

Is the Catalytic Active Silver Surface Really Growing in the Course of Development?

Vitaliy V. Gavrik

S. I. Vavilov State Optics Institute, St. Petersburg, Russia

Abstract

The photographic development is commonly considered as an autocatalytic process due to the growing developed silver surface. The "parallel" development of grains has been shown to increase the silver mass as a simple linear function of time. Its constant term corresponds to the initial soaking period. Since all the emulsion grains start developing nearly the same time, the linear kinetics stands constant for every individual grain until its undeveloped mass is completely exhausted. After the smallest grains are completely developed, the linearity gets distorted. The classic exponential kinetics correspond only to the grains each of them had wholly developed for its after-induction time being much less than the difference of induction periods of simultaneously developing grains. Some data indicated the constant rate of silver filament growth and a particular catalytic activity of their ends are discussed. Latent image (LI) nano-clusters as stabilized in statu nascendi by the metal-polymer interactions suggest themselves to be the invariable active areas.

Hypothesis on the Autocatalytic Kinetics of Photographic Development

A question in the ground theory of photographic process seems not to be solved although it promises a far-reaching effect on the development methods that provided the dramatic changes in custom properties of modern color photographic materials. Is the development process autocatalytic or not? The negative answer should follow into a fundamentally different mechanism based on the especially arranged, unchanging in the course of development, catalytic active site on a the surface of developing particle. Not hardly controlled properties of growing silver surface, but those of its invariable portion established before development.^{1,2}

The classic exponential kinetics seemed to be a rather rough approximation already for a long time. It could result from a gradual "first-order" exhaustion of undeveloped grains if the entire grain is assumed to be developed momentarily after its induction period. A basis to that approach served a concept of autocatalytic development of every single grain. The catalytically active surface of every developing silver particle has been commonly assumed to grow with the general silver surface. That seemed to result unambiguously in an autocatalytic process. A kinetics expression of that kind was suggested by Sheppard³:

$$k(t - t_0) = \log [M_\infty / (M_\infty - M)] \quad (1)$$

where k is the "first-order" rate constant, t is the development time, t_0 is the "time of induction", and M_∞ is the silver mass per unit of photographic layer area for infinite time of development. T. H. James⁴ noted that these equations hold to good approximation for some conditions, but may represent only a small portion of the entire development curve for others.

Silver halide grains have actually never developed in such a manner but in a nearly "parallel" one. T. H. James^{4a} wrote of a typical developer: "The experimental conditions correspond roughly to the first extreme, i.e., the grains developed in approximately parallel fashion. Note that the shape of the silver curve in Figure 3 differs from that of the density curve, a result of the non-linearity of the silver-density relation." A main portion of the mass curve looked a straight line. The more convex density curve looked closer to exponent a:

$$k(t - t_0) = \log [D_\infty (D_\infty - D)] \quad (2)$$

due to silver covering power variations with the developed grain size.

T. H. James wrote⁴: "The term induction period also has been used to designate a period during which no development is detected by whatever method the experimenter is employing. In microscopic examinations of development of single grains, for example, the induction period has been defined as the time elapsing before a speck of developing silver is first detected. A third use of the term depends on an extrapolation method. When the Sheppard impression was used to determine the induction period of the $\log (M_\infty - M)$ dependencies of development time, so at the time t_0 , corresponding the interception of their "straight portion" with abscissa, so considerable and growing masses of developed silver were often observed for a little-sulfite, hydroquinone developer, pH = 9.4."

Willis, and Pontius⁵ in their classical investigation of the development by ascorbic acid have also used the dependencies ($\log(M_\infty - M)$, t) to calculate the "1-order constant". The linearity was reported to extend up to over 50% reaction at the highest exposures. The linearity distortions were explained as usually by the fast exhaustion of developing species in the absence of an auxiliary buffer.

J. R. Fyson, and G. I. P. Levenson⁶ proposed to represent the development rate curves on the ($\log M$, $\log t$) scale.

They derived a formula shown an autocatalytic process to make such dependencies be in part straight lines of the slope close to 3.0. They put no special attention to the differences between $\log D$ and $\log M$ in their analysis, and applied the same transformation to the curves of both the kinds. Every curve was considered by them as really having such a straight portion. Later attempts to confirm in such a manner the autocatalytic character of development showed the expected slope to approximate roughly over two to three in all experimental points.

