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Modelling of edge effects taking account of the diffusion phenomenon

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In this paper, the results of simulation model examination of the occurrence intensity of edge effects as dependent on: time, reaction rate constant, substrate and product concentration, layer thickness and exposure intensity are presented. For that purpose, a model development process was applied, taking account of the kinetic reaction equation as well as the diffusion equation. The results obtained are represented in the form of three-dimensional plots where the intensity of edge effect occurrence is shown as a function of two variables.

1. Introduction

In the course of the photographic development process at a border of neighbouring fields of different exposures a gradient of both developing substance and that of reaction product occurs. This results from the different speed of developing the fields of different exposure. The speed of silver production is described by the kinetic equation [1]

$$\frac{\partial C_{Ag}}{\partial t} = k_1(C-k_2)(C_{Ag\infty}-C_{Ag}) \tag{1}$$

where: C_{Ag} – molar concentration of silver after time t [mol/m^3], $C_{Ag\infty}$ – molar concentration of silver after infinitely long developing time [mol/m^3], k_1 – reaction rate constant [m^{3}g^{-1}s^{-1}], k_2 – constant defining the effectiveness of reaction products in order to reduce the effective concentration of the developer (inhibiting the development process), C – molar concentration of developing agent after time t [mol/m^3], P – molar concentration of the developing reaction product obtained after time t [mol/m^3].

In the places of high exposure the developing reaction runs much quicker than that in the low exposure places. Therefore, the concentration of the developing agent falls down much quicker in the fields of stronger irradiation while the concentration of developing reaction products increases. If the field exposed to strong irradiation borders on a field of low irradiation, the gradient of concentration appearing during the development leads to the diffusion of the developing agent

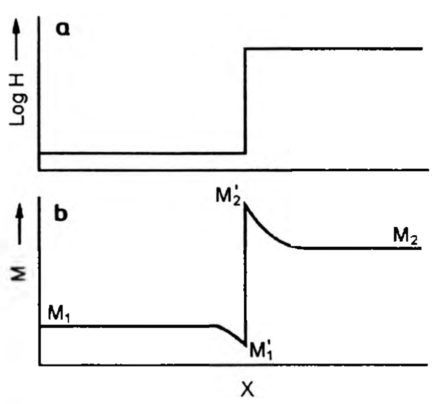

Fig. 1. Spatial distribution of the exposure (a) and spatial distribution of the mass of the appearing silver (b) expressed in grams per unit area. In figure b, the criteria of selection of minimal M'_1 and maximal M'_2 quantities of silver developed respectively on the low irradiated and high irradiated fields as well as the quantity of silver obtained outside the range of operation of the edge effects (M_1 and M_2 are shown. The quantities determined are essential for calculating the indicator of intensity of edge effects.

from the field of low exposure to the high exposure field and to the diffusion of the developing reaction products in the opposite direction. As a result of these processes the silver image appearing in the high exposure regions bordering on the low exposure regions becomes enhanced, as it is shown in Fig. 1. On the other hand, the image appearing in the low exposure regions bordering on the high exposure regions becomes weaker. In the literature these effects are called edge effects [2]. The intensity of such effects increases if the products of developing reaction have strong features inhibiting the developing process. The local increment of contrast caused by the edge effects is interpreted by the human eye as an increment of acutance of the image. In other words, by increasing the intensity of the edge effects the acutance in the photographic image can be strengthened to a high degree [2].

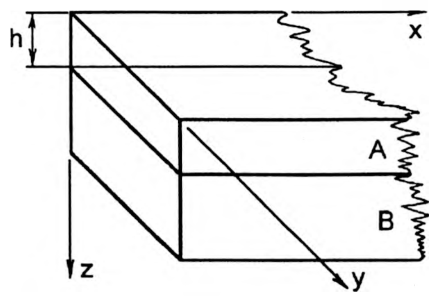

Fig. 2. Coordinate system used in formation of diffusion equations, A — light sensitive layer, B — base, h — layer thickness.

