LITH DEVELOPMENT KINETICS AND HALFTONE DOT FORMATION

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Abstract: The growth of image density during development of a lith film occurs in two distinct stages. The initial stage, the induction period, comprises nearly the entire period of development but accounts for only a minor fraction of the final developed density. The second stage, "lith effect" development, on the other hand, is a relatively short period of very rapid development during which most of the total development occurs. Although the focus of previous studies of lith development has generally been on the rapid lith-effect development stage, the imaging response, i.e., exposure dependence, of the lith process actually rests with the processes occurring during the induction period.

This paper focuses on the kinetics of the induction-period development and their relation to halftone dot formation. A model of lith induction-period development is derived that is in agreement with a number of experimentally observed induction-period effects. The model is also consistent with the observed exposure dependence of the lith induction period of typical lithographic systems. The paper concludes with a discussion relating the induction-period exposure dependence to the rates of initiation and growth of halftone dots during development of lith film exposed to a contact screen.

Introduction - Lith Versus Non-Lith Development Kinetics

The high contrast of lith films that facilitates their use in generating halftone images from continuous-tone film originals is due in large part to the rather unusual photographic development kinetics of these films. Figure 1 illustrates the principal differences in the manner by which typical non-lith and lith films increase in density during the development stage of processing. Non-lith films

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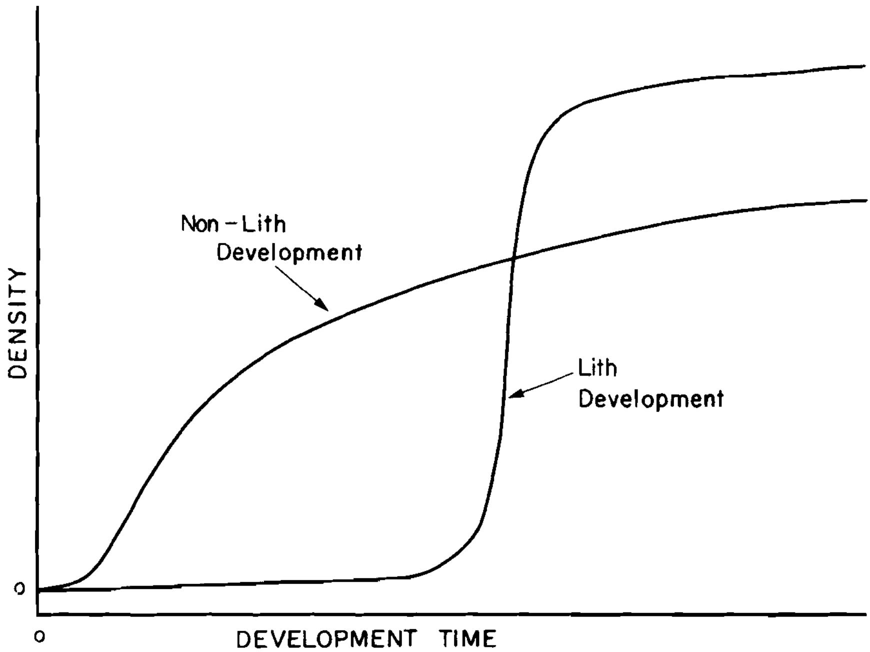

Figure 1. Lith and non-lith development kinetics.

generally show a short initial period where little if any development is observed. This portion of the development process is commonly referred to as the induction period. Following the induction period, the development rate of the non-lith film increases to a maximum and then declines gradually as the final density is approached at extended development time. Lith development, on the other hand, involves a much longer induction period of slow, though detectable, development, after which development rapidly accelerates to a maximum rate which is maintained essentially to the attainment of the final density. The final rapid stage of development, during which most of the final density is developed, is commonly called "lith effect" development.

Figure 2 illustrates the inherent differences between the effects of exposure upon the development kinetics of lith and non-lith films. The dashed curves in each case represent a lower exposure level than the curves from Figure 1 that are reproduced here as the solid curves. Lowering the exposure in the non-lith development case