Some Evidence Suggested a Non-autocatalytic Kinetics of Photographic Development

In addition to the questions above, several lines of evidence indicate the constant growth rate of silver filaments and a particular and stable catalytic activity of their ends. The development rate in a bromideless solution has remained practically constant^{7,8} until a considerable amount of microcrystals developed completely. Some kinetics calculations⁸ and experiments⁹ suggested a constant catalytic active site to exist on the surface of every developing particle. A silver filament is known to grow from its base keeping its diameter nearly constant.¹⁰ Particle growth rate remains usually constant in spite of considerable increase in the total filament surface.¹¹ Spontaneous leap-like changes in the filament growth rate and sudden growth cessation were explained by reversal poisoning of the little-atomic active area on the top of the growing filament by few absorbed inhibitor molecules or even by a single molecule.^{11d}

The multistep structure¹²⁻¹⁴ of characteristic curves, first noted by Silberstein,¹² has been recently shown¹⁴ to have a regular character induced by the atom-by-atom growth of latent image center (LIC) with light exposure.^{1,15} The structure keeps over the entire course of development process,^{1,14,15} indicating the constant catalytic properties of active sites from the beginning up to the latest stages of development. Gelatin suggested^{1a,b} to stabilize the ultradisperse silver particles of LI in the moment of their origination like even less active polymers form stable bounds to highly dispersed metals.¹⁶

The rule of size correspondences of developing species to the definite surface structure of LI particles of silver¹⁷ or non-silver nature¹⁸ could be explained also with assuming a non-changeable catalytic site. For instance, the developing ability was established for only the ions and atoms (free or bound within a molecule) close in size to a period of interatomic hollows in the closest packed surface (111) of silver.¹⁷ It then randomly occurred close packing of such particles each of them drawn in into the neighboring hollows after hitting the LIC surface, extra van-der-waals forces occur.^{17b,c} They retain particles on the surface longer. The probability to give away electrons to a salt microcrystal increases in comparison to a direct interaction with salt's surface. The atom-by-atom growth of LI centers originates more hollows and successive discrete increases in its ability to retain the developing particles.

