Numerical model for characteristic curves of photothermographic materials using semiempirical simulation method.

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Abstract

Photothermographic materials that contain silver halide grain and organic silver salts are widely used in dry processing imaging system. Klosterboer and Rutledge[1] published a primary numerical model for the characteristic curves of these materials. Hirano[4] pointed out some insufficiencies of their model, and gave improved equations. Since these previous works are based on ideal Poisson's distribution of the fraction of silver halide grains with a latent image, their estimated characteristic curves don't fit that of materials of practical use perfectly. Also they don't refer to fog. To improve these insufficiencies, a new semiempirical simulation method is studied. Hirano's equations were modified to suitable form to regression works. Some experimental characteristic curves of different development times and different development temperatures were applied to the equations using our original regression algorithm, then both development rate parameter and characteristic curve parameter were found. Using these parameters, the modified equations gave more exact estimation of characteristic curves for various development conditions than that of previous works.

Introduction

Photothermographic materials that contain silver halide grain and organic silver salts are widely used in dry processing imaging system. In these systems, latent image centers are formed on the surface of silver halide grains by light exposing. These latent image centers are grown into visible metallic silver image by physical development in thermal development process. Silver ions are supplied from organic silver salts that surround the silver halide grain.

Klosterboer and Rutledge[1] assume that only the silver from the organic silver salts within a certain radius from a silver halide latent image has the time to diffuse to the latent image and be reduced to image silver during development time. This spherical volume was named *sphere of influence*. These spheres are observed as white faint hollows using a scanning electron microscope. Based on this assumption, they gave a primary numerical model for characteristic curves. In this model, number of latent image centers is calculated from exposure and grain size, based on Poisson's distribution. Amount of developed silver is considered to be equivalent to amount of organic silver salts within the sphere of influence. Optical density is assumed to be proportional to the amount of developed silver. Radius of the sphere of influence is assumed to be limited so that the volume of the sphere of influence does not exceed the physical layer volume.

Klosterboer and Rutledge model.

$$f = \left[\sum_{p=A}^{\infty} \left(a \cdot E \cdot L^2\right)^p \frac{\exp\left(-a \cdot E \cdot L^2\right)}{p!} \right] \quad (1)$$

$$D = \frac{K \cdot f \cdot W_{SS}}{\left(T \cdot A \cdot d / W_{SH}\right) - 1} \left[\left(\frac{4}{3}\pi \left(r/L\right)^3 \right) - 1 \right] \quad (2)$$

f: fraction of silver halide grains receiving a latent

$$\frac{r}{L} \leq \left[\frac{3}{4\pi} \left(\frac{T \cdot A \cdot d}{W_{SH}} + 1 \right) \right]^{\frac{1}{3}} \quad (3)$$

image exposure

A: a latent image number of absorbed photons
E: number of photons per unit area
a: fraction of photons absorbed
L: edge length of the silver halide grain
D: optical density
K: proportional constant
Wss: coating weight of organic silver salts
T: thickness of coated layer
A: coated area
d: density of silver halide grains
W_{SH}: coating weight of silver halide grains
r: radius of sphere of influence

Though this model is famous and fundamental, it is too simple to predict the exact shape of the characteristic curve, especially its shoulder to Dmax range.[2),3)]

Hirano[4] pointed out some insufficiencies of their model, and gave improved equations. The points in an argument are as follows.

1. Overlap of the sphere of influence should be considered instead of the limitation of its radius.
2. Optical density is not proportional to the amount of developed silver. Covering power should be considered.
3. Dead volume of the undeveloped silver halide grains within the sphere of influence should be considered.

In his model, overlap of the sphere of influence was corrected by integration of its probability. The limitation for the radius of sphere of influence was repealed. Covering power was calculated from both number and radius of the developed silver particle.

