Rate of Development and Size of Latent Image Centers in Chemically Sensitized Emulsions

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This study was undertaken to examine the relation between the sizes of latent image centers and the rate of development. Information on precise development progress was given by measuring the time-dependent optical densities of layers of primitive, sulfur-sensitized and sulfur-plus-gold-sensitized emulsions at 1090 nm. Information on the size of latent image centers was obtained by applying the simulation on the basis of the nucleation-and-growth model to the measured quantum sensitivities of the emulsion layers during development. The development process of a sulfur-plus-gold-sensitized emulsion consisted of fast and slow components. The fast and slow components corresponded to the development of the grains bearing latent image centers composed of at least 5 atoms and less than 5 atoms, respectively. The fast component could be explained on the basis of electrode reaction theory, and the slow component on the basis of a one-by-one reaction mechanism that brought about a long induction period for the development of each grain.

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Introduction

The characterization of latent image centers is very important for the understanding of silver halide photographic materials. One area of interest is the size of latent image centers. Hamilton[1] proposed the nucleation-and-growth (N&G) model for the mechanism of latent image formation. As a result of a simulation on the basis of Hamilton's model, Hailstone et al. have concluded that the smallest latent image centers are composed of 3 atoms in a sulfur-plus-gold-sensitized emulsion[2] and 4 or 5 or more atoms in a sulfur-sensitized emulsion.[3]

Another area of interest is the rate of development of silver halide grains, because the difference in the rate of development between exposed and unexposed grains gives an image. The difference of rate of development of an image from that of *developer fog* is especially important. Developer fog results from development of grains that have unnucleated surfaces without any catalytic center. The fog that results from catalytic silver or gold metal specks produced during preparation of emulsion grains is called *emulsion fog*.[4] The mechanism of development is explained by the electrode reaction theory, according to which the rate of development increases in proportion to the surface area of developing silver particles, as was shown by Pontius and Willis.[5]

The discrimination between development of latent image centers from developer fog is important and is determined by the time of the initiation of development by latent image centers with respect to that for developer fog. It is obvious that the time for the initiation depends on the size of the latent image centers, because development starts with electron transfer from developer to latent image centers. Here, the redox potential of a latent image center is one of the most important parameters that controls the time to initiation of development, and the redox potential of the silver cluster becomes more negative with decreasing size.[6] Reinders[7] reported that a redox buffer solution with a potential at least 90 mV more negative than that of silver electrode was needed to initiate development. Hilson[8] reported that latent image centers formed by high-intensity exposure could be bleached by a redox buffer solution with a potential more negative than that of a solution that could bleach latent image centers formed by low-intensity exposure, supporting the inference by Burton and Berg[9] that the latent image centers formed by high-intensity exposure were smaller than those formed by low-intensity exposure. Hilson considered that the activation energy and induction period of development increase with decreasing size of latent image centers, owing to the increase in the surface energy of the centers with decreasing size.

Konstantinov and Malinowski[6,10,11] studied the redox potentials of evaporated silver clusters of various sizes. They determined the size of silver clusters in equilibrium with redox buffer solutions with variation of redox potential and concluded that in the range of cluster size not less than 20 Å the shift of redox potential of silver clusters from that of bulk silver metal was caused by its size-dependent surface potential, as given by the Gibbs–Thomson equation.

This study was undertaken to examine the relationship between the size of latent image centers and rate of development. The information on precise development progress was obtained by measuring time-dependent optical densities of layers of primitive, sulfur-sensitized and sulfur-plus-gold-sensitized emulsion layers at 1090 nm. Information on the size of latent image centers was obtained by applying a simulation on the basis of the N & G model to the quantum sensitivities of the emulsions.

Experimental

Measurement of Rate of Development. The development process was studied by measurement of the change in optical density of exposed emulsion layers at 1090 nm (i.e., IR density) during development. The apparatus for the IR density measurement is illustrated in Fig. 1. The

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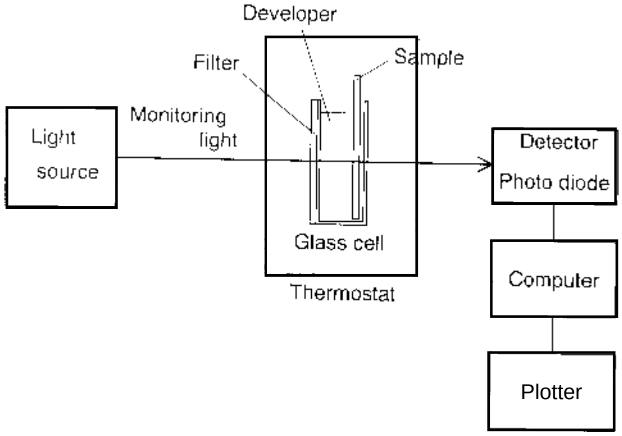

Figure 1. Apparatus for IR density measurement of a film sample during its development.

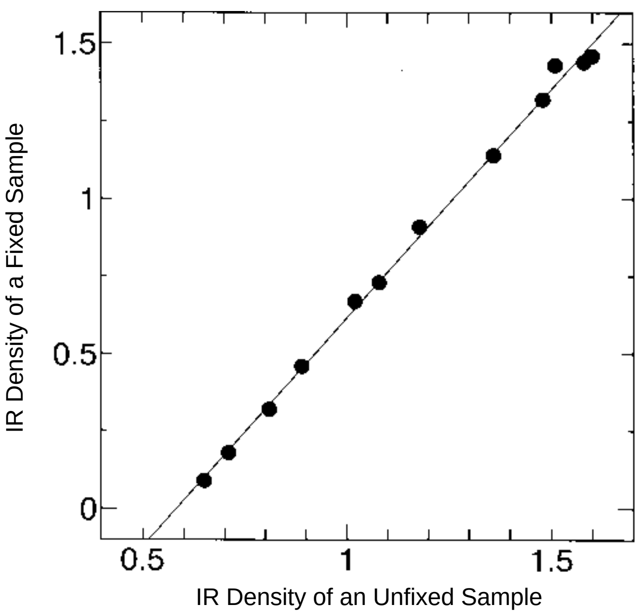

Figure 2. Relation between IR density of the fixed and unfixed samples. This figure is based on a sample of a sulfur-sensitized emulsion. The developer used was MAA-1. Development of each sample was stopped by use of tartaric acid. Fixer was by Super Fuji Fix.

light source was a halogen lamp, and light of wavelength shorter than 900 nm was removed by an IR-90 filter placed in front of the developer. The IR density was measured by a multichannel photodiode (MCPD-100 made by Photal Co. Ltd.). The data obtained were analyzed by computer (NEC 9800VX).