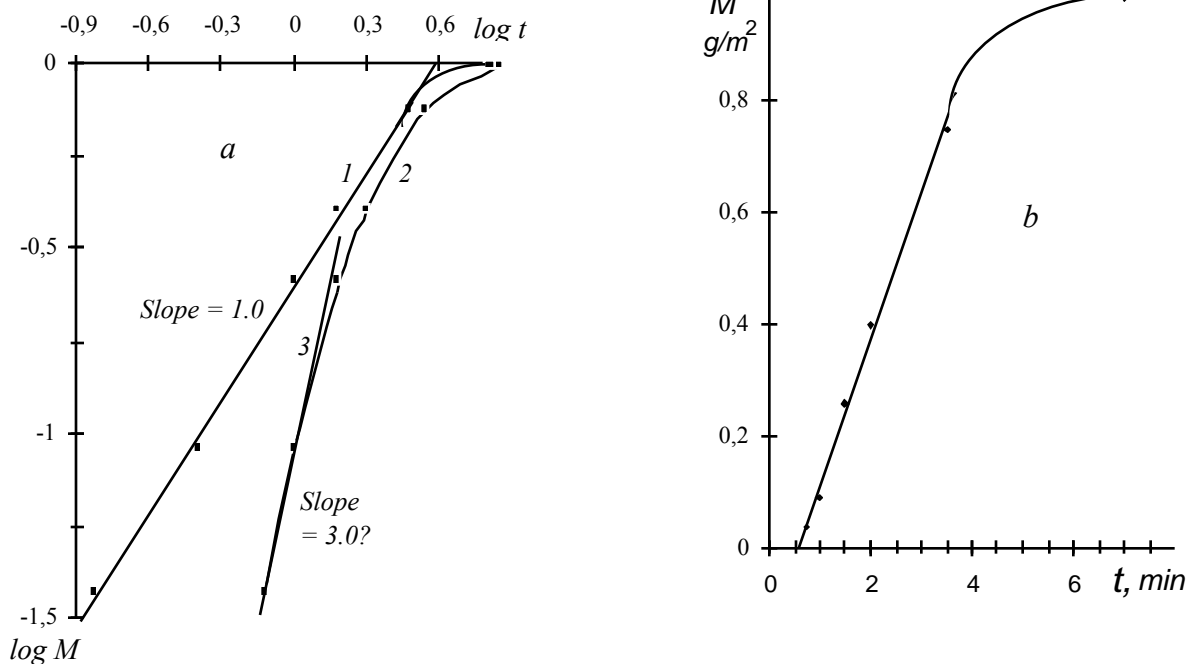


Figure 1. Silver mass growth by the "parallel" development of grains.¹⁹ a : 1 - log-time scale is $\log(t - t_0)$; 2 - original presentation³⁴; 3 - the "straight portion" of the slope 3.0. b - the same curve on the non-logarithmic scales.

Plotting the Course of Photographic Development According to Occam Suggests an Unchangeable Catalytic Active Site

The evidence above makes us expect the general silver mass per unit of photographic layer area to grow also in linear manner with the development time. This should be right before all for the "parallel" development of grains that usually displays very small induction periods. It is typical for non-charged developing species or little bromide in developer. When we report on the simple non-logarithmic scales some data considered as confirming the autocatalytic development, the developing silver mass is rather a linear function of time.

Curve 2 on Figure 1a displays a recent data carefully obtained by Miyake and Tani for the "parallel development of grains"¹⁹ (Figure 14 in the original) with N-methyl-N-(b-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate as developing agent and 0.6 g potassium bromide at pH 10.2. Figure 1b drawn on the simple non-logarithmic scales shows unequivocally a linear growth of developed silver mass with development time. The constant term $t_0 = 0.6$ min of the linear dependence could be reasonably considered as an initial soaking period. The emulsion soaking times at the room temperature are commonly known to be close to this value.

Since all the emulsion grains start developing nearly at the same time,¹⁹ the linear kinetics stands for the development rate of a grain to be constant until its undeveloped mass is completely exhausted. With exception of 1) the "induction period" while the layer is being swelled by the developing solution, and 2) the saturation portion of the kinetics curve corresponding to silver exhaustion, in the "parallel" period of non-limited development, the silver

mass grows linearly with development time:

$$M - M_{o,E} = k_E (t - t_0) \quad (3)$$

where $M_{o,E}$ is the silver mass photolytically produced by light exposure, E ; k_E is the development rate constant depending on the exposure and development conditions. Since $M_{o,E}$ of LI is negligible compared to developed silver, M , in a visible darkening :

$$M = k_E (t - t_0). \quad (4)$$

When plotted on the double-logarithmic scale ($\log M$, $\log t$), the dependence seems non-linear (curve 2 on Figure 1a). A lower portion of the curve with the slope about 3.0 seems not to be reliable straight line as involved only two experimental points and could quite increase its slope when still less silver masses would be considered. The dependence (4) should look also a straight line on the double-logarithmic scale ($\log M$, $\log (t - t_0)$) instead of ($\log M$, $\log t$):

$$\log M = \log k_E + \log (t - t_0). \quad (5)$$

Its slope should be 1.0 like the factor at the term $\log (t - t_0)$. Curve 1 of Figure 1a does display the features, thus extra confirming the validity of the kinetics equation (3). After only the smallest grains get completely developed, the linearity is distorted simultaneously for Fig.1b and curve 1 on Figure 1a. Thus, the simplest replotting the experimental kinetics data on the non-logarithmic scales is more compatible with the Occam principle⁶ than proposed by Fyson and Levenson themselves, since provided the simplest explanation to the data.