Hirano model

$$f = \left[\sum_{p=A}^{\infty} \left(a \cdot E \cdot L^2\right)^p \frac{\exp\left(-a \cdot E \cdot L^2\right)}{p!} \right] \qquad (1)$$

$$N_0 = \frac{W_{SH} \cdot A}{d \cdot L^3} \qquad (4)$$

$$N = f \cdot N_0 \qquad (5)$$

$$Pss = \frac{Wss \cdot A}{A \cdot T - N_0 \cdot L^3} \qquad (6)$$

$$M = Pss\left[AT\left\{1 - \exp\left(-\frac{4}{3}\pi r^3 \frac{N}{AT}\right)\right\} - NL^3 \right]\left(\frac{AT - N_0 L^3}{AT - NL^3}\right) \qquad (7)$$

$$D = C \cdot N\left(\frac{M}{N}\right)^{\frac{2}{3}} \Big/ A = C \cdot M^{\frac{2}{3}} \cdot N^{\frac{1}{3}} \Big/ A \qquad (8)$$

N_0: number of total silver halide grains
N: number of silver halide grains receiving a latent image exposure
Pss: density of organic silver salts in the coated layer volume
M: mass of the developed silver
C: proportional constant for covering power

Though treatment of the sphere of influence was improved in this model, calculation of the fraction of silver halide grains receiving a latent image exposure was still based on ideal Poisson's distribution. So estimated characteristic curves don't fit that of materials of practical use perfectly. Also these models don't refer to fog.

Purpose of the Study

On the development of a dry processing imaging system, it is very important to keep the shape of characteristic curves under precise control. Because the characteristic curves of photothermographic materials are very sensitive to its development condition, we often need to calculate the precise change of the characteristic curves under various development conditions.

Some problems must be solved prior to use the above models. Equation (1) is an ideal model on the assumption that the silver halide grains are uniform in sensitivity. On materials of practical use, the sizes of grains are distributed. It is difficult to examine precise distribution of their size because they are very small (less than 0.05 micrometer in edge length). Though spheres of influence are observed as white hollows using a scanning electron microscope, these are faint distorted figures. Radius of sphere of influence should be regarded as a conceptual parameter.

To solve these problems, we adopt a semiempirical method. In this study, the values of *f, r, C* are determined from experimental data.

Typical Regression Study

Experimental Data

Some pieces of same photothermographic film are exposed equally, and developed various development times and temperature. Following characteristic curves were observed.

Film: Konica Medical Imaging Film SD-P
Develop unit: DRYPRO model 722

Table 1. Development Condition

No	heat time (sec.)	temperature (C)
1	14	119
2	14	121
3	14	123
4	14	125
5	14	127
6	7	125
7	10	125
(4)	14	125
8	20	125
9	30	125

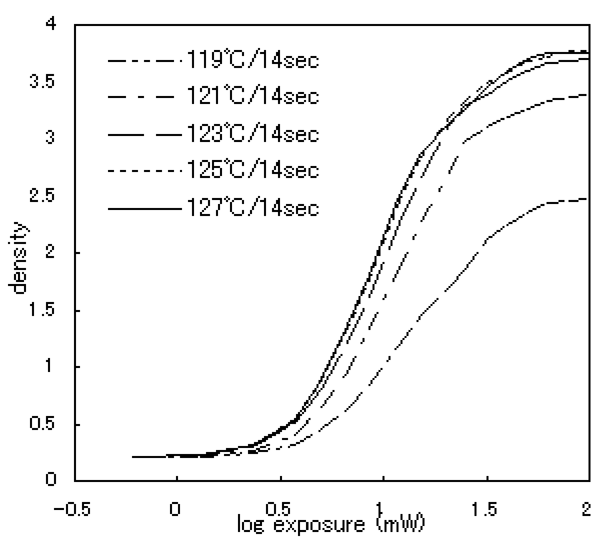

Figure 1. Characteristic curves of various temperature

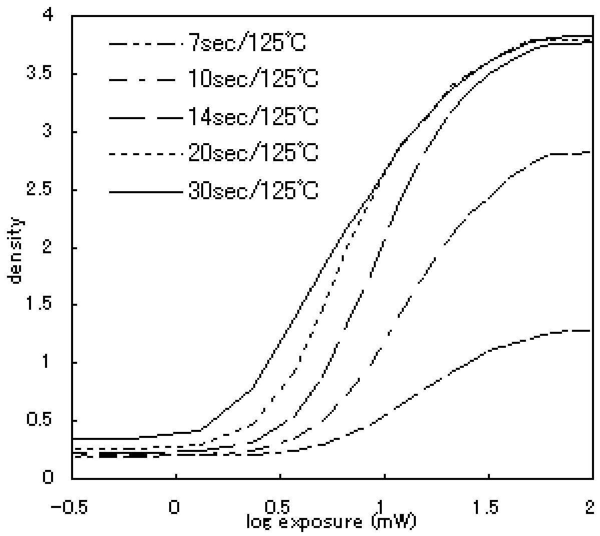

Figure 2. Characteristic curves of various times

Regression

Equation (1) of Hirano's model was repealed. Instead of it, f was treated as a look up table function. Their table values were fixed latter.