The IR density arose from light scattering by silver halide grains and light absorption of developed silver. IR density due to the light absorption of developed silver was separated from the total IR density by comparing IR density of a sample before and after fixing. As shown in Fig. 2, the relationship between IR densities of samples before and after fixing was linear during development of the primitive, sulfur-sensitized and sulfur-plus-gold-sensitized emulsions.

Figure 3 shows that the IR density and the amount of developed silver in the fixed samples, as measured with x-ray fluorescence (XRF), coincided. This result indicates that the covering power of the developed silver was constant during development and that the IR density was proportional to

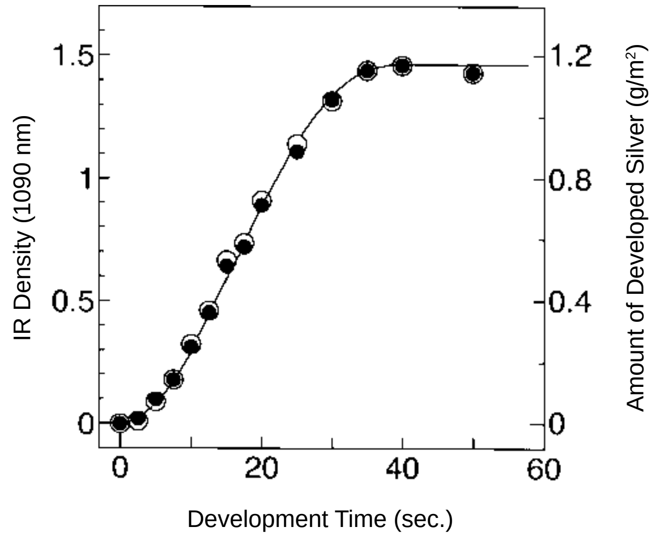

Figure 3. Relation between IR density (○) and amount of developed silver (●) of the sample shown in Fig. 2. The amount of developed silver was measured by x-ray fluorescence.

the amount of the developed silver. This result was realized regardless of the type of chemical sensitization.

Emulsion, Coating, and Processing. The emulsion used was composed of octahedral AgBr grains with equivalent diameters of 0.47 μm. The pH and pAg values of the emulsion at 40°C were 6.3 and 8.4, respectively. The sulfur-sensitized emulsion was prepared by the digestion of the emulsion in the presence of 1.5×10^{-5} mole of $Na_2S_2O_3 \cdot 5H_2O$/mole of AgBr at 60°C for 60 min. The sulfur-plus-gold-sensitized emulsion was prepared by digestion of the emulsion in the presence of 2.3×10^{-5} mole of $Na_2S_2O_3 \cdot 5H_2O$/mole of AgBr, 2.1×10^{-5} mole of $HAuCl_4$/mole of AgBr, and 8.7×10^{-4} mole of KSCN/mole of AgBr at 60°C for 60 min. Sensitization was optimized for a 10-s exposure.

The emulsions were coated on triacetate films at 1.2 g/m^2 of AgBr and 2.1 g/m^2 of gelatin. Each coated emulsion was exposed to a tungsten lamp (color temperature 2854 K) through a blue filter. The developer used was MAA-1.[12] The initial rate of development was defined as the reciprocal of the time needed to give 10% of the maximum density.

Result and Discussion

Development Processes of Primitive, Sulfur-Sensitized, and Sulfur-Plus-Gold-Sensitized Emulsions. Figure 4 shows the characteristic curves of samples used in this experiment. Each sample was developed by MAA–1 developer after a 10 s blue exposure. The exposure level of each sample is indicated in Fig. 4 by arrows. The change of IR density due to the light absorption of developed silver in each exposed emulsion layer is shown in Fig. 5 as a function of time of development. The development of an exposed sulfur-plus-gold-sensitized emulsion layer proceeded through two steps with fast and slow components. On the other hand, only the fast component was observed in the change of IR density for the development of exposed primitive and sulfur-sensitized emulsion layers.

Figure 6 shows development processes of sulfur-plus-gold-sensitized emulsion layers at several exposure levels. An exposure level of 1.0 corresponds to that indicated by an arrow in Fig. 4(c). Exposure time was 10 s. The proportion of the fast component increased as the exposure increased. On the other hand, the slow component was absent at all exposure levels for primitive emulsion layers, as shown in Fig. 7.

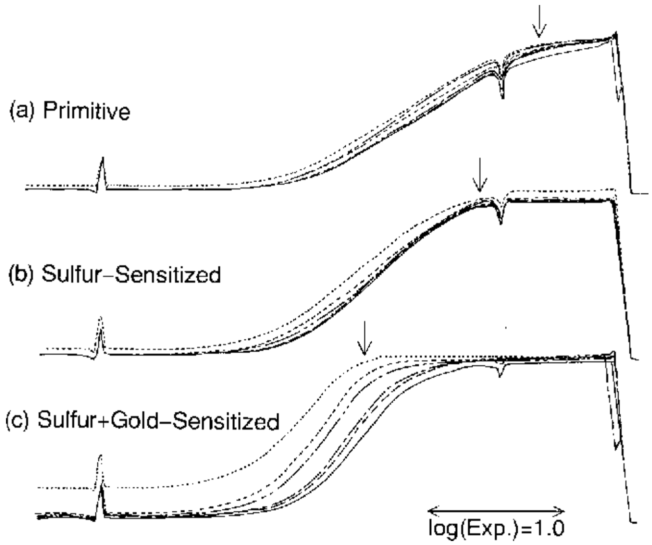

Figure 4. Characteristic curves of (a) primitive, (b) sulfur-sensitized, and (c) sulfur-plus-gold-sensitized emulsion layers. Exposure was for 10 s, and samples were developed by MAA-1 at 30°C for 30 s (———), 40 s (— — —), 50 s (— — —), 5 min (— — — —), 10 min (– – – – – –), and 30 min (·········). Relative values of exposure in log ($l \cdot t$) were (a) 1.0, (b) 0.5, and (c) 0.