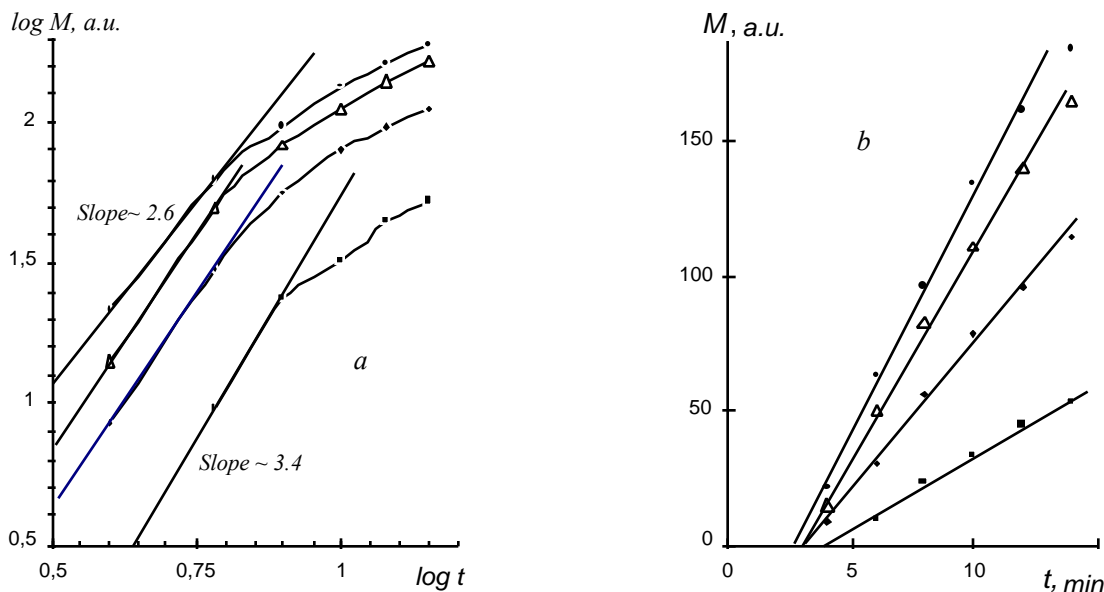


Figure 2. The kinetics dependencies of photographic development. a: from Figure 7b of the work⁶; b: the non-logarithmic representation.

Figure 2a displays the mass curves used in the classic article by Fyson and Levenson⁶ to prove the autocatalytic kinetics. They were obtained at different light exposures by Pontius and Willis²⁰ that "...had supposed that the rate would be proportional to the total available silver ion concentration. A first-order plot of the data in the form $\log Ag^+$ versus time could be interpreted as showing an induction period followed by a first-order reaction..." Yet when the same data have been replotted in terms of $\log Ag$ versus $\log t$ we find the slope for the first quarter of the development to be close to 3.0 as in Figure 7b. This shows that the early part of ordinary chemical development by ascorbic acid also proceeds as if the pre-filamentary and filamentary development mechanism. Nor is it necessary to introduce an induction period in this case just to make the later part of the reaction first order in residual silver ion."

The other curves in article⁶ including main Figure 9 seem to be rather optical density curves. The authors made no special difference in the text between both the kinetics dependencies (note, for example, their indication that their Figures 4 and 5 were plotted on the " $\log D$ or Ag " scales that both express "the proportion of silver reduced") and put no attention to a bromide content in the developers used. The slopes of short "straight portions" on their Figure 9 sometimes dramatically depend on the points corresponding to the relative densities of several tenth percent. The non-logarithmic presentation of density curves also proved to have deciding advantages in comparison to the double-logarithmic scale (one could prove it easily by oneself).

The curves on Figure 2a seem to possess no real straight portion. One could make a linear interpolation over

three initial points of every curve. It would be nothing but a more or less rough linear interpolation of a concave curve. The slope of "linear" portions is not constant. It varies regularly with exposure, exceeding 3.0 and tending to increase some more at lower $\log M$.

The data, replotted on the non-logarithmic scale (Figure 2b), does display straight lines including all the points besides sometimes of the last one influenced by a considerable portion of completely developed grains. The highest M values presented in Figure 2 in arbitrary units corresponded closely to $M/M_\infty \approx 100\%$.^{6,20} Thus, the linear kinetics includes not only "the first quarter of development"⁶ but about the entire course of development.

