

Influence of the rate of photographic development process on the edge effects

BOGUMIŁ RAJKOWSKI

Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland.

In the paper, the results of simulation examinations of the dependence of both intensity and direction of edge effects on the rate of the photographic development process are presented. In the examination a model of the development process was applied taking account of the kinetic equation of the chemical reaction as well as the diffusion equation. Four most important cases occurring during selective reduction of the silver ions taking place in the development process have been analyzed.

1. Introduction

Considering equations of the kinetics of chemical reactions taking place during photographic development and analyzing the diffusion equations for substrates and products of these reactions in a swelled light-sensitive layer at least four different courses of the development process can be distinguished:

- development process is limited only by the kinetics of reduction reaction of the silver halide,
- development process is limited by the diffusion rate of the developing agent in the swelled light-sensitive layer,
- development process is limited by the diffusion rate of both the developing agent and the development reaction products of properties inhibiting this process,
- development process is limited by the diffusion rate of both the developing agent and the development reaction products of properties accelerating this process.

We deal with the first case when the circulation of the developer solution is sufficiently strong while the light-sensitive layer is thin to such a degree that the differences in concentrations of the developing agent and the products of development reaction observed between the layer and the developer solution are balanced in an infinitely short time. Under these circumstances no differences in concentrations of the developing agent and the products of development reaction occur at the border of differently exposed fields. Then, this way of chemical processing is recognized as a development process taking place without contribution of the edge effects.

The second case takes place when the products of the silver ion reduction have no influence on the kinetic of development process. The gradient of the developing agent

concentration occurring during the development at the border between differently exposed fields is responsible for creation of edge effects connected with the due inhibition of the development process.

In the third case the intensity of edge effect occurrence increases since the products of the silver ion reduction reaction inhibit the development process.

The fourth case refers to the situation in which the products of the reducing reaction are accelerators of the development process. Then edge effects may occur the direction of which is consistent with the direction of effects connected with the acceleration of the development process.

2. Model examinations

In order to analyse the influence of the development method on the profile of the spatial distribution of density at the border of differently exposed fields some calculations based on the diffusion model were performed; the details of the latter being described in the works [1], [2]. In this model, the instantaneous concentrations of the developing agent, the concentration of one of the products of silver ion reaction and that of the metallic silver at a definite place of the developed light-sensitive layer are determined by the following equations:

$$c_{i,j+1} = c_{i,j} + \frac{D_c \Delta t}{(\Delta x)^2} (c_{i-1,j} - 2c_{i,j} + c_{i+1,j}) + \frac{D_c \pi^2 \Delta t}{4h^2} (c_0 - c_{i,j}) - m_1 (c_{Ag_{i,j+1}} - c_{Ag_{i,j}}), \quad (1)$$

$$c_{p_{i,j+1}} = c_{p_{i,j}} + \frac{D_p \Delta t}{(\Delta x)^2} (c_{p_{i-1,j}} - 2c_{p_{i,j}} + c_{p_{i+1,j}}) + \frac{D_p \pi^2 \Delta t}{4h^2} c_{p_{i,j}} + m_2 (c_{Ag_{i,j+1}} - c_{Ag_{i,j}}), \quad (2)$$

$$c_{Ag_{i,j+1}} = c_{Ag_{i,j}} + k_1 (c_{i,j} + k_2 c_{p_{i,j}}) (c_{Ag_{\infty}} - c_{Ag_{i,j}}) \Delta t, \quad (3)$$

where: c_0 – concentration of developing agent in the developer solution [mole/m³], c – instantaneous concentration of the developing agent in the light-sensitive layer [mole/m³], c_p – instantaneous concentration of the development products in the light-sensitive layer [mole/m³], $c_{Ag_{\infty}}$ – molar concentration of silver obtained after an infinitely long development time [mole/m³], c_{Ag} – concentration of silver obtained after time t [mole/m³], k_1 – reaction rate constant, k_2 – constant determining the efficiency of the reaction products of silver ion reduction as far as change of the

effective concentration of the developing agent is concerned, m_1 – constant determining the number of moles of the developing agent necessary to produce one mole of metallic silver, m_2 – constant determining the number of moles of the products of silver ion reduction reaction which are reduced during production of one mole of metallic silver, D_c – diffusion coefficient for the developing agent [m^2/s], D_p – diffusion coefficient for the product of silver ion reduction reaction [m^2/s], h – thickness of the light-sensitive layer, Δt – elementary time interval of the development process [3], i – index denoting the changes in the direction of x axis, j – index denoting the time changes.

