unique values of  $p$  and  $k$  irrespective of the initial parameters used in the calculations. However, it was

found that the calculated rate parameters were sensitive to the extent of reaction achieved in the experiments because  $f$  is dependent on OD (or  $m$ ). Tests with data sets where development completion was achieved showed that  $k$  and  $p$  changed when OD (or  $m$ ) were substituted with values obtained prior to the end point of the reaction. The changes were significant since lowering OD by about 13% decreased  $p$  by 59% and increased  $k$  by 40%. Thus, only  $k$  and  $p$  values obtained from curves that reached complete development (11 data sets of Ag mass vs.  $t$  and 4 sets of OD versus time) were considered reliable. In these cases further tests were performed to verify that the kinetic parameters obtained from the simulations can adequately reproduce the kinetic data. Autocatalytic processes are characterized by a maximum reaction rate, the expression for the time at which the maximum takes place,  $t_{\max}(\text{calc})$ , was derived from equation 4 and is represented by equation 7 is:

$$t_{\max}(\text{calc}) = -\ln p / k(1 + p) \quad (7)$$

The agreement between the calculated values of  $t_{\max}$  and those obtained from plotting the instantaneous reaction rates versus time,  $t_{\max}(\text{exp})$ , was very good, in most cases the deviation between experimental and calculated  $t_{\max}$  was  $\leq 10\%$ . Larger deviations (15-30%) occurred only for development curves where the number of data points available was insufficient for an accurate determination of  $t_{\max}(\text{exp})$ .

Since the initial concentrations of  $\text{Ag}^+$  present in the films were rarely reported in the original publications, it was not possible to extract  $k_2$  from  $k$  and, therefore, comparisons between the autocatalytic rates constants of different systems are not meaningful. On the other hand,  $k_1 = p k$  and, in general,  $k_1$  was between 2 and 6 orders of magnitude smaller than  $k$ . This is not unexpected because the first-order growth of clusters was assumed to be slower than the autocatalytic step. The former step is most significant during the early stages of development, and plays a smaller, but not negligible, role once self-acceleration becomes the predominant process.

## Conclusions

Development kinetic data can be understood in terms of an autocatalytic step of silver particle formation coupled with a parallel growth step of Ag clusters. The kinetic model derived from this mechanism is able to fit very well all the 50 data sets of physical and direct development that were analyzed. Metal deposition is governed initially by the slow growth of silver clusters and this step still contributes at longer times when autocatalytic Ag formation predominates. Quantitative comparisons of the obtained rate constants require more accurate experimental results than those currently found in the literature.

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## Biography

Dr. German Mills earned his Ph.D. in Physical Chemistry from the Technical University of West Berlin in 1985. He then conducted postdoctoral studies at Argonne National Laboratory until 1987. Between 1987 and 1989 he was a Research Fellow in Environmental Engineering at Caltech. Dr. Mills joined the Department of Chemistry of Auburn University as an Assistant Professor in 1989, he was tenured and promoted to Associate Professor in 1995. His research interests include adaptive systems, Photocatalysis and properties of nanomaterials.