The Application to Classic Data on the Silver Speck Size at the Early Stages of Development

Early prefilamentary stages of development comprehensively studied by Pontius and Willis^{21,22} also confirm the linear kinetics of grain growth. The silver particles under study seemed to be compact and about globular in shape²¹. It was difficult to measure a filamentary growth since the filaments were bent and twisted. The graphs ($S^{1/2}, t$) on Figure 3a, where S is the mean developed grain projection, are taken from the original work.^{21a} The scale has been derived by Pontius and Willis as to be linear for autocatalytic kinetics. An unsensitized cubic emulsion was developed in a solution containing 0.01 M ascorbic acid, 0.25 M sodium carbonate, and 0.09 M sodium bicarbonate at pH 10, ionic strength 1.0, and the temperature of 20°C. The curves of Figure 3a correspond to very low concentrations of potassium bromide in the solution as typical condition of parallel development with negatively charged active species.

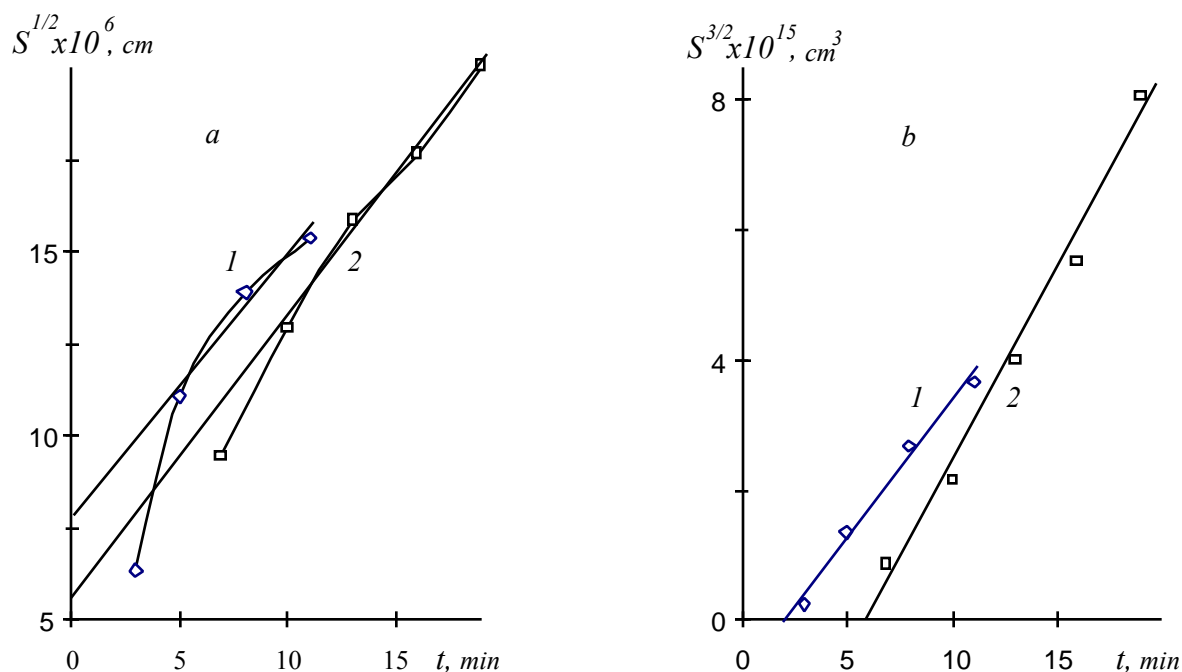


Figure 3. Kinetics of prefilamentary silver formation in single emulsion grains^{21a}: 1 - 0.001g/l KBr; 2 - 0.01 g/l KBr. a: original data presentation^{21a}; b: data presentation proposed in this paper.

If one does not take into account the first experimental point on every curve that stands regularly out of the best straight-line approximation, the lines extrapolated to $t = 0$ give overestimate the mean diameter of LI centers (80 or 60 nm). If one interpolates over all the experimental points, the estimates will decrease by about a half. LI centers are known to consist of several silver atoms or to be by two orders of magnitude less. Therefore, the approximations seem not to have any actual physical meaning.