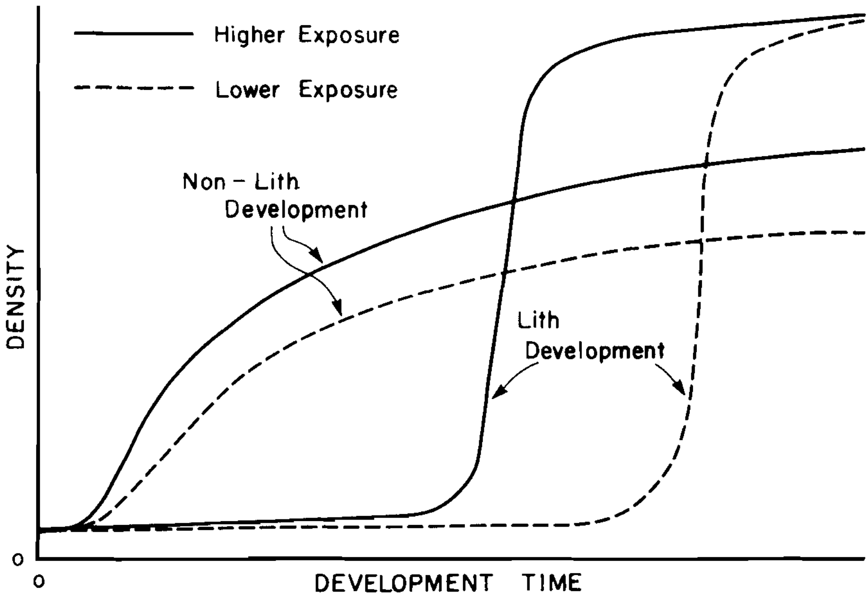

Figure 2. Exposure dependence of lith and non-lith development kinetics.

shows little effect upon the induction period, but the general overall development rates and the final level of density approached at long development times are both reduced by lower exposures. The main effect of lower exposure upon lith development kinetics, on the other hand, is a lengthening of the induction period. The final-stage lith-effect development is, however, little affected by exposure either in terms of rate or final extent.

These features of lith development kinetics translate into a high-contrast response, as illustrated in Figure 3. Here two lith development rate curves for two exposures, A and B, differing by a small amount, Δ log E, are plotted. A development time intermediate to the induction periods of these two curves, indicated by the arrow, will result in a high developed density at exposures equal to or greater than A, but essentially no developed density at exposures less than or equal to B. The result is a large density change for a small exposure difference at this development time; in other words, a high contrast. The corresponding thought experiment for non-lith development leads to a much smaller developed density difference for a given exposure difference, hence a lower contrast response.

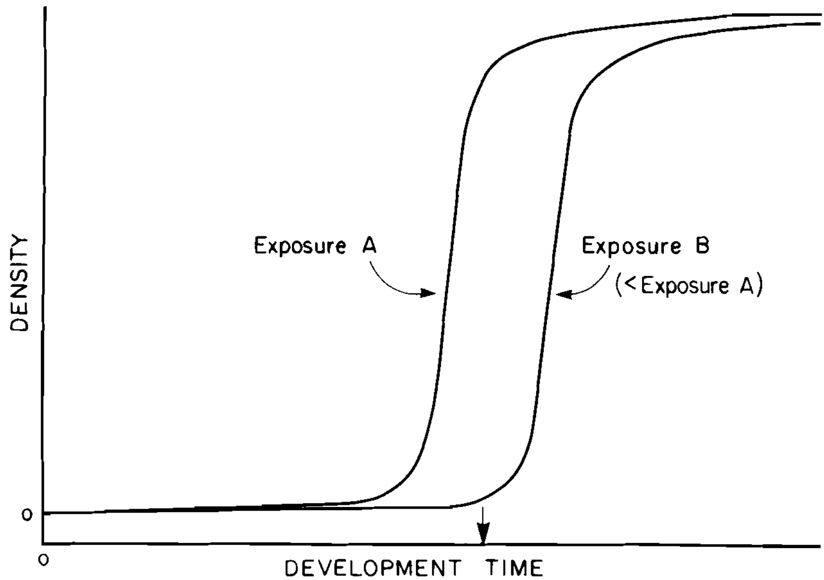

Figure 3. Why high contrast results from lith development kinetics.

The Mechanism of Lith Development

Figure 2 illustrates the important point that the exposure dependence, and hence the photographic utility of the lith process, is associated with the events that occur during the induction period. Previous studies of the lith development process (for example, Yule, 1945 and Austin, 1974) have pointed out the importance of semiquinone, a much more active developer than hydroquinone, in promoting the rapid late-stage lith-effect development. The following reactions summarize how semiquinone is formed during lith development.

$$\underset{\text{(hydroquinone)}}{HQ^{=}} + \underset{\text{(exposed silver halide)}}{2Ag^{*}X} \xrightarrow{\text{slow}} \underset{\text{(silver)}}{2Ag^{0}} + \underset{\text{(quinone)}}{Q} + \underset{\text{(halide ion)}}{2X^{-}} \quad (1)$$

$$HQ^{=} + Q \underset{\longleftarrow}{\xrightarrow{\text{fast}}} \underset{\text{(semiquinone)}}{2SQ^{\overline{\cdot}}} \quad (2)$$

$$Ag^{*}X + SQ^{\overline{\cdot}} \xrightarrow{\text{fast}} Ag^{0} + Q + X^{-} \quad (3)$$

$$\underset{}{Q} + \underset{\text{(sulfite)}}{SO_3^{=}} \xrightarrow{\text{fast}} \underset{\text{(hydroquinone monosulfonate)}}{HQS} \quad (4)$$

Reactions (2) and (3) show how the concentration of semiquinone can autocatalytically build up as development of the silver halide grain proceeds. According to reaction (4), however, sulfite reacts rapidly with quinone to form hydroquinone monosulfonate, a relatively weak developer, and thus moderates the rate of semiquinone buildup. Lith developers are therefore formulated with fairly low levels of free sulfite to permit sufficient semiquinone generation to sustain lith-effect development.