$$f = g(Ex) \quad 0 \leq f \leq 1 \quad \text{Ex: exposure} \tag{9}$$

Equation (4) to (8) were arranged into one equation by substituting N_0, N, Pss, and M.

$$D = h(f, r, C, W_{SH}, Wss, L, A, T, d) \tag{10}$$

In these equation, following parameter were already known: W_{SH}, Wss, L, A, T, d. Differ from original Hirano's model, f is independent of L. L works on the dead volume correction of the silver halide grains only. So a rough average value is enough for this calculation.

Maximum density was given by putting 1 in the place f and putting infinity in the place r in the equation (10).

$$D\max = C \cdot Wss^{2/3} \cdot \left(\frac{W_{SH}}{d \cdot L^3}\right)^{1/3} \tag{11}$$

$$C = D\max \cdot Wss^{-2/3} \cdot \left(\frac{W_{SH}}{d \cdot L^3}\right)^{-1/3} \tag{12}$$

Parameter C was fixed by putting observed Dmax value into equation (12). To get a correct Dmax value, the exposure should be in the range of practical use, because extreme exposure causes the formation of latent image on in_situ silver halide, and gives excessive density.

Now r and f remain to be solved. To fix these, a reverse function of equation (10) was defined.

$$f = h^{-1}(D, r, C, W_{SH}, Wss, L, A, T, d) \tag{13}$$

Though the algebraic expression of above function is difficult to solve, numerical solution of above is calculable by iterative routines such as Newton-Raphson method. On equation (13), putting 1 micrometer as initial value in the place r and putting experimental density (base density was subtracted) in the place D, following f were calculated.

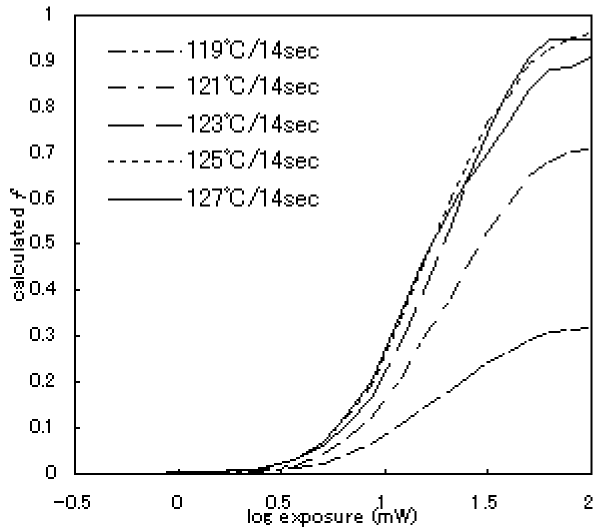

Figure 3. Calculated f when r was NOT optimum values.

Above f values are NOT correct. Because all samples are equal in the sensitivity and exposure condition, all lines should gather in almost one line. Since r is an only undecided parameter in the right hand side of equation (13), r-value should be fixed to gather the lines. This assumption is a key principle of our method. Following error function was defined for the optimum calculation of r.

$$\overline{D_i} = \frac{1}{n}\sum_{j=1}^{n} D_{i,j} \qquad Err = \sum_{j=1}^{n}\sum_{i=1}^{m}\left(D_{i,j} - \overline{D_i}\right)^2 \tag{14}$$

i : number of wedge, j: number of samples

Parameter r for each sample was adjusted to give minimum Err by Marquardt[5] method. Average of the calculated f for each sample was adopted as final value for f. Using these r and f, characteristic curves were calculated by equation (10).

