

# A New Equation of Characteristic Curves of Photothermographic Material

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## Abstract

A new equation of photographic characteristic curves of photothermographic material was derived on the basis of Klosterboer-Rutledge model for thermal developing of the material. Three points were newly considered to improve the equation. 1.The equation for optical density is derived using Nutting equation from amount of developed silver. 2.The overlap of "sphere of influence" was correctly evaluated. 3.The calculation was extended to include the condition under which some silver halide grains are contained in a sphere of influence. The new equation succeeds in describing the results of Gisser's experiment on maximum density of the material. With using the equation, it became possible to simulate many features of photothermographic materials.

## Introduction

Photothermographic material consisting of silver halide grains and silver soap is commercially available and known as *Dry Silver*. Klosterboer and Rutledge proposed a model for thermal development of the material<sup>1</sup>. On the basis of the model they derived an equation of photographic characteristic curve for the material. The equation was experimentally examined by Gisser<sup>2</sup>. There was, however, a clear discrepancy between experimental and calculated values of maximum densities.

Although other equations have been recently proposed for the characteristic curve of the system<sup>3,4</sup>, they have not yet succeeded in reproducing correctly the optical density of the material.

In this paper we have re-examined the K-R equation and derived a new equation of the characteristic curve of the photothermographic material on the basis of Klosterboer - Rutledge model. The new equation has described the result of Gisser's experiment and has made it possible to simulate some features of the photothermo-graphic materials.

## Klosterboer-Rutledge model

The photothermographic material consists of silver halide

grains, silver soap (mainly silver behenate), chemical components such as developers and toners, and binder. Latent images are formed on the silver halide grains by optical exposure. The thermal development is physical, and silver ions for the development are supplied from silver behenate and reduced to developed silver. Silver halide itself is not assumed to be developed. As the development proceeds, silver ions of silver behenate around the developing center are consumed and there appears a region which does not contain silver behenate, and outside of which no silver ions is consumed(Fig.1). This region was named *sphere of influence* of the developing center.

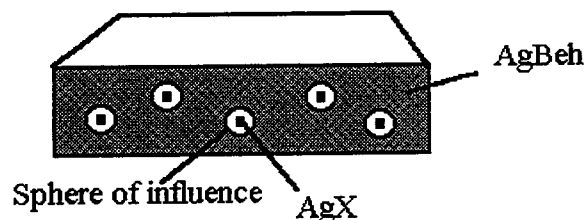


Fig.1 Schematic diagram of Klosterboer-Rutledge model

On the basis of this model, they derived an equation of the *optical density* of the system,

$$D = k \frac{W_{ss}}{(AT - N_0 L^3)} \left( \frac{4\pi}{3} r^3 - L^3 \right) N \quad (1)$$

where optical density is assumed to be proportional to the amount of developed silver with proportional constant  $k$ ,  $A$  is the area,  $T$  is thickness of the developed layer,  $N_0$  is number of silver halide grains contained,  $L^3$  is the volume of the silver halide grains (in this case cubic grain with edged length  $L$  is assumed),  $W_{ss}$  is coated amount of silver soap per unit area,  $r$  is radius of the sphere of influence, and  $N$  is number of silver halide grains developable. The second factor in the right-hand side of eq.(1) is a density of silver behenate ( $\rho_{ss}$ ) in the volume except that where silver halide is present. The third factor,  $(4\pi r^3/3 - L^3)$ , is the volume where silver ions of silver soap were consumed.

