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A STUDY FOR DEVELOPMENT OF FILM NEGATIVE IN BULK REACTION CASE

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ABSTRACT. We study a mathematical modeling for development of film negative and concentrate the bulk reaction problem. We prove nonnegativeness of developer, coupler and dye function in two dimensional case. Also we prove stability of our numerical scheme. Finally, we discuss numerical example which have specified constants.

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1. Mathematical Model

Film development is of major interest to many industries, yet the modeling of the process is not fully understood. We consider the development of a color film negative. The film developing process is roughly that the *reduced developer* R, after reacting with the exposed silver halide grains(after giving up its electrons), becomes the *oxidized developer* T. It then diffuses and reacts with a coupler C in the oil droplet to form a *dye* Y(which is immobile) and an *inhibitor* P. The inhibitor P diffuses and some of it adsorbs to the surface of the silver grain blocking halides from dissociating.

Let R, T, C, D, P, and P^* be density functions. Note that P^* represents the adsorbed inhibitor and S denotes the surface area of the silver halide grains per unit volume. Then, It's known that using the conservation of mass, the developing process is described by the following system of differential equations[1,2].

That is,

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$$\frac{\partial R}{\partial t} = D_R \Delta R - f_{dev}(R,P,S,P^*)E \tag{1}$$

$$\frac{\partial T}{\partial t} = D_T \Delta T + f_{dev}(R,P,S,P^*)E - k_1 TC \tag{2}$$

$$\frac{\partial C}{\partial t} = -k_1 TC \tag{3}$$

$$\frac{\partial Y}{\partial t} = k_1 TC \tag{4}$$

$$\frac{\partial P}{\partial t} = D_P \Delta P + k_1 TC - k_2 PS + k_3 P^* \tag{5}$$

$$\frac{\partial P^*}{\partial t} = k_2 PS - k_3 P^* \tag{6}$$

$$\frac{\partial S}{\partial t} = -k_4 S^{-\frac{1}{2}} f_{dev}(R,P,S,P^*) - k_2 PS + k_3 P^*, \tag{7}$$

where $E \geq 0$ is a given exposure function and D_R, D_T, D_P, and the k_i are all positive constants. The factor $S^{-\frac{1}{2}}$ in the last equation comes from the fact that $dV = k_5 S^{\frac{1}{2}} dS$ where dV is the volume element.

2. Bulk reaction problem

The solution of the previously described equations with appropriate initial and boundary conditions is a formidable task; more so because f_{dev} is not quite known and must be fitted to experimental results. However, we can get some flavor of the analysis by concentrating on a special case, which deals only with the *bulk reaction*. In this model we ignore the silver halide grains. The reason for doing this is not only to simplify the analysis but to be in use directly to some industrial problems[1,2]. We simply assume that the oxidized developer T diffuses through the emulsion and react only coupler C distributed in the oil droplets. We take for simplicity $f_{dev} \equiv \gamma$, a positive constant. Then the equations

$$\frac{\partial T}{\partial t} = D\Delta T + \gamma E(x,y) - kTC \tag{8}$$

$$\frac{\partial C}{\partial t} = -kTC \tag{9}$$

hold in the solution where $0 < x < M_1, 0 < y < M_2, t > 0$. And we must give initial conditions

$$T(x,y,0) = T_0(x,y), \quad 0 \leq x \leq M_1, \quad 0 \leq y \leq M_2 (T_0 \geq 0), \tag{10}$$

$$C(x,y,0) = C_0(x,y), \quad 0 \leq x \leq M_1, \quad 0 \leq y \leq M_2 (C_0 \geq 0) \tag{11}$$

and boundary conditions, say,

$$T(0,y,t)=0, \quad T(M_1,y,t)=0 \quad \text{for} \quad t>0,\ 0\le y\le M_2 \tag{12}$$
$$T(x,0,t)=0, \quad T(x,M_2,t)=0 \quad \text{for} \quad t>0,\ 0\le x\le M_1. \tag{13}$$

We wish to study the above problem.

Now we analyze the solution of this bulk reaction problem. Let A be the cubic region $0 < x < M_1,\quad 0 < y < M_2$, and $0 < t \le T$, while B is the part of the boundary of A contained in the five planes $x = 0$, $x = M_1$,$y = 0$,$y = M_2$ and $t = 0$. The proof of the following theorem is based on the one-dimensional version in [2].

Theorem 1 (The Maximum Principle). *If $T = T(x, y, t)$ is continuous in $A \cup B$, and satisfies the inequality*

$$\frac{\partial T}{\partial t} - D\Delta T + cT \ge 0 in A,$$

where D is a positive function and c is any bounded function, and if $T \ge 0$ on B, then $T \ge 0$ in A.

The maximum principle yields the following useful result.

Theorem 2 (Comparison theorem). *If u(x,y,t) and v(x,y,t) are such that the function T=u-v satisfies the condition described in Theorem 1, then u≥v in $0 \le x \le M_1,\ 0 \le y \le M_2,\ 0 \le t \le T$.*

Now consider our problem (8)-(9). By inspecting, (9) yields

$$C(x,y,t) = C_0(x,y)\exp\left(-k\int_0^t T(x,y,s)ds\right).$$

By the fact that the exposure function is nonnegative, our problem satisfies the condition of the maximum principle with $c = kC$. Hence, by the comparison theorem, $T \ge 0$. It follows that $\partial C/\partial t \le 0$, that is, $C(x, y, t)$ is monotone non increasing in t. What we really want to study is the dye Y. Note that the rate of change of the dye Y plus coupler C must be zero by the system equation (3) and (4). This means that

$$Y = C_0 - C. \tag{14}$$

Hence we can calulate the dye Y by means described in this equation directly after calculate coupler C numerically. Computational discussion is following after the inspecting algorithm to obtain developer T and coupler C.