Since prefilamentary silver particles are not loose in contrast to filamentary silver clumps, the mean grain mass should be approximately $M = k_s \delta S^{3/2}$, where k_s is a shape factor, $\delta = 10.5 \text{ g/cm}^3$ is the bulk silver density, and $S^{3/2}$ is proportional to the mean grain volume. Then, the kinetics expression (4) could be re-written in terms of the grain size data:

$$S^{3/2} \approx k_E (t - t_o) / k_s \delta. \quad (6)$$

Figure 3b displays the graphs ($S^{3/2}, t$) that look really as straight lines. The reasonable constant terms of the dependence corresponding to the induction period can be defined by their intersection points with the time axis. The induction periods increase with bromide content in the solution with negatively charged developing ascorbate ions. The developer containing 0.001g/l *KBr* showed the 2.5 min induction, and 0.01g/l *KBr* showed that 6 min long. Both the emulsion soaking itself and the difference in penetration rates of solution components capable to shift a characteristic curve as a whole along the log-exposure axis,^{1,9} contribute into the constant.

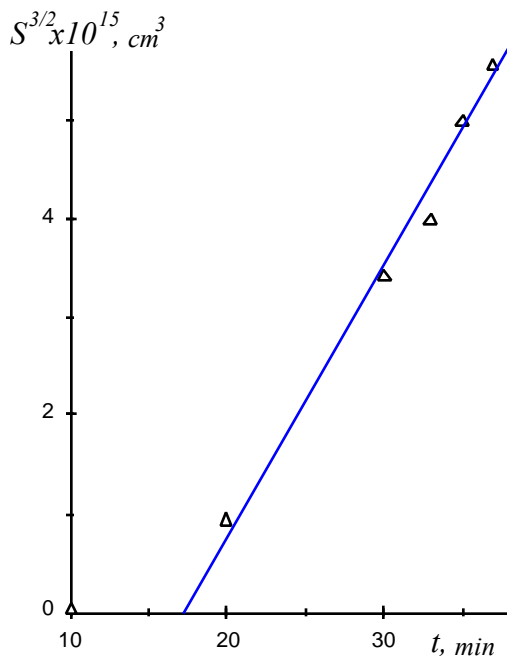


Figure 4. Kinetics of prefilamentary silver formation in single emulsion grains²² at 1.0 g/l *KBr* concentration in the developing solution.

Another data^{21,22} indicate higher bromide concentrations slightly violate the linear kinetics. Figure 4 for 1 g/l *KBr* demonstrates also a simple linear dependence of mean silver particle volume upon the development time with the 17 min long induction period.

Discussion

Thus, the idealized kinetics expression should look at this case as follows:

$$M = M_\infty M_{o,E} k_d (t - t_o) = M_\infty (t - t_o) / (t_c - t_o) \text{ at } t_o \leq t \leq t_c, \quad (7a)$$

$$M = 0 \text{ at } t < t_o, \quad (7b)$$

$$M = M_\infty \text{ at } t > t_o \quad (7c)$$

where k_d is the rate constant reflecting only the development conditions; $M_{o,E}$ is the activity of LIC; and t_c is the idealized time required for every grain to develop completely. The catalytic activity, $M_{o,E}$ varies with light exposure in a multisteped manner¹⁴ induced by the atom-by-atom growth in the largest LIC in grain.¹

The linear kinetics occurs always in every individual grain. In a photographic layer as a whole, it could be observed under conditions providing the parallel development. Ideally, the grains should start being reduced simultaneously and their silver halide masses should become completely reduced at the same moment. Eq. (7) is most suitable to the thin emulsion layers with grains identical in size as well in the depth where they occur within the emulsion layer.

Why have not photographic classics note the simple dependence? Four explanations could be proposed.

(1) Early 20th century, they have had little data on the mass curves and rested predominantly on the density curves that were strongly violated by the variations in covering power due to the gradual silver grain growth²³ in the course of parallel development. The grains vary also in silver compactness: from quasi-spherical pre-filamentary particles of compact silver through its long and randomly twisted filaments up to the loose clumps of filaments.

(2) They deal predominantly with polydisperse emulsions. The kinetics curves of a polydisperse emulsion should have a more extensive non-linear saturation portion than those of a modern monodisperse emulsion. The emulsion grains of different size need significantly different times to be completely developed. Therefore, the modern emulsions with small size variation coefficients should give the mass curves with shortened saturation portions and fit a straight line up to the latest stages of development.

(3) They deal with thick emulsion layers where even the initial swelling times could be comparable to the time of complete after-induction development of grain. The layers should violate the linearity at the initial after-induction stages of development. Microcrystals situated at different depth in such an emulsion layer could considerably differ in times of developer components to reach them.