The number of silver halide grains developed,  $N$ , is given with using fraction of developable silver halide  $f$  by

$$N = fN_0 \quad (2)$$

and  $f$  is given by Silverstein's expression<sup>5)</sup>,

$$f = \sum_{p=M}^{\infty} q^p \left(\frac{e^{-q}}{p!}\right) = 1 - \sum_{p=0}^{M-1} q^p \left(\frac{e^{-q}}{p!}\right) \quad (3)$$

where  $q$  is number of photons absorbed by a grain,  $M$  is minimum number of photons necessary for producing developable latent image. Total number of silver halide grains coated,  $N_0$ , can be calculated by use of coated amount of silver halide,  $W_{SH}$ , and density of silver halide,  $d$ ,

$$N_0 = \frac{W_{SH}A}{dL^3} \quad (4).$$

### Discussions on K-R equation

In eq.(1), Klosterboer and Rutledge assumed that optical density was proportional to the amount of developed silver. It is well known, however, that when the covering power of developed silver is different, the optical density is different despite of the same amount of developed silver. So K-R equation is not available for the comparison between systems with different covering power. A simple way to take account of the difference of covering power is to use Nutting equation for the density, which is adaptable to optical density of black and white photosensitive material<sup>6)</sup>.

$$D = C_d Na / A \quad (5)$$

where  $C_d$  is constant (0.434 in a simple case),  $a$  is projected area of a developed silver.

Moreover, K-R equation does not consider the overlap of the spheres of influence. The equation can be adapted only to the case where the spheres of influence are isolated from each other. Although the spheres of influence were recognized to be isolated from each other in the low density region, they overlap with each other in high density region, especially in the maximum density region.

Klosterboer *did* refer to the overlap. They postulated that in the material such that all silver soap was developed at the maximum density, the volume of sphere of influence was limited to the value, (total volume of emulsion /number of AgX grains) at *any* density. This postulation was clearly incorrect.

Kong has pointed out this insufficiency of K-R equation<sup>4)</sup> and derived an improved equation for amount of developed silver. His consideration of the overlap was a little complicated. He took account of the overlap of *mass* of developed silver in the overlapped sphere of influence. In this report, we will simply consider the overlap of *volume* of the spheres of influence according to physical meaning of the sphere of influence.

Thirdly, we consider exclusion of silver soap by silver halide grains. Exclusion of silver soap by *developed* silver

halide at the center of the sphere of influence was correctly taken into account in K-R equation. However, we should also take account of exclusion of silver soap by *undeveloped* silver halide grains in the sphere of influence. This exclusion will become un-negligible if silver halide density in the material increases.

### Derivation of the new equation

#### Amount of developed silver

When number of silver halide grains become from  $N$  to  $N+dN$  (in the layer volume  $AT$ ), the total volume fraction of sphere of influence increases from  $V$  to  $V+dV$ ,

$$dV = \frac{4\pi r^3}{3AT} (1-V)dN \quad (6)$$

where  $(1-V)$  is a probability that the newly added volume of sphere of influence does *not* overlap with other spheres of influence. Eq.(6) is integrated

$$\int_0^V \frac{dV}{1-V} = \int_0^N \frac{4\pi r^3}{3AT} dN \quad (7)$$

and we obtain

$$V = 1 - \exp\left(-\frac{4\pi r^3}{3AT} N\right) \quad (8).$$

We can calculate amount of developed silver  $M$  from

$$M = \rho_{ss} (ATV - \text{volume of AgX in the sphere of influence}) \quad (9)$$

where  $\rho_{ss}$  is the density of silver soap in the layer except that where silver halide grains are present;

$$\rho_{ss} = \frac{W_{ss}A}{[AT - N_0L^3]} \quad (10).$$

Volume of AgX in the sphere of influence is the sum of the volume of *developed* AgX at the center of the sphere of influence and the volume of *undeveloped* AgX contained in the sphere of influence. The number of the latter grains is  $N_0 - N$  in the volume considered, and they distribute homogeneously in the volume where developed AgX grains are not present. Thus the density of these undeveloped AgX is

$$\frac{N_0 - N}{AT - NL^3} \quad (11)$$

and they distribute within the volume of

$$ATV - NL^3 \quad (12).$$

Therefore, also taking account of the volume of developed AgX at the center, eq.(9) becomes,