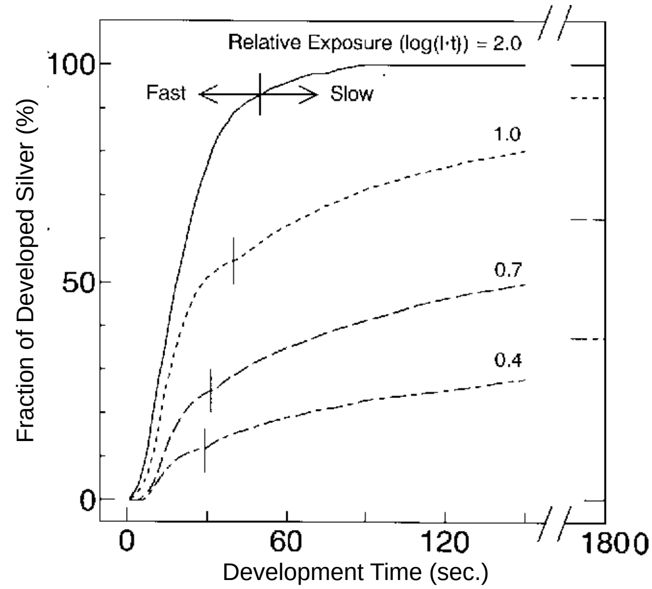

Figure 6. Development profile of a sulfur-plus-gold-sensitized emulsion at various exposures. Relative exposure 1.0 is indicated by an arrow in Fig. 4(c). Each sample was exposed for 10 s and developed at 30°C in an MAA-1 developer.

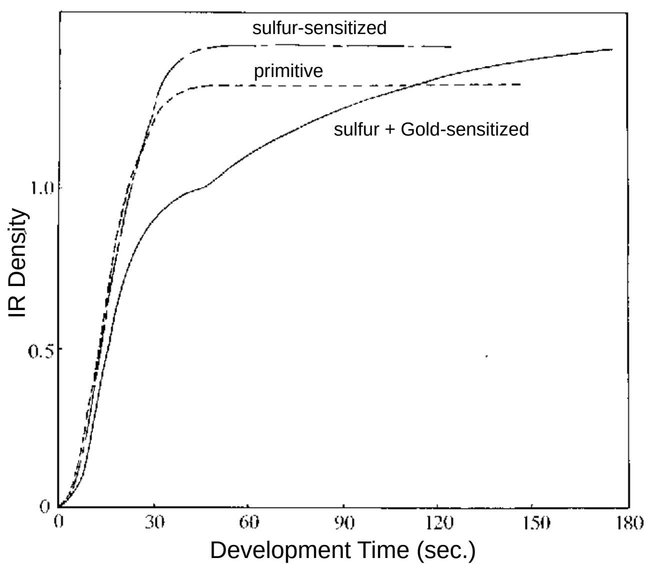

Figure 5. Increase in IR density as a function of development time for primitive (– – – – – –), sulfur-sensitized (— — —) and sulfur-plus-gold-sensitized (———) emulsion layers. Exposure time was 10 s and exposure level is shown by arrows in Fig. 4. Development was performed at 30°C in an MAA-1 developer.

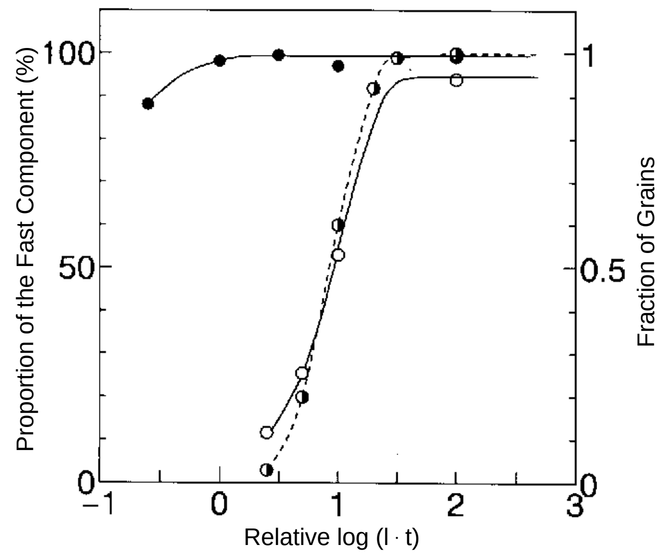

Figure 7. The proportion of the fast component in a primitive emulsion (●) and in a sulfur-plus-gold-sensitized (○) emulsion as a function of exposure. Relative exposure 1.0 is indicated by arrows in Figs. 4 (a) and (c). Each sample was exposed for 10 s and developed at 30°C in an MAA-1 developer. The simulated fraction of the grains with a latent image center composed of at least 5 atoms as a function of exposure is also shown in the figure (◑). The simulation was based on the N&G model.

Figure 8 shows the proportion of the fast component of sulfur-plus-gold-sensitized emulsion at the exposure ($I \cdot t$) with variation of exposure time (t) and light intensity (I) to give the shoulder density. The proportion of the fast component was independent of exposure until exposure time exceeded 1 s; then it increased with increasing exposure time and reached unity at about 100 s of exposure.