(4) And finally, the conditions required are practically realized in slow developers containing no negatively charged developing species or little bromide anions and thus producing readily fog. They were not available in rapid developers containing much anionic antifoggant that were predominantly used several decades ago.

Small bromide anions penetrate an emulsion layer more rapidly than larger developing molecules do.²⁴ They adsorb readily on the LI centers and form an electrostatic repulsion layer that increases the induction period of grain⁹. Since the ions are replaced gradually by developing anions, more and more grains are involved in the process.^{9a} If the typical period of complete grain development is much less than the time of considerable increase in number of simultaneously developing grains, one can observe a non-parallel, "granular" development like with the D-72 developer used by Miyake and Tani.¹⁹

It fits formally a "first-order" Sheppard kinetics (Eq.1), reflecting a gradual accumulation of completely developed grains with a constant covering power (Figures 2, 3 and 5 in the article¹⁹). Nevertheless, they are substantially different. The rate constant in the "granular" development is determined by the timing difference of grains to start being reduced. It depends on the developer composition and the statistical size distribution of the largest LI centers formed by light exposure in every grain. Since the occurrence probability of LIC is an exponential function of its size¹ and the surface interactions at a catalytic site obey the linear kinetics, one can positively expect a quasi-first-order kinetics for the "granular" development. Every individual grain develops at a constant rate but too fast and at its own time. A combined kinetics depend on the ratio of grain induction and grain complete reduction times.

The findings are of importance for the progress in the photographic technology. Instead of considering the growing silver grain surface of uncertain features, one could now manage a development process as occurring from its beginning to its end at the well known closest-packed (111) surface of unchangeable catalytically active silver center formed by light exposure.

Summary

The silver mass kinetics dependencies show the development process not to be autocatalytic. Their transforms proposed earlier to prove the autocatalysis keep over much less experimental points than the simple linear presentation of the same data. The kinetics of "parallel" development is linear with an induction period when no perceptible silver mass is produced, a period of a constant development rate, and a saturation period when a perceptible number of grains is developed completely. The induction period by the development of "parallel" type depends predominantly on the initial swelling of emulsion layer in a developer solution.

Every individual grain develops with a constant rate and its catalytic sites do not change in the course of development. The rates of individual grain development vary in regular multisteped manner with increasing exposure. The steps correspond to the atom-by-atom growth of the largest LIC in every grain. The silver LI centers may be stabilized in statu nascendi by the surrounding gelatin and act in the course of development as unchangeable catalytic sites of especial surface structure that does induce the catalytic interaction with developer molecules.

The quasi-first-order kinetics typical to the "granular" development may reflect actually the exponential distribution of induction periods for catalytic active sites that could be derived from the exponential size distribution of LI centers and vary fast after-induction development of individual grains. The induction period by the "granular" development suggests to depend predominantly on the replacement rate of fast penetrating non-developing anions by developing agents from the size of most catalytically active sites produced by a given light exposure.