Table I Parameters used in the calculations

	area A m <sup>2</sup>	thick.T μm	radius of SoI r μm	coated Ag W <sub>ar</sub> g/m <sup>2</sup>	AgX size L μm	min. photon M	coated SS* W <sub>ss</sub> g/m <sup>2</sup>
Fig.3	1	10	0.5	0.2	0.08	10	1
Fig.4	1	10	var,	0.05	0.06/0.1	3	1

$$M = \rho_{ss} \left\{ AT \left[ 1 - \exp \left( - \frac{4\pi}{3} \frac{r^3}{AT} N \right) \right] - NL^3 \right\} \left( \frac{AT - N_0 L^3}{AT - NL^3} \right) \quad (13)$$

In the limit that all spheres are isolated  $(4\pi^3/3)N \ll AT$  and that silver halide grains are sparse  $(AT \gg N_0 L^3 > NL^3)$ , eq.(13) gives the same equation as K-R equation (1);

$$M(\text{low density}) \approx \rho_{ss} \left\{ \frac{4\pi}{3} r^3 N - NL^3 \right\}$$

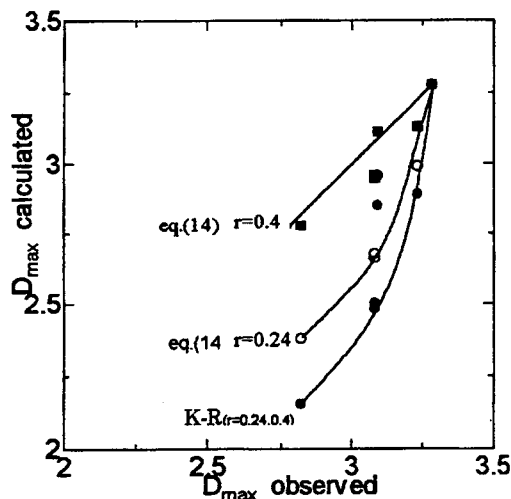


Fig.2 Comparison of calculated  $D_{max}$  with Gisser's experimental  $D_{max}$ . K-R equation (solid circle), eq.(14) with  $r=0.24$  (open circle) and  $r=0.4$  (solid square)

### Optical density

The simple way to convert the amount of developed silver, M, to the optical density, D, is to use Nutting equation (5). The amount of developed silver per a sphere of influence is given by eq.(13) divided by N. The projection area  $a$  of the developed silver is proportional to square of cube-root of the volume of the developed silver. This volume is proportional to the amount of developed silver. Thus, using eq. (5), we obtain

$$D = C \left\{ \rho_{ss} \left\{ AT \left[ 1 - \exp \left( - \frac{4\pi}{3} \frac{r^3}{AT} N \right) \right] - NL^3 \right\} \left( \frac{AT - N_0 L^3}{AT - NL^3} \right) \right\}^{\frac{1}{3}} \frac{1}{A} \quad (14)$$

where  $c$  is constant. If we take constant in Nutting equation as 0.434 and the developed silver forms dense sphere, constant  $c$  becomes  $0.434 \times 4\pi(3/4\pi)^{2/3}$ .

[ 10<sup>6</sup>]

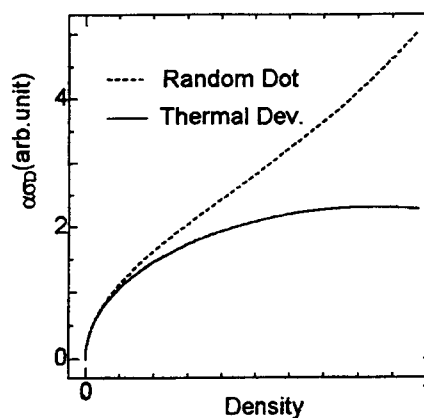


Figure 3. Comparison of granularity. Random dot model (dot) and photothermographic material (solid).

### Comparison of $D_{max}$ with experiments

Gisser<sup>2)</sup> observed maximum densities and sensitivities of photothermographic materials with different amounts of coated silver for two sizes of silver halide grains. In Fig. 2 we compared her data with values calculated from the K-R equation and the equation (14). Numerical factors were normalized to the point of  $D_{max}=3.28$  for both equations. K-R equation gave the same maximum density in spite of different radius of sphere of influence. As is already described, the equation is inadequate to estimate maximum density because there are overlapping of the spheres of influence in her experiments. Calculation with different radius of the sphere of influence,  $r$ , in equation (14) are shown in Fig.2. The values with the radius of  $0.4\mu\text{m}$  were in good agreement with those of experiments. This radius was the typically observed radius of sphere of influence in the developed photothermographic materials<sup>1)</sup>. Therefore, new equation (14) describes correct maximum densities of the photothermographic materials.