Temperature dependence of the initial rate of development is shown in Fig. 9. The rate of development of the fast component of a sulfur-plus-gold-sensitized emulsion layer coincided with development rates of primitive and sulfur-sensitized emulsion layers at any temperature from 30° to 80°C. The activation energy of the rate of development of the fast component was 12.2 kcal/mol. On the other hand, the development process of the sulfur-plus-gold-sensitized emulsion was composed of only the slow component, when exposed for 10^{-5} s to render ~50% of grains developable. The temperature dependence of the initial rate of development of the slow component is also shown in Fig. 9. The activation energy of the slow component was 17.7 kcal/mol.

Figure 10 shows electron micrographs of developed silver and remaining AgBr grains in sulfur-plus-gold-sensitized emulsion layers, which were exposed to render ~50% of the grains developable when developed at 20°C for 10 min in MAA-1. In the case of an exposure for 1000 s, almost all of the developable grains had small developed

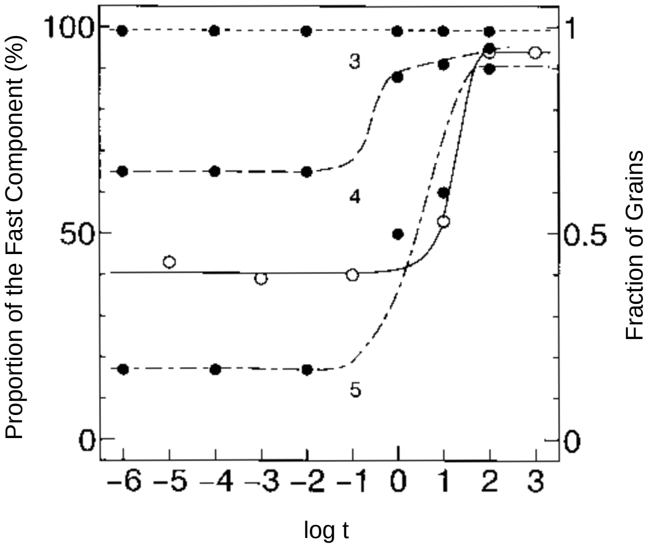

Figure 8. The proportion of the fast component of development of sulfur-plus-gold-sensitized emulsion layers as a function of exposure time (◯). Each sample was exposed to give the shoulder density in its characteristic curve. Development was 30°C in an MAA-1 developer. Comparisons of the proportion of the fast component with the simulated fractions of the grains having latent image centers consisting of various number of atoms (●) as a function of exposure time are also shown in the figure. The numbers shown in the figure indicate the minimum size of the latent image center of the grain.

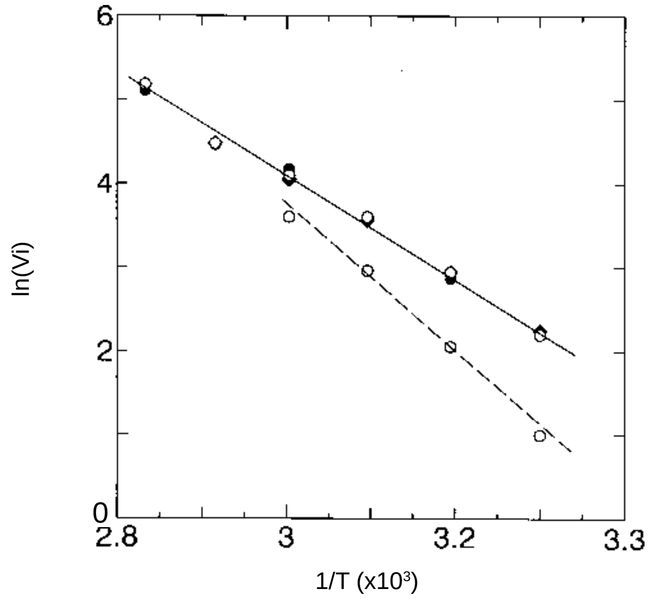

Figure 9. Temperature dependence of the rate of development (V_i) of primitive (●), sulfur-sensitized (◆), and sulfur-plus-gold sensitized (◯) emulsions. *Solid* and *broken lines* represent the rates of the fast and slow components, respectively. The activation energies were 12.2 and 17.7 kcal/mol for the fast and slow components, respectively.