The generation of semiquinone in low-sulfite, hydroquinone lith developers provides an explanation for the drastic increase in development rates between the induction period and lith-effect stages of development. However, it is still not clear what triggers the onset of lith-effect development; that is, when development becomes controlled by reaction 3 rather than reaction 1. The rather obvious possibility that semiquinone gradually accumulates during the induction period up to some critical level seems unlikely in the face of results of model lith sensitometry experiments such as those reported by James (1967). We have run analogous lith development rate experiments using an apparatus where the density of the lith film is monitored during development, in real time, using infrared radiation. The following examples of these experiments clearly contradict the position that accumulation of semiquinone during the lith induction period is important in triggering the onset of lith-effect development.

The first of these results is illustrated in Figure 4. Two identically exposed samples of KODALITH MPII Ortho Film 2577 were developed in our development rate apparatus using KODALITH MPII Developer. In the first case, developer was flowed past the film continuously until the rapid lith-effect development was complete. In the second case, development was begun as before, but at the end of the normal induction period, just before the onset of lith-effect development, the developer flow was turned off and a 60-sec water wash was given the film. The development process is arrested by this wash, as shown by the horizontal

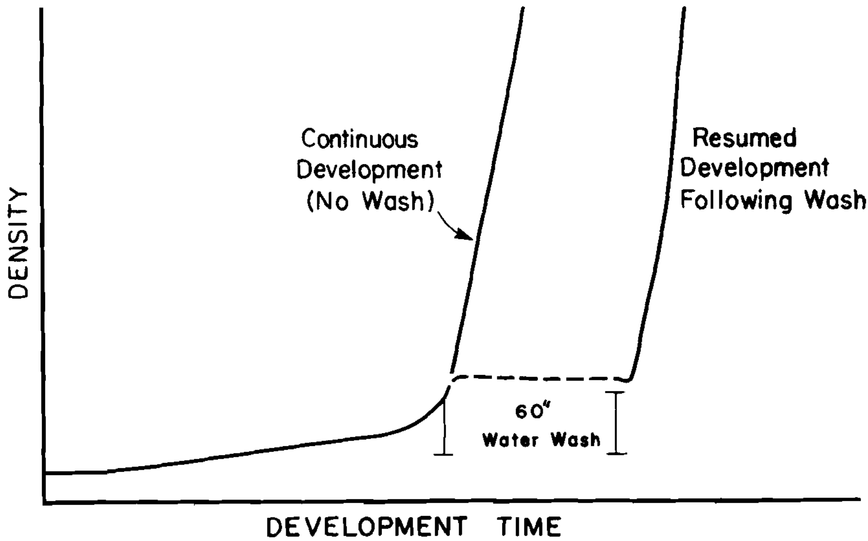

Figure 4. Effect of intermediate water wash on lith development kinetics.

dashed line. When developer flow was resumed after the water wash, lith-effect development initiated immediately. The water wash introduced in the late stage of the induction period would be expected to wash out accumulated semiquinone and thereby delay the onset of lith-effect development upon resumption of developer flow. The absence of any significant delay in the initiation of lith-effect development following the water wash is strong evidence that semiquinone accumulation is at best a minor factor in the triggering of the lith-effect stage of lith development.

A second experiment with the same film and developer combination involves "split" high/low sulfite development and further illustrates that semiquinone development activity is confined principally to the lith-effect, as opposed to the induction-period, stage of lith development. In Figure 5, the development rate curve is shown for the case where development is started in a lith developer having 10 times the normal sulfite concentration. The generation of semiquinone should be lowered substantially in this developer according to reactions (2) and (4). However, if development is carried out with this sulfite-doctored lith

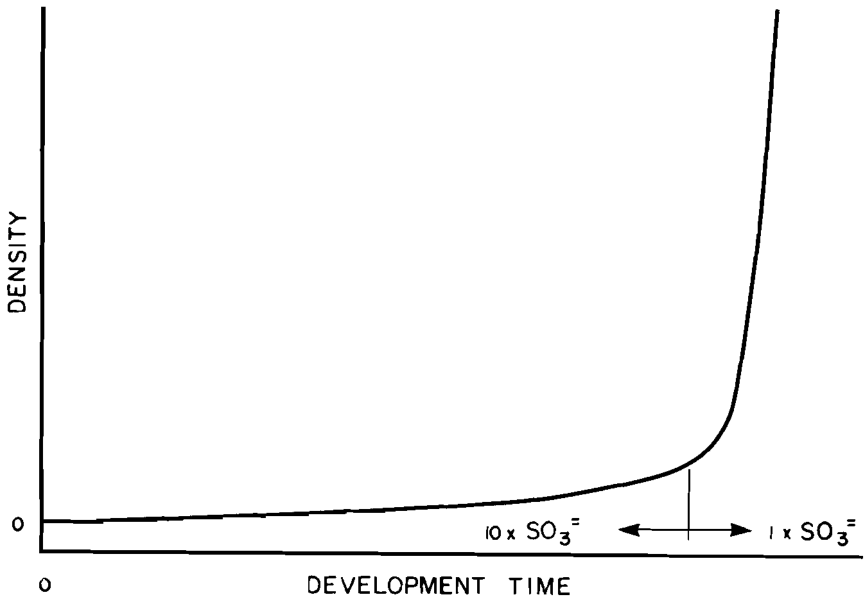

Figure 5. Split high/low-sulfite development.