### Applications

One important application of equation (14) is estimation of granularity. Random dot model is known to describe well

the granularity of black and white photosensitive material<sup>7</sup>. If  $aN/A \ll 1$ , then granularity is given by

$$\alpha^{1/2} \sigma_D = 0.434a(N/A)^{1/2} \quad (15).$$

In the ideal black and white conventional material with monodisperse developed silver, projection area  $a$  is constant all over the layer. In the case of photothermographic material,  $a$  varies with density. Namely, the size of developed silver decreases with increasing the degree of the overlap of the spheres of influence. Thus granularity is smaller in higher densities. On the basis of eq.(15), granularity of photothermographic material is given from eq.(15) by

$$\alpha^{1/2} \sigma_D = c' \left[ \rho_{ss} \left\{ AT \left[ 1 - \exp \left( - \frac{4\pi r^3 N}{3 AT} \right) \right] - NL^3 \right\} \left( \frac{AT - N_0 L^3}{AT - NL^3} \right) \right]^{2/3} N^{1/6} \quad (16).$$

In Fig.3, granularity with eq.(16) is compared with that with random dot model. Parameters used in the calculation are listed in Table I.

The second application of eq.(14) is to the thermal developing process. As the thermal developing proceeds, the radius of the spheres of influence along with density increases. This behavior can be simulated as a function of  $r$  in Fig.4 for tow sizes of silver halide grains with the same amount of silver halide coated. As the development proceeds, maximum density is attained where all silver soap is consumed, and density elsewhere continues to increase. The number of development centers and therefore the rate of development increases with decreasing the size of silver halide grains.

### Conclusion

The new equation for characteristic curves of photothermographic materials, which consist of silver halide grains and silver soap, has been obtained by taking account of

1. optical density by using with Nutting equation
2. overlap of spheres of influence.
3. the exclusion of silver soap by silver halide grains.

The equation predicts correctly Gisser's experimental data of maximum density. The equation is applicable to simulate many features of the system, e.g. granularity, covering power and developing process in photothermographic materials.

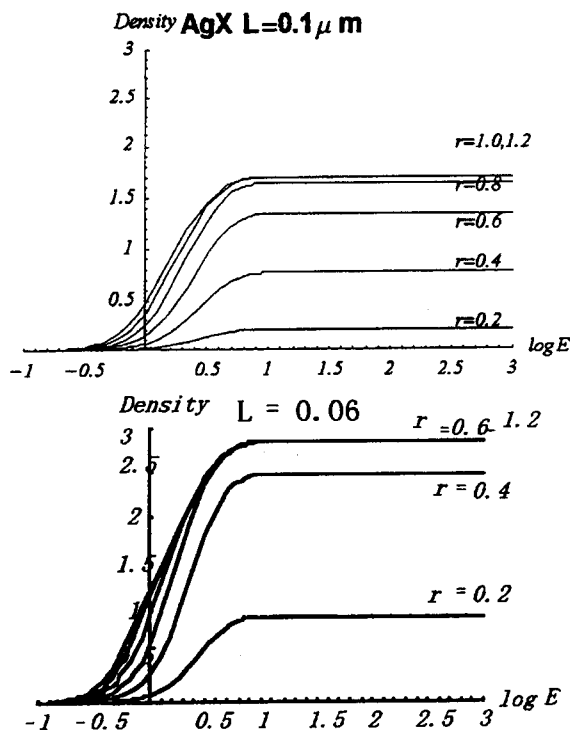


Fig.4 Calculated characteristic curves of photothermographic materials for two sizes of silver halide grains(0.06μm and 0.1μm). As a function of radius of sphere of influence, r.

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