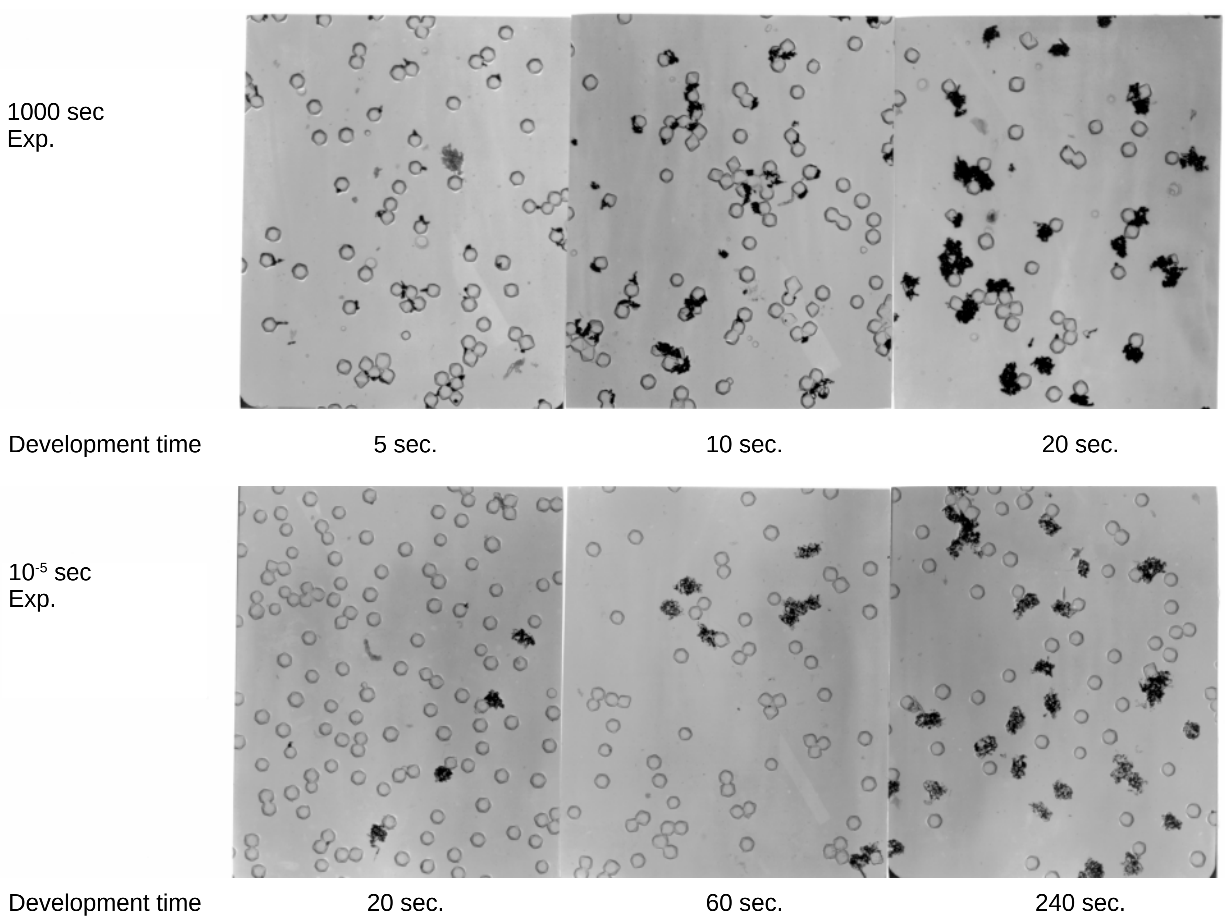

Figure 10. Electron micrographs of developed silver and remaining AgBr grains at various development times. The emulsion was sulfur-plus-gold-sensitized and exposed to render ~50% of grains in the emulsion layer developable when developed in MAA-1. Exposure times were 1000 s (upper row) and 10^{-5} (lower row).

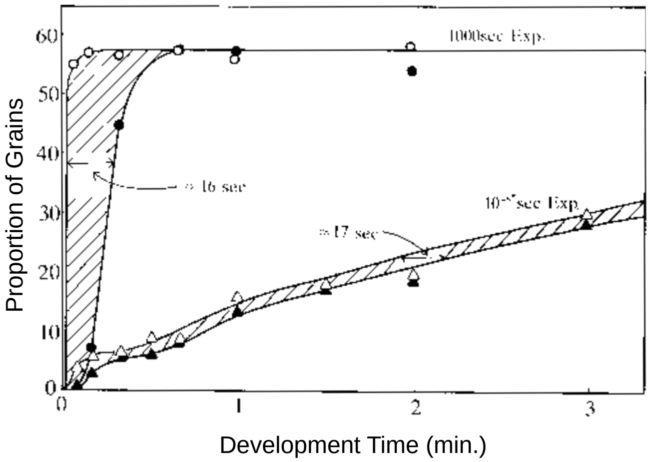

Figure 11. Proportions of developed grains and developing grains as a function of rate of development for sulfur-plus-gold-sensitized emulsion layers exposed to make ~50% of the grains developable. Solid circles and solid triangles indicate the proportions of developed grains exposed for 1000 and 10^{-5} s, respectively. The sums of proportions of developed and developing grains for the corresponding exposure time are indicated by open circles and open triangles, respectively. Accordingly, the hatched region indicates the proportion of developing grains.

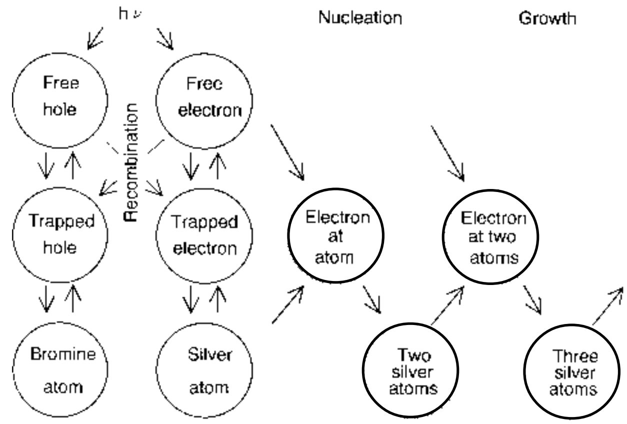

Figure 12. Schematic of N&G model.

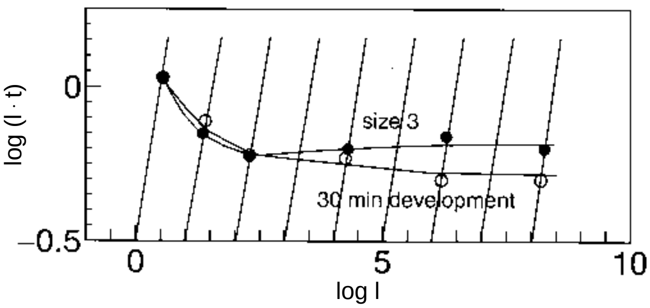

Figure 13. Reciprocity curves of a sulfur-plus-gold-sensitized emulsion with development at 30°C for 30 min in MAA-1 (◯) and of the N&G model simulation (●) under the assumption that the smallest latent image centers consisted of 3 atoms.

silver clusters after 5 sec of development. Then the developed silver clusters grew on each grain in a similar manner. On the other hand, in the case of the 10^{-5} s exposure, development of grains was initiated one after another during the development for 240 s.