developer to the point where the developed density is equal to that normally attained during the induction period, and then switched to a normal (low) sulfite lith developer, lith-effect development initiates almost immediately. Reversing the sequence, that is, starting development in the low-sulfite developer and continuing past the onset of lith-effect development before switching to the 10X normal-sulfite developer, results in a drastic reduction in the rate of lith-effect development after the switchover (Figure 6).

It was demonstrated earlier that the exposure dependence of a lith film is really determined by the exposure dependence of the induction-period processes. This fact, when considered with regard to the lith development reactions (1) through (4), suggests that the exposed silver halide term in reaction (1) is in some way the underlying controlling factor in the induction-period kinetics. The reduced silver metal that forms as a result of photographic development such as described by reaction (1) takes the form of a concentrated deposit or speck that remains attached to the silver halide grain as it grows during development. At the start of development, the silver speck consists of those few atoms of silver formed by photolytic decomposition of silver halide during exposure. The development process itself is,

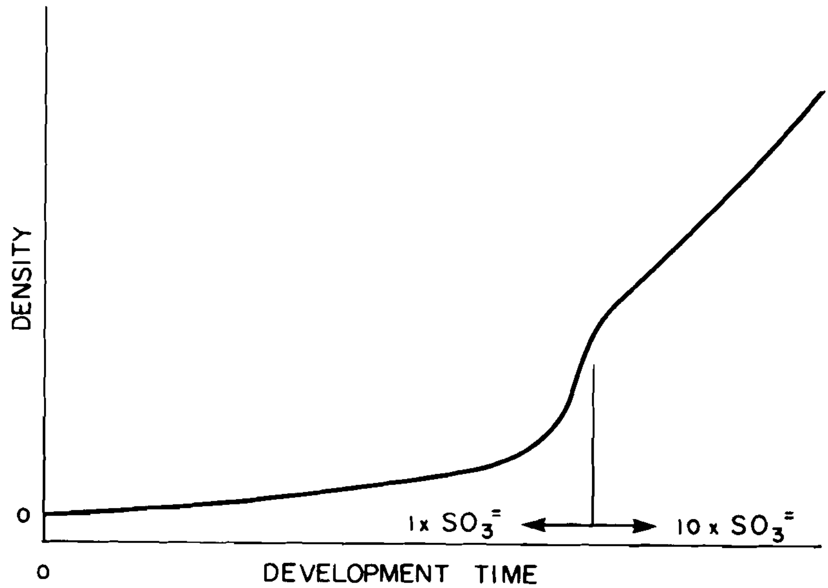

Figure 6. Split low/high-sulfite development.

to a degree, autocatalytic. That is, the rate increases the larger the silver speck size (Pontius and Willis, 1973 and James, 1977). Therefore the rate of development will continuously increase, owing to the growth of the silver speck during development even without accumulation of an active developing agent such as semiquinone.

Previous studies of the autocatalytic nature of silver halide development such as those cited above have been concerned with the development kinetics of silver specks that are at least a factor of 10^5 larger than the latent-image size. In this size range the specks can be sized by use of electron microscopy. Thus a direct measure of the development rate dependence upon developed silver can be determined. These data typically show that the development rate is proportional to the surface area of the speck at each instant. In other words, the development rate is proportional to the mass of developed silver, raised to the 2/3 power.

There is evidence (Fyson and Levenson, 1977) that the surface-area-dependent model of development does not, however, account for the exposure dependence of the earliest stages of the silver speck growth, that is for $1 < Ag^0/Ag^0_{LI} < \sim 10^4$. For this reason, we have explored the possibility that the early-stage latent-image growth follows an autocatalytic silver dependency different from a surface-area dependency. A simple kinetic model of early-stage (induction period) development, with general Nth order ($N > 0$) autocatalytic silver dependence, was therefore derived and tested against observed lith induction period kinetics. The detailed derivation of the model is presented in Appendix I, but it will be briefly described here. A general Nth order autocatalytic dependence of the silver development rate upon already-developed silver is assumed:

$$\frac{dAg^0}{dt} = kAg^{0^N} \quad ; \quad N > 0 \tag{5}$$

with the initial condition that:

$$Ag^0 = Ag^0_{LI} \text{ at } t = 0 \tag{6}$$

In other words, the initial silver speck is the latent-image speck produced by exposure. The integrated equation was compared to actual lith kinetics, and a close similarity was demonstrated between the actual kinetics and the general model case for $N > 1$. For this case, the size of the growing silver speck, as a function of the development time (t) and initial reduced-silver speck size (i.e., the latent image, Ag^0_{LI}), is given by:

$$Ag^0 = Ag^0_{LI} \left[\frac{(1-N)\ kt}{\left(Ag^0_{LI}{}^{(1-N)}\right)} + 1 \right]^{\frac{1}{1-N}} \quad ; \quad N > 1 \tag{7}$$

Mathematically this relation predicts that complete grain development occurs as development time approaches the value given by the following relation:

$$t = \frac{Ag^0_{LI}{}^{(1-N)}}{(N - 1)k} \tag{8}$$

A typical silver versus time curve calculated using equation (7) and assuming N = 2 is plotted in Figure 7.