As was mentioned earlier the diffusion phenomenon in the photographic layer is responsible for the appearance of edge effects which can be considered in a three-dimensional coordinate system [3], shown in Fig. 2. In accordance with the diffusion equation the concentration of the developing substance in given place of the photographic layer in the definite time t is [1], [3], [4]

$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 C}{\partial x^2} + D_c \frac{\partial^2 C}{\partial y^2} + D_c \frac{\partial^2 C}{\partial z^2} - m_1 \frac{\partial C_{\mathrm{Ag}}}{\partial t} \tag{2}$$

where: C – molar concentration of the developing agent in a definite place (x, y, z) after time t [mol/m^3], D_c – diffusion coefficient of the developing substance [m^2/s], m_1 – constant defining the number of moles of the developing agent required to produce one mole of the metallic silver.

In an analogous way the concentration of the reaction products at a given point can be described by the equation

$$\frac{\partial P}{\partial t} = D_p \frac{\partial^2 P}{\partial x^2} + D_p \frac{\partial^2 P}{\partial y^2} + D_p \frac{\partial^2 P}{\partial z^2} + m_2 \frac{\partial C_{\mathrm{Ag}}}{\partial t} \tag{3}$$

where: P – molar concentration of the developing reaction product in a definite place (x, y, z) obtained after some time t [mol/m^3], D_p – diffusion coefficient of the developing reaction product [m^2/s], m_2 – constant defining the number of moles of the developing reaction product which are liberated during creation of one mole of metallic silver.

The second derivatives of the concentration in the directions x and y corresponded to the diffusion stream inside the layer. On the other hand, the second derivative of concentration in the z direction corresponds to the exchange of components between the light sensitive layer and the developer solution.

Changes in the acutances caused by the edge effects can be expressed in the form of an indicator of the relative edge enhancement designated as REE (relative edge enhancement) [5]. The value of REE is determined from the equation

$$\mathrm{REE} = \frac{(M'_2 - M'_1) - (M_2 - M_1)}{M_2 - M_1} \tag{4}$$

where: M_1 – average quantity of the developed silver (mass per unit area) determined outside the range of edge effect operation in the low exposure field [g/m^2], M'_1 – minimal quantity of the developed silver determined within the range of the edge effect operation in the low exposure field [g/m^2], M_2 – average quantity of the developed silver (mass per unit area) determined outside the range of edge effect operation in the high exposure field [g/m^2], M'_2 – maximal quantity of the developed silver determined within the range of the edge effect operation on the high exposure field [g/m^2].

2. Characteristic of the model

An irreplaceable tool in the theoretical examinations of the appearance of edge effects and their influence on the quality of the photographic image are investigations of theoretical model. They can be classified into two groups. The first one is the group of empirical models in which the chemical spread function is used to describe the phenomena occurring during development [6]–[17]. The other group is composed of so called diffusion models, which exploit the diffusion equations and equations of chemical reactions occurring during the developing process [1], [18]–[22]. The diffusion models can be divided into two groups differing in the approach to the solution of the diffusion equation. The first group comprises models in which the diffusion equation is solved analytically [18], [19], while the other group is formed by models solved numerically [1], [20]–[22].

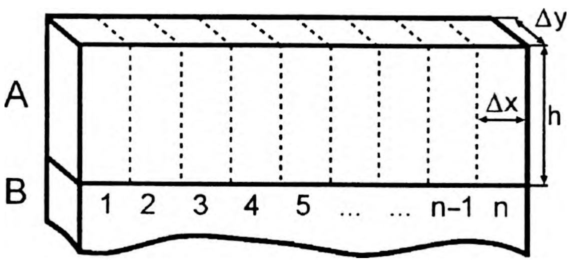

Fig. 3. Scheme of the photographic material structure applied in the diffusion model A – light sensitive layer, B – base.

For our calculations the last of the above mentioned types of models was applied. The light sensitive layer is divided into an equal fragments of length Δx, width Δy and height h. The exchange of both the developer components and the reaction products occurs along the layer and between the layer and the solution in the z-direction (Fig. 3). In this model the following assumption have been accepted:

– only diffusion of the developing agent and one product of developing reaction are taken into account,

– gradient of the developing agent concentration and that of the reaction product in the y-direction is equal to zero,

– developing agent concentration and that of the developing reaction product in the z-direction are averaged,

– laminar layer between the light sensitive layer and the developer solution is infinitesimally thin, which means that there exist a strong circulation of the solution during developing.