The changes of the spatial distribution of the reduced silver as a function of development duration for the case where development is limited by the kinetics of silver halide reduction reaction were determined from Eq. (3) in which, in place of the instantaneous concentration c of the developing agent, the concentration of the developing agent in the developer solution c_0 was substituted. The concentration of the development product c_p in the light-sensitive layer during the whole process has been assumed to be equal to zero. Since for this type of development process the diffusion rates of the developing agent and the product of development are infinitely great, Eqs. (1) and (2) have been neglected in calculations. For the remaining cases of development Eqs. (1)–(3) have been applied in unchanged form.

Taking account of the data available in the literature [3]–[5] and the results of our own investigation [2] the following values of the initial parameters have been assumed:

- surface silver concentration obtained after infinitely long development time on the faintly exposed field ($M_{1,\infty} = 0.5 \text{ [g/m}^2\text{]}$),
- surface silver concentration obtained after infinitely long development on the strongly exposed field ($M_{2,\infty} = 1.5 \text{ [g/m}^2\text{]}$),
- developing agent concentration in the developer solution ($c_0 = 5 \times 10^3 \text{ [g/m}^3\text{]}$),
- reaction rate constant ($k_1 = 1 \times 10^{-5} \text{ [m}^3\text{g}^{-1}\text{s}^{-1}\text{]}$),
- elementary time interval of the development process ($\Delta t = 4.9 \times 10^{-3} \text{ [s]}$),
- thickness of the developed light-sensitive layer ($h = 1 \times 10^{-4} \text{ [m]}$),
- elementary length of a fragment of the light-sensitive layer subjected to the development process ($\Delta x = 8 \times 10^{-7} \text{ [m]}$),
- elementary width of a fragment of the light-sensitive layer subjected to the development process ($\Delta y = 8 \times 10^{-7} \text{ [m]}$),
- diffusion coefficient of the developing agent in the swelled light-sensitive layer ($D_c = 5.2 \times 10^3 \text{ [g/m}^3\text{]}$),
- diffusion coefficient of the developing reaction product in the swelled light-sensitive layer ($D_p = 5.2 \times 10^3 \text{ [g/m}^3\text{]}$).

The value of constant k_2 defining the capability of the development reaction product to change the effective concentration of the developing agent was chosen from the range -0.5 to 2.0 while the positive value of the constant indicates the acceleration

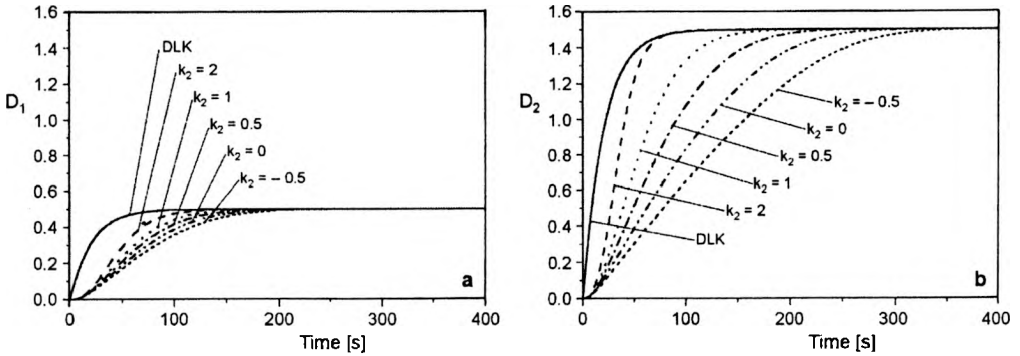


Fig. 1. Influence of both duration and the way of development on the increment of the density determined outside the range of edge effects on the faintly exposed field (a) and strongly exposed field (b). The solid line represents the course of the changes determined for the development process limited only to the kinetics of the silver halide reducing reaction. The remaining lines mark the courses of changes determined for the development process limited by the diffusion of reagents in the exposed light-sensitive layer.