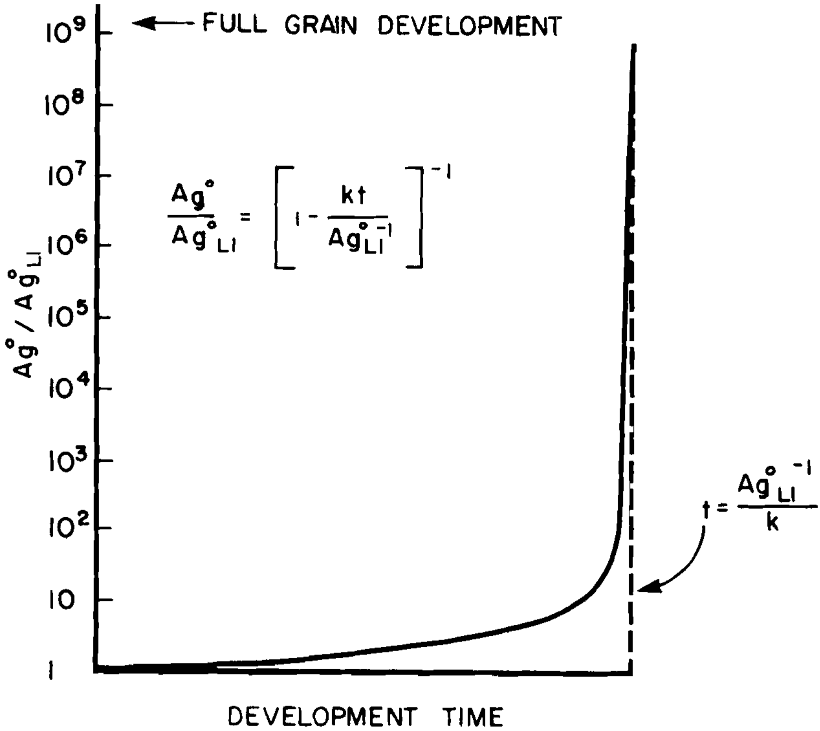

Figure 7. Calculated silver development for N = 2 (Equation 7).

The shape of this curve suggests that Equation (8) can be taken as a close approximation to the induction period, t_{IP}, since only a minor fraction of the development occurs before this time asymptote is closely approached. Equation (8) can be differentiated with respect to latent-image size, which is assumed to be proportional to exposure, to yield the following relation between exposure and induction period:

$$\frac{d \log E}{d \log t_{IP}} = \frac{1}{1 - N} \qquad (9)$$

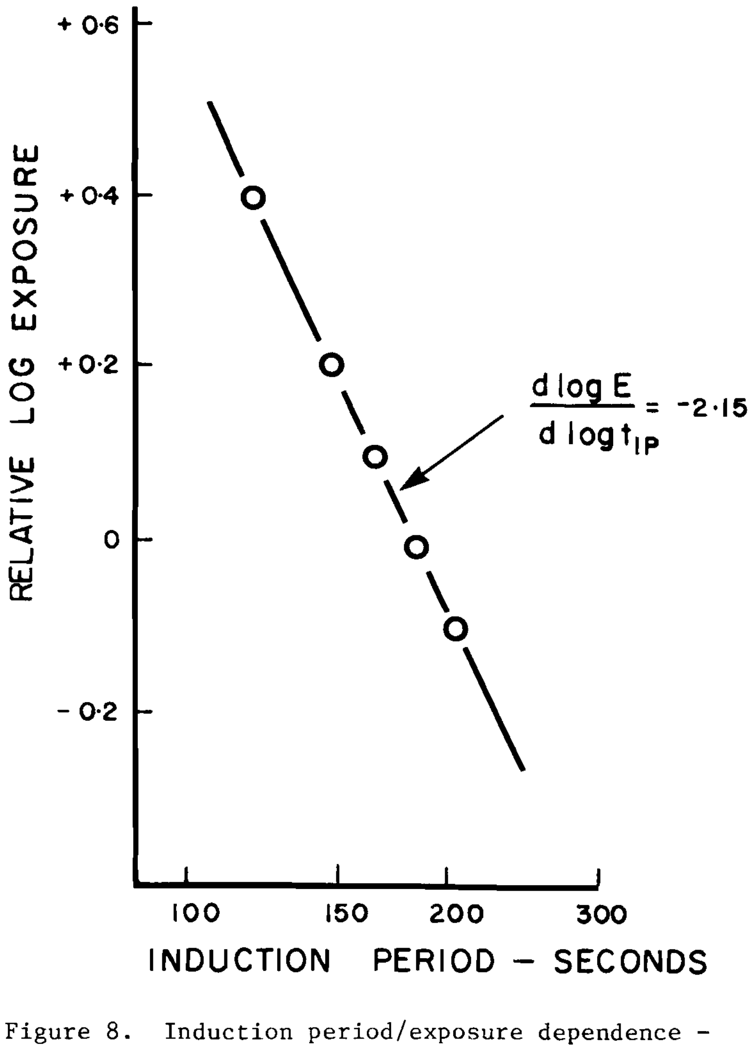

Figure 8. Induction period/exposure dependence - KODALITH Ortho Film, Type 3 in KODALITH Super RT Developer.

Equation (9) predicts a linear relationship between log exposure and log induction period, the slope of which depends on the autocatalytic silver reaction order N. A log/log plot of induction periods of KODALITH Ortho Film 2556, Type 3 developed in KODALITH Super RT Developer for a series of exposures (Figure 8) is linear, as predicted by Equation (9). The slope of this line (-2.15) corresponds to a reaction order N = 1.47.

The characteristics of lith development kinetics and the relationship between exposure and induction period just discussed will now be related to the process by which first-generation halftone dots are formed by the lith process. The first step in the process is exposure of the film to a continuous-tone film original through a halftone contact screen. The contact screen imparts a periodic exposure pattern of relatively high spacial frequency (60 to 300 lines per inch) with an amplitude of somewhat greater than 1.0 log E peak-to-valley. The absolute exposure at any given point on the lith film is determined by the sum of the densities of the continuous-tone film original plus the pointwise density of the contact-screen pattern. An example of the exposure profile the lith film "sees" is illustrated in Figure 9 for two density levels of the continuous-tone original. According to the inverse relationship between

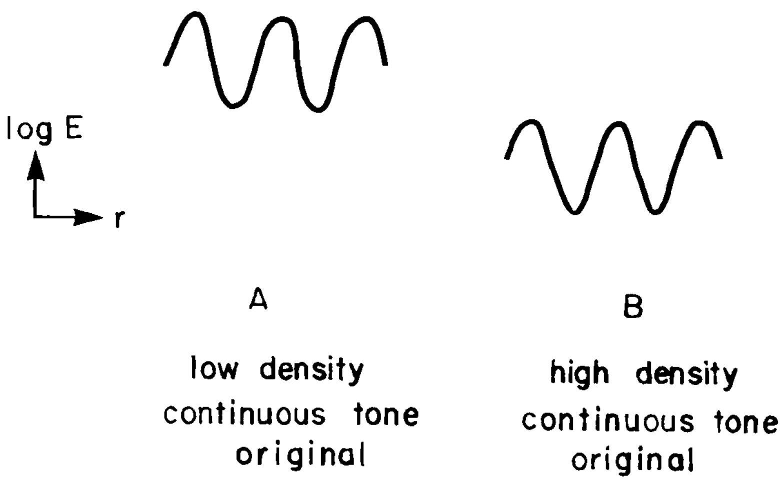

Figure 9. Halftone exposure pattern.

exposure and the lith induction period, the first points to initiate lith-effect development will be the peak exposures of the pattern produced by the low-density continuous-tone original (A). Lith-effect development is then initiated at the lower exposures outside of these peaks as development time is extended. In effect, the centers of the dots form first and then the dots grow radially with extended development time. The same process occurs in the area exposed to the high-density original (B), except the entire process is shifted to later times, owing to the overall lower exposures involved.

The initiation of halftone dot development at the core is described by the exposure/induction period relations of Equations (8) and (9). The dot growth process is essentially the same process of lith-effect development initiating at continuously decreasing exposures as development time is extended. As such, an equation can be derived as follows to describe the halftone dot growth process:

$$\text{growth rate} = \frac{dr}{dt} = \frac{d \log E/dt}{d \log E/dr} = \frac{\frac{1}{2.303t}\,\frac{d \log E}{d \log t}}{d \log E/dr} \qquad (10)$$

Since d log E/d log t is constant, as previously shown, and the spacial gradient of the contact-screen pattern can be approximated as a constant, Equation (10) becomes

$$\frac{dr}{dt} \approx \frac{K}{t} \qquad (11)$$

where,

$$K = \frac{\frac{d \log E}{d \log t}}{2.303\,\frac{d \log E}{dr}} \qquad (12)$$

Integrating Equation (11) with the initial condition

$$r = 0 \text{ at } t = t_{IP,\ \log E\ peak} \qquad (13)$$

yields the following relation for dot radius as a function of time:

$$r = 2.303\ K \log\ [t/t_{IP,\ \log E\ peak}] \qquad (14)$$

A development time series of similarly exposed uniform KODALITH Ortho Film 2556, Type 3 halftone tints was processed in KODALITH Super RT Developer. The halftone dot radii were measured by using a microscope and plotted versus the log of development time in Figure 10. The straight line obtained is in good qualitative agreement with the relationship