Thus, the instantaneous concentration of the developing agent in definite place of the layer is determined from the following equation, while the above assumptions are taken into account:

$$C_{i,j+1} = C_{i,j} + \frac{D_c \Delta t}{(\Delta x)^2}(C_{i-1,j} - 2C_{i,j} + C_{i+1,j})$$
$$+\frac{D_c}{4h^2}(C_0 - C_{i,j}) - m_1(C_{Agi,j+1} - C_{Agi,j}) \tag{5}$$

where: C_0 – developing agent concentration in the developer solution [mol/m^3], C – instantaneous concentration of the developing agent in the layer [mol/m^3], D_C – diffusion coefficient for the developing substance [m^2/s], h – thickness of the light sensitive layer [m], Δt – developing time interval [s], i – index denoting changes in the x-direction, j – index denoting changes in time.

In an analogous way the equation for the product of developing reaction can be written

$$P_{i,j-1} = P_{i,j} + \frac{D_p \Delta t}{(\Delta x)^2}(P_{i-1,j} - 2P_{i,j} + P_{i+1,j})$$
$$-\frac{D_p}{2h^2} P_{i,j} + m_2(C_{Agi,j+1} - C_{Agi,j}) \tag{6}$$

where P denotes the instantaneous concentration of the development product in the layer.

Instantaneous concentration of the metallic silver occurring during development time in a given place is determined from the equation

$$C_{Agi,j+1} = C_{Agi,j} + k(C_{i,j} - P_{i,j})(C_{Ag\infty i} + C_{Agi,j})\Delta t. \tag{7}$$

3. Results

Based on the present model the examinations of the changes in intensity of edge effect occurrence at the border of two differently irradiated fields were carried out. The development time has been restricted to two hundred seconds since after this time no essential changes in the intensity of the edge effect occurrence appear. As the measure of intensity of edge effect the value of the relative indicator of relative edge enhancement was chosen. The calculations were performed considering the dependence of the edge effect intensity on the following parameters:

– developing time t,
– surface concentration of the developed silver M,
– thickness of the wet light sensitive layer h,
– concentration of the developing agent in the developer C_0,
– value of the constant rate of the developing reaction k_1,
– degree of inhibiting the developing process by the products of reaction k_2,
– value of the diffusion coefficient for the developing reaction in the layer D_p.

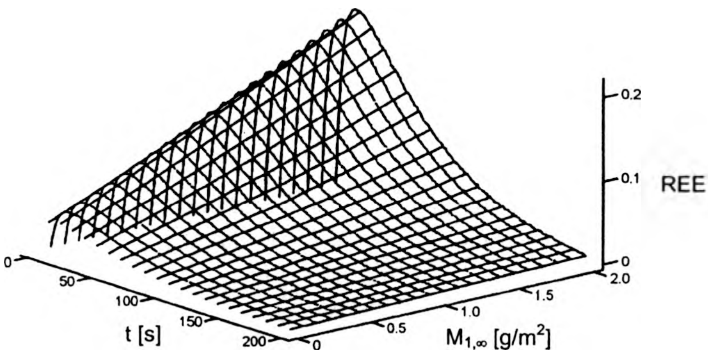

Fig. 4. Changes in intensity of the edge effect determined as a function of both developing time and the surface silver concentration in the field of low exposure. The difference in the silver concentration between the fields of high and low exposures, respectively, is equal to unity ($M_{2,\infty} - M_{1,\infty} = 1$). The symbol ∞ means the quantity of silver obtained after the infinitely long time developing.