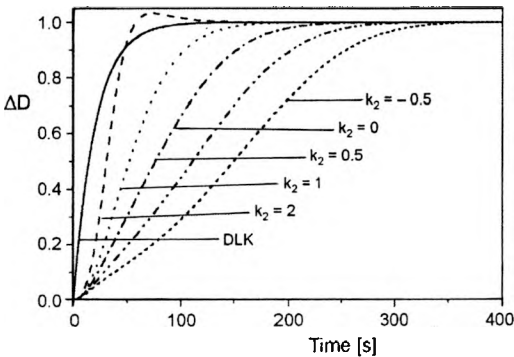


Fig. 2. Influence of time and the way of development on the course of the changes in density difference between the strongly exposed and faintly exposed fields, respectively, determined outside the range of edge effects. The solid line shows the course of changes determined for the development process limited only by the kinetics of the silver halide reduction. The other lines represent the course of changes for the development limited by the diffusion of reagents in the exposed light-sensitive layer.

of the development process while its negative value speaks for inhibition of that process. In this way a set of edge functions was obtained representing the spatial distribution of the density for chosen ways of photographic development.

The obtained results of the changes in parameters of the edge function as a function of development process duration are illustrated in Figs. 1–3. Figure 1 presents the changes of respective density in the bright and the dark fields D_1 and D_2 in the image determined outside the range of edge effects, while Fig. 2 presents the changes in the value of the density difference ΔD in both fields. Different ways of performing the photographic development process determined by the magnitude of the constant k_2 are denoted by corresponding kinds of curves while the changes of the edge function

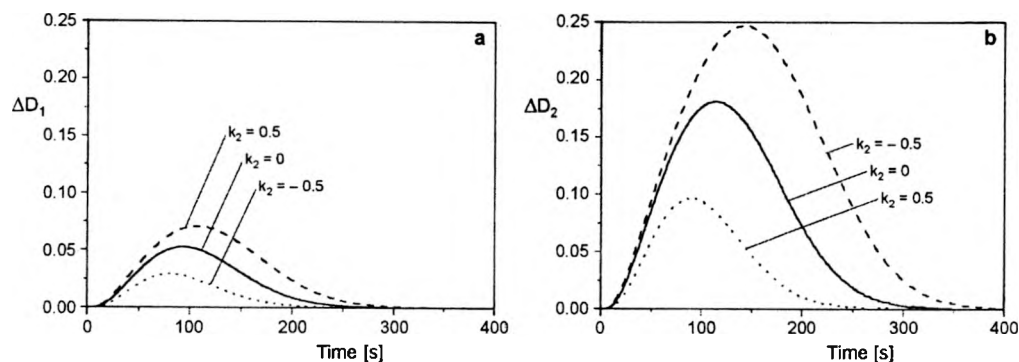


Fig. 3. Influence of the development process duration on the intensity of edge effect action which is expressed as a difference in the density ΔD_1 determined in the lower part of the edge function (a) and a difference in density ΔD_2 determined in the upper part of the edge function (b).

parameters for the case of the development process limited only by the rate of silver ion reduction reaction are denoted by a solid line (marked by DLK – development limited by kinetics). In Figure 3, changes in the intensity of edge effects versus development process duration are illustrated, with the intensity of those effects being expressed in terms of the density difference ΔD_1 in the bright image field and ΔD_2 in the dark image field, respectively. These dependences are determined for three values of the constant k_2 responsible for the course of the photographic development process. For positive values of the constant k_2 the development reaction product increases the effective concentration of the developing agent while its negative value indicates diminishing of the developing agent concentration. The zero value of k_2 denotes lack of chemical activity of the development product.

3. Discussion of results

Assuming constant concentration of developing agent in the developer solution the course of changes in the image field density depends only on the exposure of this field when development is limited merely by the rate of silver ion reduction. The intensity of development increases with the exposure level of the field being developed within which the used substance is immediately replaced with the fresh one. In such an ideal case the strongly exposed field is developed in a shorter time (see Fig. 1b) than the faintly exposed one (Fig. 1a).

In the process of photographic development that is limited by the diffusion rate of reagents inside the swelled light-sensitive layer one can distinguish three principal stages. In the first stage, the developing agent starts to diffuse from the developer solution to the inside of the light-sensitive layer being subjected to chemical processing. Due to the low concentration of the developing agent in the photographic layer the development in its initial stage proceeds very slowly. This is demonstrated by the concave part of the dependences illustrated in Figs. 1 and 2 in the range of very