Figure 11 shows the change in the proportion of developed grains and developing grains as a function of development time for the sulfur-plus-gold-sensitized emulsion layer, taken from the micrographs in Fig. 10. In the case of the 1000-s exposure, the development of each developable grain was initiated shortly after the start of development and was completed in about 30 s. On the other hand, in the case of the 10^{-5} s exposure, the initiation of development of each grain was much delayed and fluctuated among grains. In both cases, it took about 16 s to develop one grain completely after detectable developed silver was observed. It is reasonable to consider that the development of the emulsion layers that were exposed for 1000 s and 10^{-5} s correspond to the fast and the slow components, respectively, which were observed in the development process of the layers exposed for 10 sec.

Analysis on the Basis of the N&G Model. The size of latent image centers was estimated on the basis of the N&G simulation model. In the N&G model, an absorbed photon generates an electron–hole pair. Then, electrons and holes take part in the recombination, nucleation, and growth processes (see Fig. 12). First one must decide the recombination rate Γr, nucleation rate Γn, and growth rate Γg. Here the important parameters are the ratios of these rates. The ratio $\Gamma r/\Gamma g$, which is called ω, indicates the probability of recombination. The ratio $\Gamma n/\Gamma g$, which is called η, indicates the probability of nucleation.

These two parameters were determined so as to reproduce the experimental characteristics (quantum sensitivity, reciprocity law failure, gradation) of samples. Development at 30°C for 30 min in MAA-1 was used to complete the development of the slow component. Under this development condition, the quantum sensitivity of a sulfur-plus-gold-sensitized emulsion layer was 9 absorbed photons/grain with ~19% fogged grains. For the emulsion used here, 1 and 0.5 were adopted as the values of ω and η, respectively. These parameters gave a quantum sensitivity of 10 absorbed photons/grain as the result of the simulation. The agreement between experimental and observed reciprocity law failure curves was confirmed in Fig. 13.

The result of the simulation on the basis of the N&G model with the above parameters is shown in Fig. 14, as the fraction of developable grains as a function of exposure when the smallest latent image centers are composed of 2, 3, 4, 5, and 6 atoms. Figure 11 indicates that the fast component of the development was completed within 30 s. Then the characteristic curves given by development for 30 s and for 30 min were compared with curves shown in Fig. 14. The result is shown in Fig. 15. The curve given by development for 30 s coincided with the simulated curve having the smallest latent image centers composed of 5 atoms. On the other hand, the curve given by development for 30 min corresponded to the simulated curve with the smallest latent image centers composed of 3 atoms. It is therefore considered that the fast component of development was caused by latent image centers composed of at least 5 atoms and the slow component was caused by latent image centers composed of 3 atoms.

As seen in Fig. 15, the gradations of the simulated characteristic curves were higher than those of the corresponding experimental ones. We consider this result to arise from the assumption in the N&G model that all grains were completely similar, contrary to the fact that grains in a real emulsion were not necessarily the same in sensitivity.

As shown in Fig. 7, the experimentally observed proportion of the fast component of development of a sulfur-plus-gold-sensitized emulsion layer as a function of exposure was in good agreement with the simulated fraction of the grains with latent image centers composed of 5 or more atoms.

Similar comparison was made in Fig. 8 between the proportion of the fast component of development of a

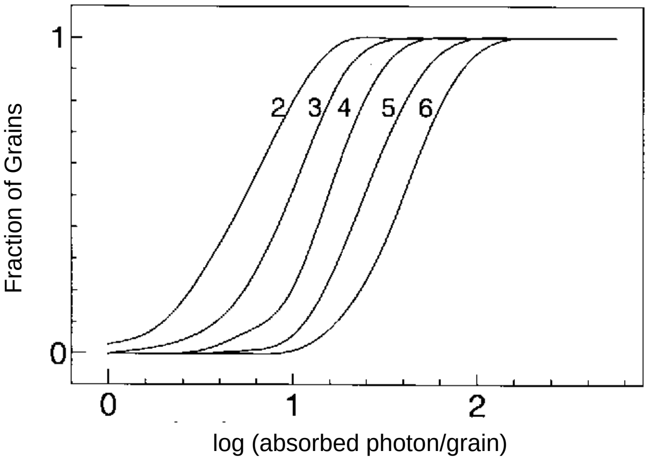

Figure 14. Set of characteristic curves simulated on the basis of the N&G model. The ordinates represent the fraction of developed grains on which the smallest latent image centers were composed of 2 to 6 atoms.

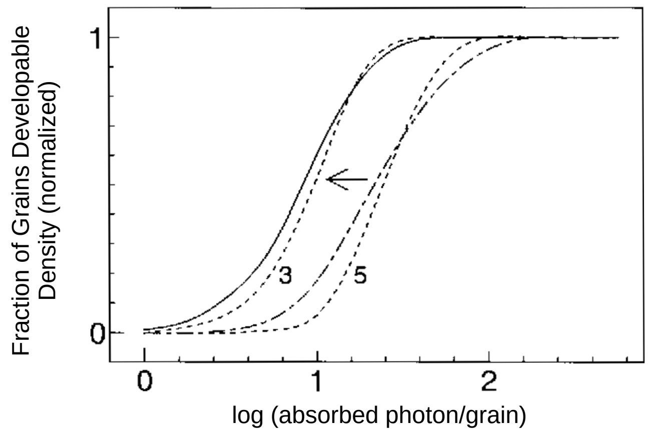

Figure 15. Comparison of experimental characteristic curves with simulated ones. Experimental curves were for sulfur-plus-gold-sensitized emulsion layers, which were exposed for 10 s and developed at 30°C for 30 s (— — —) and 30 min (———) in MAA-1. Simulated curves (– – – – – –) were based on the N&G model. Numbers in the figure indicate the numbers of atoms in the smallest latent image centers.

sulfur-plus-gold-sensitized emulsion layer when exposed to give the shoulder of the characteristic curve and the fraction of grains with latent image centers composed of at least 3, 4, or 5 atoms, according to the simulation, as a function of exposure time. With increasing exposure time, both the proportion of the fast component of development and the fraction of the grains with latent image centers composed of at least 5 atoms were independent of exposure time when exposure was shorter than 0.1 s, then increased and approached unity when exposure time exceeded 10 s.