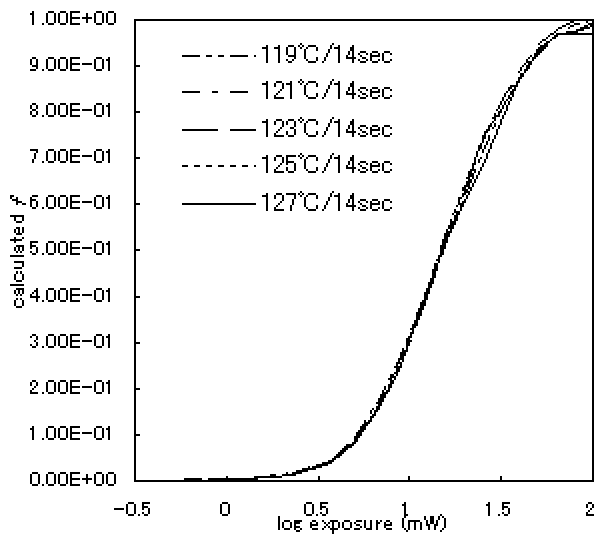

Figure 4. Calculated f of optimum r-values.

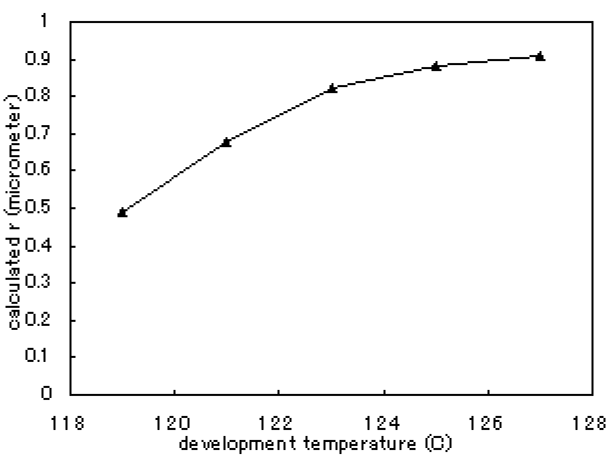

Figure 5. Calculated r vs. development temperature.

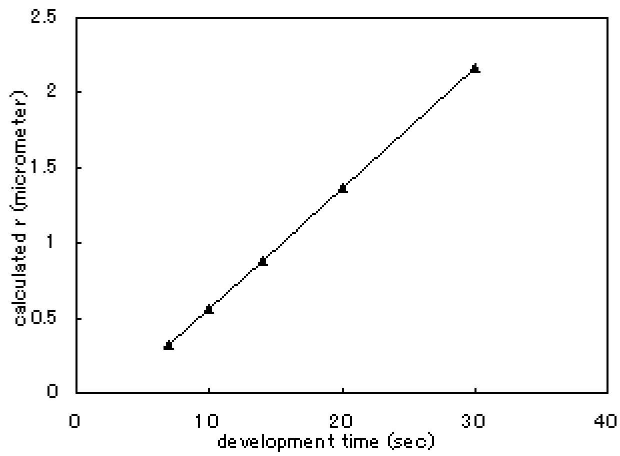

Figure 6. Calculated r vs. development time.

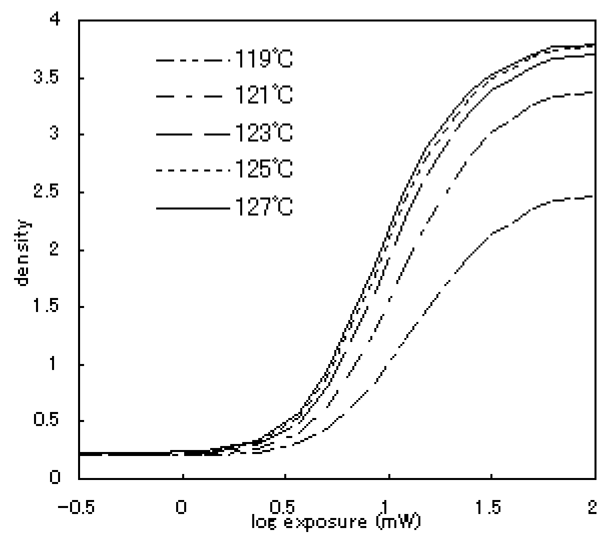

Figure 7. Calculated characteristic curves of various temperatures.