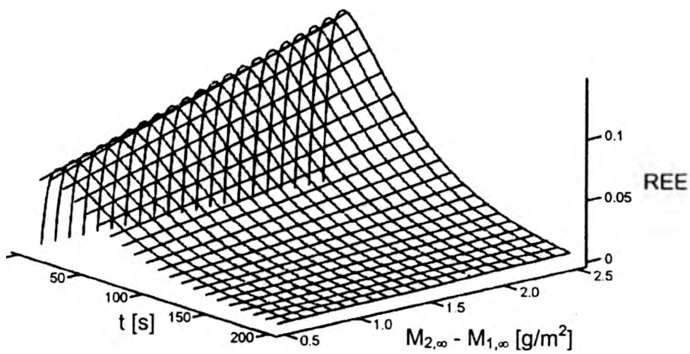

Fig. 5. Changes in intensity of the edge effect determined as a function of both developing time and the difference in the surface silver concentration in the fields of high and low exposures, respectively. The value of the surface concentration $M_{1,\infty}$ is constant and amounts to 0.5 [g/m²]. The symbol ∞ means the quantity of silver obtained after the infinitely long developing time.

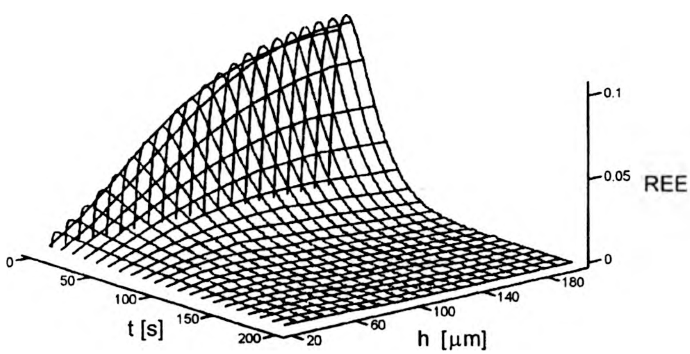

Fig. 6. Changes in intensity of the edge effect determined as a function of both developing time and the thickness of developed layer.

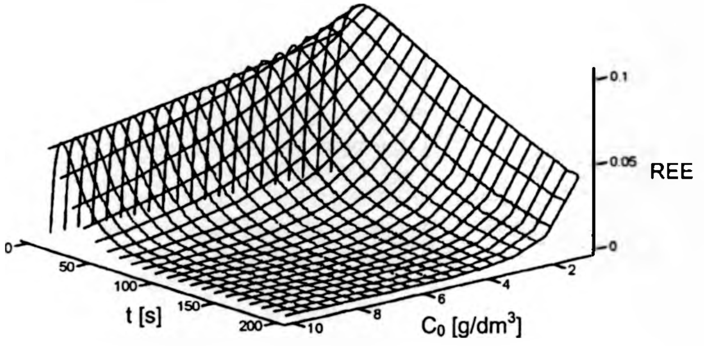

Fig. 7. Changes in intensity of the edge effect determined as a function of both developing time and initial concentration of the developing agent in the developer solution.

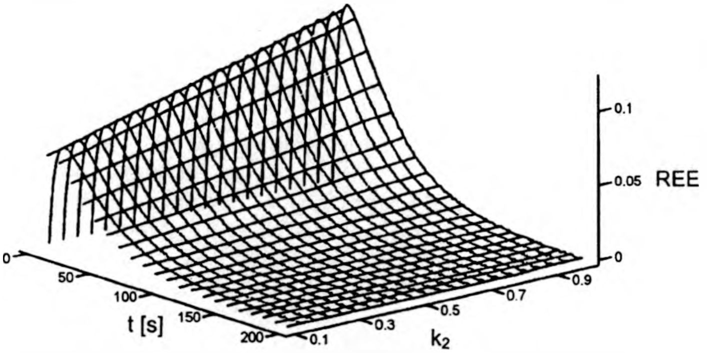

Fig. 8. Changes in intensity of the edge effect determined as a function of both developing time and changes of coefficient k_2 defining capability of reaction product inhibiting the developing process.

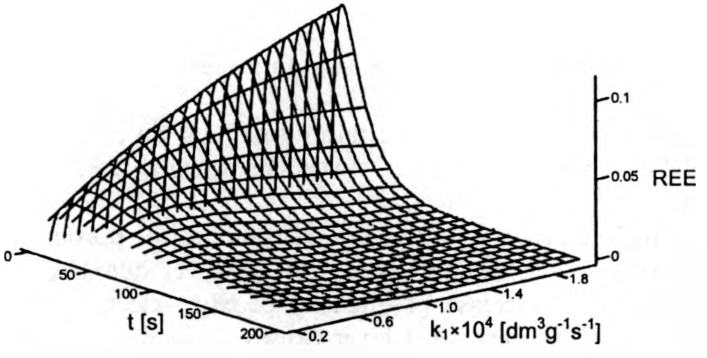

Fig. 9. Changes in intensity of the edge effect determined as a function of both developing time and the reactivity of the developing agent.