The proportion of the fast component of development was qualitatively in accord with the fraction of grains with latent image centers composed of at least 5 atoms, supporting the idea that development of the grains with latent image centers composed of at least 5 atoms gave rise to the fast component of development. In Fig. 8, in the high-intensity exposure region, the proportion of the fast component is larger than the fraction of grains with latent image centers composed of at least 5 atoms. The reason is not now clear.

The speed increase caused by sulfur-plus-gold-sensitization could be attributed to the decrease in the size of the minimum latent image center. According to the analysis by Hailstone et al., the sizes of the minimum latent image centers were 3 atoms in sulfur-plus-gold-sensitized emulsions and 5 atoms in primitive and sulfur-sensitized emulsions. However, as shown in this study, sulfur-plus-gold-sensitization was associated with the decrease in rate of development, because the initiation of development of a latent image center composed of 3 atoms was very slow.

Simulation of Development Process. The development profile of a sulfur-plus-gold-sensitized emulsion is simulated in this section. At the early stage of the fast developing process, spherical developed silver was observed by an electron microscope (see Fig. 10), and optical density, which was proportional to the amount of silver formed, increased in proportion to t^3. This result indicates that the rate of development was proportional to the surface area (S) of developed silver. Therefore the reaction mechanism could be explained by the electrode reaction theory.[4] The reaction is represented as follows.

$$d[\mathrm{Ag}]/dt = \kappa S, \qquad (1)$$

$$[\mathrm{Ag}] = (4/3)\,\rho\pi r^3, \qquad (2)$$

$$S = 4\pi r^2, \qquad (3)$$

where r and ρ are radius and specific gravity of developed silver, respectively. Taking into account the condition $r = 0$ when $t = 0$,

$$[\mathrm{Ag}] = \mathrm{K}t^3, \qquad (4)$$

$$K = (4/3)\,\pi\kappa^3/\rho^2. \qquad (5)$$

Assuming that half of the grains have latent image centers comprising at least 5 atoms, Eq. 4 leads to Fig. 16 as a fast-development profile. A grain was developed in 16 s. Hence, κ was given as 9.7×10^{-8} mol/cm$^2 \cdot$ s.

On the other hand, the one-by-one reaction mechanism was applied to the slow development process, during which a latent image center consisting of 3 atoms grows to a larger center:

$$\mathrm{LI}_3 \xrightarrow{k_1} \mathrm{LI}_4 \xrightarrow{k_2} \mathrm{LI}_5,$$

where LI_n indicates a latent image center consisting of n atoms. A latent image center on a grain in a sulfur-plus-gold-sensitized emulsion may include Au atoms. Then,

$$-d[\mathrm{LI}_3]/dt = k_1[\mathrm{LI}_3], \qquad (6)$$

$$-d[\mathrm{LI}_4]/dt = k_2[\mathrm{LI}_4] - k_1[\mathrm{LI}_3], \qquad (7)$$

where $[\mathrm{LI}_n]$ represents the ratio of grains having latent image centers consisting of n atoms. Then the initial ($t = 0$) conditions with $[\mathrm{LI}_3] = [\mathrm{LI}_3]_0$, $[\mathrm{LI}_4] = [\mathrm{LI}_4]_0$, and $[\mathrm{LI}_3] + [\mathrm{LI}_4] + [\mathrm{LI}_5] = [\mathrm{LI}_3]_0 + [\mathrm{LI}_4]_0$ lead to the following equations:

$$[\mathrm{LI}_3] = [\mathrm{LI}_3]_0\exp(-k_1t), \qquad (8)$$

$$[\mathrm{LI}_4] = [\mathrm{LI}_3]_0(k_1/(k_2 - k_1))\{\exp(-k_1t) - \exp(k_2t)\} + [\mathrm{LI}_4]_0\exp(k_2t) \qquad (9)$$

Changes of $[\mathrm{LI}_3]$, $[\mathrm{LI}_4]$, and $[\mathrm{LI}_5]$ in the case of $k_1 = 0.06$ s^{-1} and $k_2 = 0.0098$ s^{-1} are shown in Fig. 17. According to the N&G model simulation, $[\mathrm{LI}_3]_0 = 0.2$ and $[\mathrm{LI}_4]_0 = 0.3$ at the

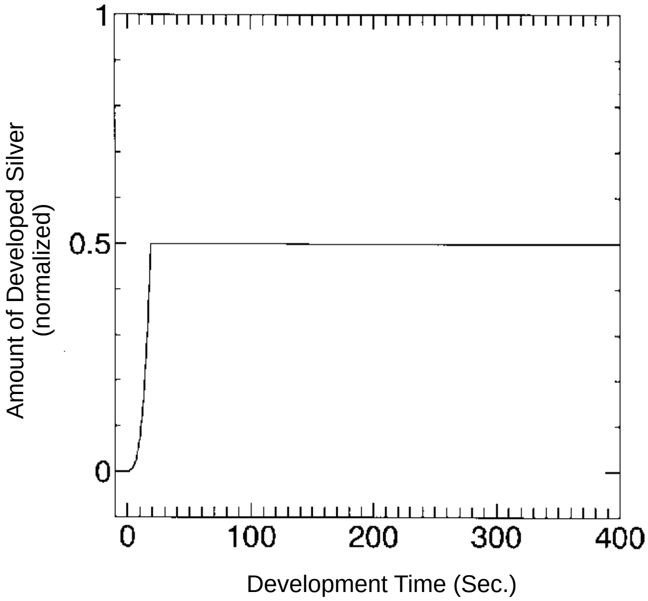

Figure 16. The simulated amount of developed silver of the fast component on the basis of the electrode reaction theory.