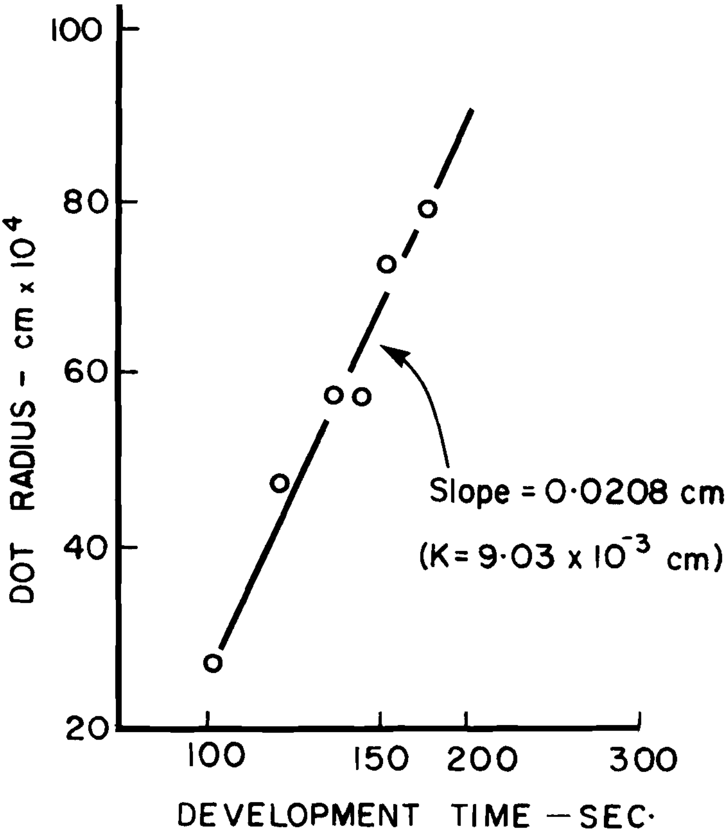

Figure 10. Halftone dot radius as a function of development time, KODALITH Ortho Film, Type 3 in KODALITH Super RT Developer.

predicted by Equation (14). The slope of this straight line corresponds to a value of $K = 9.03 \times 10^{-3}$ cm, which is in good quantitative agreement with the value of $K = 1.08 \times 10^{-2}$ cm calculated from Equation (12). Parameters used to calculate K were: d log E/d log t = -2.15 from Figure 8, and a d log E/dr gradient of 86.2 cm^{-1} estimated for the KODAK Gray Contact Screen (Negative) that was used to expose these dots.

The difference, about 20%, between the experimental and calculated values of dot growth constant, K, could be due to uncertainties in establishing the d log E/dr gradient of the screen. Another possibility is that microscale adjacency effects occur during dot growth whereby products of development formed just inside the advancing dot edge, e.g. halide ion, diffuse outward to alter the initiation of lith-effect development outside the dot edge and thereby affect dot growth. A detailed discussion of such adjacency effects is beyond the scope of this paper, but the reader should be aware that deviations of dot-growth kinetics from the basic model described by Equations (12) and (14) may occur where such secondary effects are significant.

Acknowledgments

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Appendix

Derivation of Nth Order Ag^0-Dependent Development Rate Model

During the induction-period stage of lith development, the principal development reaction is:

$$Ag^0{}_n/Ag_zX_z \quad + \quad HQ^{=} \xrightarrow{k'} Ag^0{}_{n+2}/A^+_{z-2}X^-_{z-2}$$

(silver halide grain with silver speck) (hydroquinone)

$$+ \quad Q \quad + \quad 2X^- \qquad (1A)$$

(benzoquinone) (halide ion)

This reaction is heterogeneous in the sense that the silver/silver halide is a solid phase and the hydroquinone is dissolved in the developer solution. Even though the net effect of the development reaction is the reduction of silver ion to silver metal, silver metal catalyzes the reaction. It is this catalyst role of silver metal in the development process that makes possible imagewise development of exposed photographic film. If the reduction of silver ion to silver metal were to occur equally in the presence and absence of silver metal, there would be no way to discriminate between exposed and unexposed grains.

The role of silver metal as a development catalyst suggests that the rate of development might be written as:

$$\frac{dAg^0}{dt} = k'[HQ^{=}][Ag^+][Ag^0]^N \; ; \; N > 0 \qquad (2A)$$

However, since we are concerned only with the induction-period development during which no significant depletion of hydroquinone or silver ion would be expected, the rate expression reduces to:

$$\frac{dAg^0}{dt} = k\, Ag^{0^N} \qquad (3A)$$

At the beginning of development, t = 0, the size of the silver speck is simply the so-called latent image consisting of those atoms of silver metal that result from photolytic decomposition of silver halide during exposure. That is,

$$Ag^0 = Ag^0{}_{LI} \text{ at } t = 0 \qquad (4A)$$

Equation (3A) can be integrated to yield the following two general solutions, depending on whether N = 1 or N ≠ 1. For N = 1,

$$Ag^0 = Ag^0_{LI}\ e^{kt} \tag{5A}$$

and for N ≠ 1,

$$Ag^0 = Ag^0_{LI}\left[\frac{(1 - N)\ kt}{\left(Ag^0_{LI}\ ^{(1-N)}\right)} + 1\right]^{\frac{1}{1-N}} \tag{6A}$$