References

1. a) V.V.Gavrik. *IS&T's 48th Annual Conference "Imaging on the Information Superhighway"*, Washington, 1995, pp. 246 - 251; b) *Zh. nauch. prikl. fotogr. (Sci. Appl.Phot. Cinem)*, 1996, v. 41, # 4, pp. 58 - 67.
2. V.V.Gavrik, O.N.Kononova, and N.V.Lugovaya. *IS&T's 8th Int. Symp. on Photofinishing Technologies, Atlanta, 1994*, pp. 28 - 31.
3. S.Sheppard and C.E.K.Mees. *Investigations on the Theory of the Photographic Process*, L., 1907.
4. a) T.H.James, *Phot.Sci.Eng.*, 1970, v.14, # 6, p. 371-383; b) *J.Phys.Chem.*, 1940, v. 44, p. 42.
5. R.G. Willis and R.B.Pontius, *Phot. Sci. Eng.*, 1970, v.14, pp. 384 - 390.
6. J.R. Fyson and G.I.P. Levenson, *J.Photogr.Sci.*, 1977, v.25, pp.147 - 153.
7. a) A.H.Nietz. *The Theory of Development*. Rochester, 1922; b) T.H.James. *The Theory of the Photographic Process*. Macmilan, 1977.
8. E.R. Brown and L.K.J. Tong, *Phot. Sci. Eng.*, 1975, v.19, p.314.
9. a) V.V.Gavrik, G.I.Barantseva and O.N.Kononova, *J. Inf. Rec. Mater.*, 1985, v. 13, p. 409; b) V.V. Gavrik and O.N. Kononova, in: *The Physical Processes in Light-Sensitive Salts*, Kemerovo, 1986, v. 2, p. 69.
10. a) E. Klein, *Z.Elektrochem.*, 1958, v.62, p. 505; b) E.P.Senchenkov and K.V.Chibisov, *Zh. nauch. prikl. fotogr. (Sci. Appl. Phot. Cinem)*, 1968, v.13, p. 447; c) H.J. Metz, *J. Photogr. Sci.*, 1972, v. 20, p. 111; d) C.R. Berry, *Phot. Sci. Eng.*, 1969, v.13, p. 65.
11. a) A.G. Samartcev, *Acta Physicochim. URSS*, 1942, v.16, p. 206; b) K.M. Gorbunova and A.I. Zhukova, *Zh. Fiz. Khim. (J. Phys. Chem.)*, 1949, v. 23, p. 616; c) D.A.Vermilyea., *J.Electrochem.Soc.*, 1959, v.106, p. 66; d) W.G. Courtney, *J. Chem. Phys.*, 1957, v. 27, p. 1349.
12. a) L.Silberstein, *J.Opt.Soc.Am.*, 1942, v.32, p. 474; b) L.Silberstein, A.P.H.Trivelli, *ibid.*, 1945, v.35, p.93; c) A.P.H.

- Trivelli, *J. Frankl. Inst.*, 1946, v. 241, p. 1.
13. D.A.Pitt, M.L.Rachu, and M.R.V.Sahyun, *Phot. Sci. Eng.*, 1977, v. 21, p. 331.
14. a) V.V.Gavrik, *J.Inf.Rec.Mater.*, Dresden, 1975, v. 3, p. 125; b) *ibid.*, p. 133; c) V.V. Gavrik, A.A.Barantseva and G.I.Barantseva, *Int.Congr. Phot.Sci., Rochester, 1978*, p. 202; d) V.V.Gavrik and A.A.Barantseva, *J.Inf.Rec.Mater.*, Dresden, 1980, v. 8, p. 167; e) V.V.Gavrik, and G.I. Barantseva, *ibid.*, 1980, v. 8, p. 83.
15. V.V. Gavrik and O.N. Kononova. Permanence of size distribution of silver nanoclusters produced in silver halide by light exposure or chemical fogging and partly oxidized with photolytic halogen. *IS&T'S 50th Annual Conference, May 1997, Cambridge, Mass.*
16. M.P.Andrews and G.A.Ozin, *Chemistry of Materials*, 1989, v.1, p.174.
17. a) V.V.Gavrik, *Mendeleev Communications, Cambridge, UK*, 1994, v. 4, # 5, p.191; b) V.V.Gavrik, *Int .Congr. Phot. Sci., Rochester,1994*, p.353; c) V.V. Gavrik, O.N. Kononova and N.V. Lugovaya, *II Int..Conf. "Modern Trends in Chemical Kinetics and Catalysis"*, Novosibirsk, 1995, PPK-22.
18. V.V. Gavrik. *IS&T's 49th Annual Conference "Digital Imaging and Conventioll Silver Halide"*, Minneapolis, 1996, pp. 185 - 189.
19. K. Miyake and T. Tani, *J.Imag.Sci.Technol.*, 1995, v. 39, p. 355.
20. R.B. Pontius and R.G. Willis, *Phot. Sci. Eng.*, 1970, v. 14, p. 141.
21. a) R.B. Pontius and R.G. Willis, *Phot. Sci. Eng.*, 1973, v. 17, p. 21; b) *ibid.*, p. 157.
22. R.B. Pontius, R.G. Willis and R.J. Newmiller, *Phot. Sci. Eng.*, 1972, v. 16, #6, p. 406.
23. V.V. Gavrik, *J. Photogr. Sci.*, 1996, v. 44, # 1, pp. 5 - 7.
24. H. Iwano, *J. Photogr. Sci.*, 1972, v. 20, p. 135.