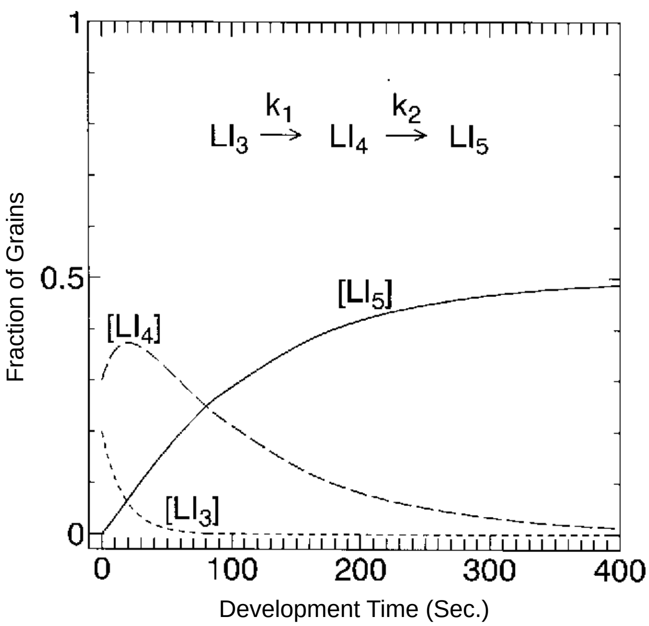

Figure 17. Growth of latent image centers by the one-by-one reaction mechanism, where $[LI_n]$ represents the fraction of grains with a latent image center consisting of n atoms. Initial conditions are $[LI_3] = 0.2$, $[LI_4] = 0.3$, $[LI_5] = 0.0$, $k_1 = 0.06\ s^{-1}$, and $k_2 = 0.0098\ s^{-1}$.

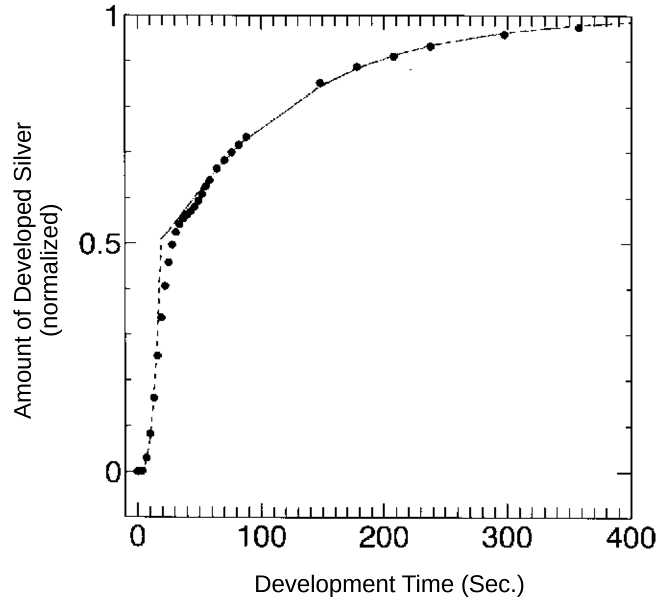

Figure 18. Simulation of the development process. *Dotted line* shows the increase in the IR density of a sulfur-plus-gold sensitized emulsion layer as a function of development time, reproduced from the solid curve in Fig. 5. The *dashed* and *solid lines* were derived from the electrode reaction model and the one-by-one reaction model, respectively.

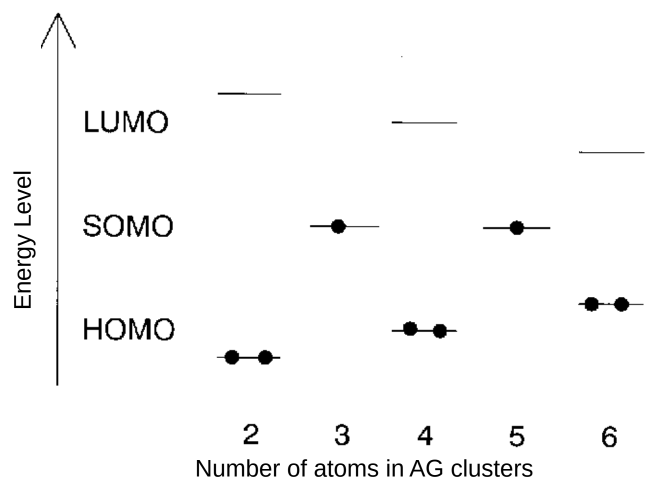

Figure 19. Energy levels of the frontier molecular orbitals of silver clusters composed of various number of atoms. LUMO, SOMO, and HOMO represent the lowest unoccupied, the singly occupied and the highest occupied molecular orbitals, respectively.

exposure that gives the shoulder of the characteristic curve corresponding to the smallest latent image center composed of 3 atoms (see Fig. 14).

Because a grain with a latent image center composed of 5 atoms was developed in 16 s, adding 16 s to time t, the simulated curve for change of $[LI_5]$ will represent the slow component of development. The two simulated curves for the fast and the slow components of development of a sulfur-plus-gold-sensitized emulsion were combined and compared with the experimental one in Fig. 18. In the boundary region between the fast and the slow components, the simulated curve did not coincide well with the experimental one. However, the simulated curve was in good agreement with the experimental one in the slow development region, which was a main point of argument in this study. This result indicates that the slow development process proceeded through a one-by-one reaction mechanism.

We note that the rate constant k_1 was larger than k_2. This could be explained by the following consideration. On the basis of molecular orbital theory, LI_3 with an odd number of valence electrons has a singly occupied molecular orbital (SOMO) whose energy level is lower than that of the lowest unoccupied molecular orbital (LUMO) of LI_4, as shown in Fig. 19. This consideration also supports the idea that the smallest latent image center consists of an odd number of atoms.

Conclusions

1. The development process of a sulfur-plus-gold-sensitized emulsion consisted of fast and slow components.

2. The fast and slow components corresponded to the development of the grains bearing latent image centers composed of at least 5 atoms and less than 5 atoms, respectively.
3. The fast component could be explained on the basis of the electrode reaction theory, and the slow component could be explained on the basis of a one-by-one reaction mechanism, which brought about an induction period for the development of each grain.

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