short duration times of the development process (about 10 s). The duration of the first stage of the development process depends on the diffusion rate of developing agent inside the photographic layer. In the second stage, some state of balance between the processes of the wearing away of developing agent in the light-sensitive layer and the diffusion of the fresh substance from the developer solution is established. Since the rate of diffusion of the developing agent deep into the layer is limited, a shortage of developing agent occurs above certain concentrations of the exposed crystals of silver halide capable of being reduced. These phenomena are the reason for local inhibition of the development process. In the final stage of development, when the concentration of the exposed silver halide is relatively small the rate of the development process becomes slower. Then, the concentration of the developing agent increases in the layer since the gradient of its diffusion from the developer solution deep inside the layer is greater than that following from the consumption of this substance under conditions of slowly proceeding reducing reaction of the silver ions in the final stage of development. It can be stated that the difference in concentration of the developed light-sensitive layer and the developer solution diminishes to zero. As a result of the phenomena that follow the scheme described above, the image fields of high exposure level need more development time (Fig. 1b) compared to the fields faintly exposed (Fig. 1a).

During the exposure limited by the diffusion rate of developing agent inside the swelled layer at the border between the differently exposed fields, edge effects occur connected with the inhibition of the development. The intensity of these effects increases during some time interval reaching its maximum at some point after which it weakens down to a complete decay. The course of these changes is illustrated in Fig. 3. The intensity distribution of edge effects is different on the faintly exposed field adjacent to a strongly exposed field (fringe effect) from that observed on a strongly exposed field adjacent to a faintly exposed one (border effect). The maximum of the intensity of adjacent effects (Fig. 3b) appears for longer times of the development with respect to the time the maximum of the intensity of fringe effect is recorded (Fig. 3a). If the reaction products are inhibitors of the development process their action is equivalent to diminishing the effective concentration of developing agent in a definite place of the light-sensitive layer being developed. Also, the gradient of the effective concentration of developing agent at the border between the differently exposed fields increases which results in intensifying the edge effects. The course of those changes is illustrated by dependences determined for $k_2 = -0.5$ and shown in the form of corresponding plots in Figs. 3a and b.

If the products of silver ion reduction have the properties accelerating the development process a situation corresponding to the increase of effective concentration of the developing agent in a definite place on the light-sensitive layer takes place due to which the gradient of concentration of this substance at the border between the differently exposed fields is diminished. This results in diminishing the intensity of edge effects connected with inhibition of the development process. These

changes are illustrated by two plots in Figs. 3, where the dependences determined for $k_2 = 0.5$ are presented.

The total decay of edge effects connected with the inhibition of development occurs when accelerator of the development process appear in such an amount which completely compensates the losses in effective concentration of the developing agent following from its consumption during the silver ion reduction. Such a situation takes place when the constants m_1 and m_2 being the numbers of moles of developing agent and the active product of the development reaction are equal to each other and the constant k_2 expressing the activity of the product of this reaction is equal to unity. In this case, the development proceeds in a way similar to that of the process limited exclusively by the rate of silver ion reduction. The further increase of the accelerator reactivity in the development process (increase of constant k_2) leads to the situation in which the effective concentration of the developing agent in the strongly exposed field becomes higher than on the field exposed faintly. This, in turn, leads to an increase of the difference in the development rate between the strongly exposed field and faintly exposed one. In such a case the direction of the edge effects suffers from a change, *i.e.*, there appear some edge effects connected with the acceleration of development process.

In the final stage of the photographic development process, a significant increment in spatial contrast is observed between the image and its background. These changes are illustrated in Fig. 2 by a dependence of the density difference ΔD in dark and bright fields, respectively, determined as a function of development duration for $k_2 = 2$. In the final phase of the photographic development process, when the strongly exposed field achieves its maximal optical density, a slow decay of increasing the spatial contrast appears which stops completely at the moment of achieving the maximal density in the bright field of the image.

Acknowledgements – This work was supported by the grant No. 341992 of the Faculty of Chemistry, Wrocław University of Technology, Poland.

References

- [1] RAJKOWSKI B., NOWAK P., *Opt. Appl.* **31** (2001), 489.
- [2] RAJKOWSKI B., *Investigations of edge effects, as a factors affecting the acutance in the silver halide materials for image information recording* (in Polish), TINTA, Wrocław 2001.
- [3] NAGAO K., [In] *Symposium on Image Analysis and Evaluation*, Toronto 1976, p. 64.
- [4] FRIESER H., PFLUGBEIL M., *Z. Angew. Phys.* **22** (1967), 336.
- [5] FRIESER H., *Photographische Informationsaufzeichnung*, The Focal Proces, London and New York, 1975, Chapt. 3.

Received November 19, 2001