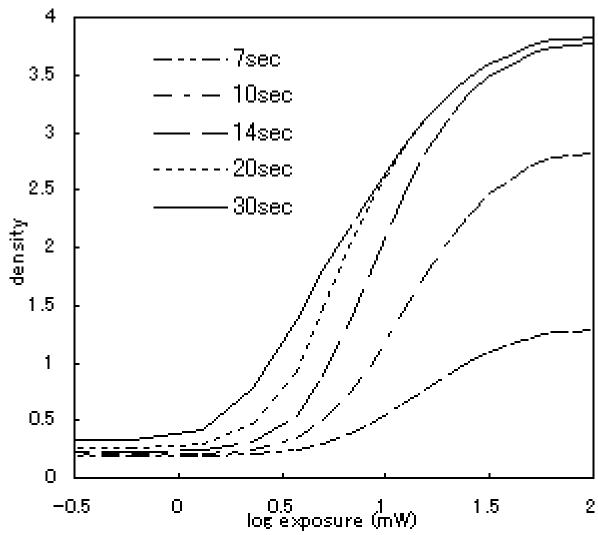

Figure 8. Calculated characteristic curves of various times.

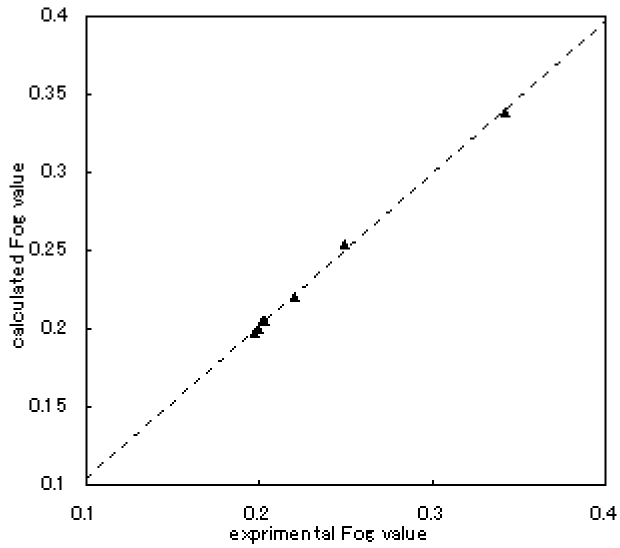

Figure 9. Experimental Fog vs. calculated Fog.

Discussion

Various figure of characteristic curves were explained on change of the *r* in equation (10) with common *f*. Parameter *f* is an intrinsic value of film, and it describes photo-sensitive character of the film. Fog was explained on minimum *f* value, which is above zero. Parameter *r, i.e.,* radius of sphere of influence varies with the condition of development.

It is noteworthy that linear relationship exits between the *r*-value and the development time in figure 6. It means that the diffusion rate of silver ion within sphere of influence isn't rate-determining step. The consumption rate of organic silver salts must be proportional to the square of *r*. It means that the development rate is proportional to the surface area of developed silver or sphere of influence.

In figure 6, the intercept of the plot to horizontal axis probably means heating time before the film temperature increased enough.

The increasing rate of r is a function of temperature. If once the function was defined exactly, the characteristic curve at the end of development with complicated history of temperature is calculable.

$$r'(temp) = \frac{dr}{dt} \qquad r = \int r'(temp(t))dt \tag{15}$$

$$D = h\,(f,\, r,\, C,\, W_{SH},\, Wss,\, L,\, A,\, T,\, d) \tag{10}$$

Conclusion

Change of characteristic curves with various development conditions was studied. And we found a new regression method for modified Hirano model. This method leads both photosensitive character and development degree from the experimental characteristic curves of several development conditions. Given parameters are useful for analysis of development rate. Once the parameters were defined, exact characteristic curves of any development conditions are calculable.

References

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Biography

Tsukasa Ito received his B.S. degree in Chemistry from the Tokyo Institute of Technology in 1982 and a Master in Chemistry from Tokyo Institute of Technology in 1984. Since 1984 he has worked in the Research and Development Center at Konica Corporation in Hino-shi, Tokyo. His work has primarily focused on the development process, including color negative film, photographic paper and photothermographic materials. He is a member of the Chemical Society of Japan.