Calculated curves of Ag^0/Ag^0_{LI} as a function of development time for the cases N = 0, 0.67, 1.0, and 2.0 are compared in Figure 1A. The appropriate rate constants, k, in

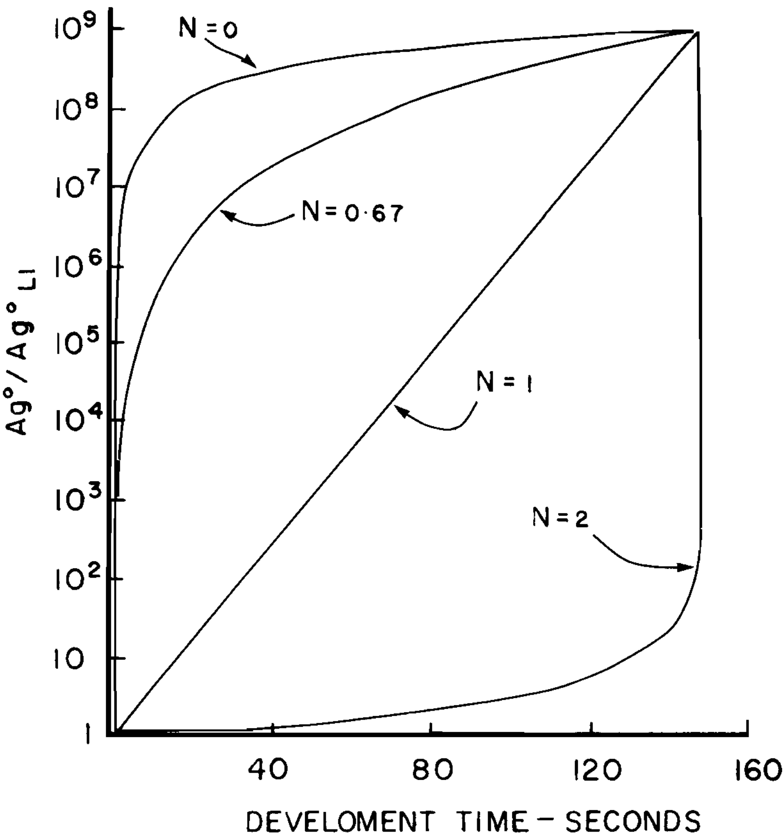

Figure 1A. Calculated silver development curves from Equations (5A) and (6A).

each case were chosen so complete grain development ($Ag^0/Ag^0_{LI} = 10^9$) is achieved in 150 sec of development. Of these four cases, only the N = 2 case shows a limited extent of development over most of the development period to parallel observed lith induction-period behavior and also to justify the assumption of insignificant silver ion and hydroquinone depletion. It further holds that the general shape of the N = 2 case applies to all $N > 1$ cases. For the general case of $N > 1$, Equation (6A) gives real, positive values of developed silver metal only in the time range from:

$$0 < t < \frac{(Ag^0_{LI})^{1-N}}{(N - 1)\ k} \tag{7A}$$

Furthermore, since only a minor fraction of the total development occurs before the upper time limit is closely approached, this limit can be taken as a good approximation of the induction period,

$$t_{IP} \quad \frac{(Ag^0_{LI})^{1-N}}{(N - 1)\ k} \tag{8A}$$

When it is assumed that the latent-image speck size is proportional to exposure, Equation (8A) expresses the dependence of induction period upon exposure. Furthermore, taking the log of both sides of Equation (8A), written in terms of exposure, and differentiating with respect to log t_{IP} yields the following relation for the gradient d log E/ d log t_{IP}:

$$\frac{d\ \log E}{d\ \log t_{IP}} = \frac{1}{1 - N} \tag{9A}$$

The straight-line dependence of log induction period upon log exposure that is observed experimentally is thus accounted for in terms of the Nth-order silver dependence of the induction-period development.

The assumptions entailed in the model, that is, insignificant hydroquinone and silver ion depletion, are invalid for the late stages of actual lith development where these species are consumed rapidly. Furthermore, the results of the previous studies of silver development at $Ag^0/Ag^0_{LI} > 10^5$ cited earlier also limit the application of the $N > 1$ induction period model to the earliest stages of latent-image growth. Figure 1A clearly shows, however, that the rapid acceleration in development rates attributable to $N > 1$ autocatalytic silver dependence is achieved at $Ag^0/Ag^0_{LI} < 10^3$. It is postulated that the acceleration in development rate due to $N \geq 1$ autocatalytic silver dependence results in sufficient $SQ^{\bar{\cdot}}$ generation to sustain the rapid, though surface-area-dependent ($N = 2/3$), lith-effect stage of lith development.