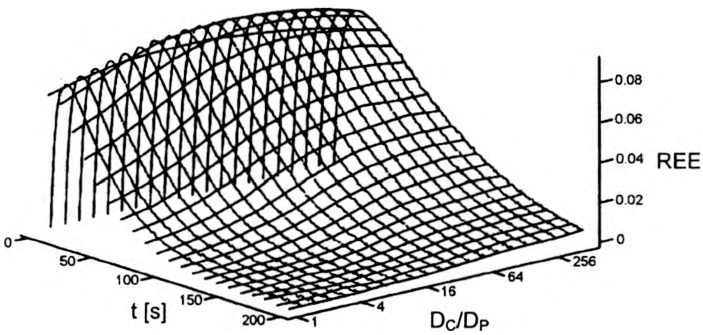

Fig. 10. Changes in intensity of the edge effect determined as a function of both developing time and the changes in diffusion coefficient of the developing process inhibitor.

The following initial values of the parameters exploited in model calculations have been assumed [1], [3], [20]:

$M_{1,\infty} = 0.5$ [g/m^2],
$M_{2,\infty} = 1.5$ [g/m^2],
$D_C = D_T = 5.2\cdot10^{-11}$ [m^2/s],
$C_0 = 5.0\cdot10^3$ [g/m^3],
$k_1 = 1\cdot10^{-7}$ [m^{3}g^{-1}s^{-1}],
$k_2 = 0.2$,
$h = 1\cdot10^{-4}$ [m],
$\Delta t = 4.9\cdot10^{-3}$ [s],
$\Delta x = \Delta y = 8\cdot10^{-7}$ [m].

The results of calculations have been presented in the form of three-dimensional plots (Figs. 4 – 10), where the relative edge enhancement shown as a function of two variables.

4. Conclusions

The results of the simulation model examination allow us to formulate the following conclusions:

– the intensity of edge effect increases within certain developing time interval reaching a maximum at a definite point after which it weakens down to complete disappearance (Figs. 4 – 10),

– both an increase in the surface silver concentration difference at the border of inequally irradiated fields as well as an absolute increase of the silver quantity in these fields (Figs. 4 and 5) causes an increase of intensity of edge effect,

– increment of the thickness of the developed layer causes an increase in the intensity of the edge effect as well as some small shift of the maximum of this function towards the longer times, as shown in Fig. 6,

– dilution of the reducing substance (Fig. 7) leads both to an increase of the intensity of the edge enhancement occurrence and the time interval for which the occurrence of the edge enhancement is observed,

– stronger slowing down of the developing process by the products of reaction (Fig. 8) causes similar changes in intensity of edge effect such as the increment of the surface concentrations of silver M_1 and M_2 (Fig. 4 and 5),

– an increase of the value of the developing reaction rate constant (Fig. 9) resulting from the change of temperature or pH of the developer leads to an increase of the intensity of the edge effect accompanied by a shift of the maximum of this function towards the short time intervals and also to a reduction of the time of their occurrence,

– a drop in the value of the diffusion constant of the developing process inhibitor (Fig. 10) causes an increase of the time interval in which the edge effects occur and results in a shift in the maximum intensity of their occurrence towards the longer time.

Summing up, it should be recognized that the application of diffusion model to the examination of the nature of the edge effects offers a possibility of taking account of many essential physicochemical parameters of the process of photographic development. Additionally, all the changes could be followed as a function of time. It should be expected that taking account, in the model, of changes of the laminar layer thickness occurring between the light sensitive layer and the developer solution will permit to widen the range of the model examinations to include the influence of the intensity of circulation of the developer solution on the edge enhancement occurrence. Besides, when taking into consideration the changes of gradient of developing agent concentration as well as the products of chemical reactions appearing in the light sensitive layer in the z-direction the examination of the multilayer light sensitive systems becomes possible.

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