3. Numerical algorithm and stability

In order to verify the above mathematical analysis computationally, we consider the following system of equations with an exposure function $E(x, y)$;

$$\frac{\partial T}{\partial t} = D\Delta T - \kappa TC + \gamma E(x,y), \tag{15}$$
$$\frac{\partial C}{\partial t} = -\kappa TC \tag{16}$$

where $(x,y) \in (0,M) \times (0,M)$, $0 < t$, the initial conditions are

$$T(x,y,0) = T_0(x,y) = 0, \tag{17}$$
$$C(x,y,0) = C_0(x,y), \tag{18}$$

and the boundary condition is

$$T(x,y,t) = 0 \text{ where } (x,y) \in \partial((0,M) \times (0,M)) \text{ for all } t \geq 0, \tag{19}$$

with positive constants D, γ, κ, and M.

The above system has a non-linear term. Hence we linearize that system then solve the equations iteratively. *i.e* first solve the equation (16) solely as a linear ordinary differential equation with respect to the function C where T is regarded as a just coefficient function already known. And then solve the diffusion equation (15) with respect to the function T where the coefficient function C is obtained from the first step. The equation (16) can be solved by the backward difference scheme considering $T^n_{m,l}$ as a constant already computed from the equation (15) where k is the size of the time step.

$$C^{n+1}_{m,l} = \frac{1}{1 + k\kappa T^n_{m,l}} C^n_{m,l}. \tag{20}$$

In order to solve the above system (15) and (16) iteratively, we must consider a scheme which can solve the diffusion equation (15) in two dimensions. We solve this equation by the Peacemann-Rachford scheme. Let L_1 and L_2 be the differential operators defined by $L_1(f) = D\frac{\partial^2 f}{\partial x^2} - \frac{\kappa}{2}Cf$ and $L_2(f) = D\frac{\partial^2 f}{\partial y^2} - \frac{\kappa}{2}Cf$, and L_{1h} andL_{2h} be the difference operators with respect to L_1 and L_2. Then, the Peacemann-Rachford scheme becomes

$$\left(I - \frac{k}{2}L_{1h}\right)\tilde{T}^{n+\frac{1}{2}} = \left(I + \frac{k}{2}L_{2h}\right)T^n + \frac{k\gamma}{2}E^{n+\frac{1}{2}} \tag{21}$$
$$\left(I - \frac{k}{2}L_{2h}\right)T^{n+1} = \left(I + \frac{k}{2}L_{2h}\right)\tilde{T}^{n+\frac{1}{2}} + \frac{k\gamma}{2}E^{n+\frac{1}{2}}. \tag{22}$$

If we use the central difference scheme for $\frac{\partial^2}{\partial x^2}$ and $\frac{\partial^2}{\partial y^2}$ then we obtain the following difference formulas:

$$-\tilde{T}^{n+\frac{1}{2}}_{m-1,l} + \left(\frac{2\mu}{D} + 2 + \frac{\kappa k\mu}{2D}C^{n+1}_{m,l}\right)\tilde{T}^{n+\frac{1}{2}}_{m,l} - \tilde{T}^{n+\frac{1}{2}}_{m+1,l}$$

$$= T^n_{m,l-1} + \left(\frac{2\mu}{D} - 2 - \frac{\kappa k\mu}{2D}C^{n+1}_{m,l}\right)T^n_{m,l} + T^n_{m,l+1} + \frac{k\gamma h^2}{D}E_{m,l}, \tag{23}$$

$$-T^{n+1}_{m,l-1} + \left(\frac{2\mu}{D} + 2 + \frac{\kappa k\mu}{2D}C^{n+1}_{m,l}\right)T^{n+1}_{m,l} - T^{n+1}_{m,l+1}$$

$$= \tilde{T}^{n+\frac{1}{2}}_{m-1,l} + \left(\frac{2\mu}{D} - 2 - \frac{\kappa k\mu}{2D}C^{n+1}_{m,l}\right)\tilde{T}^{n+\frac{1}{2}}_{m,l} + \tilde{T}^{n+\frac{1}{2}}_{m+1,l} + \frac{k\gamma h^2}{D}E_{m,l} \tag{24}$$

where $\mu = \frac{h^2}{k}, 1 \le m \le M-1, 1 \le l \le M-1$ and $E_{m,l} = E(mh, lh)$.

Note that the variables $\tilde{T}^{n+\frac{1}{2}}$ should be thought of as intermediate or temporary variables in the calculation and not as approximations to $u(x, y, t)$ at any time t.

First we consider the nonnegativity of $C^n_{m,l}$ and $T^n_{m,l}$.

Theorem 3. *Suppose that* $k \le \frac{4h^2}{4D + \kappa h^2 C^n_{m,l}}$ *with* $4D + \kappa h^2 C^n_{m,l} \ge 0$ *for all* l, m *and* n. *Then* $C^n_{m,l}$ *and* $T^n_{m,l}$ *are nonnegative for all nonnegative exposure data* $E_{m,l}$.

Proof. We use induction on n for both $C^n_{m,l}$ and $T^n_{m,l}$. For $n = 0$, it's trivially true because the initial data is nonnegative. For $n = 1$, we first solve the equation (20). Then, since $T^0_{m,l} = 0$, $C^1_{m,l} = C^0_{m,l}$. That implies the nonnegativeness of $C^1_{m,l}$. For the nonnegativeness of $T^1_{m,l}$, we consider the $T^{\frac{1}{2}}_{m,l}$. The matrix constructed by the equation (23) is real irreducibly diagonally dominant and has negative values for the off-diagonal entries while the diagonal entries are strictly positive. Since $C^1_{m,l} \ge 0$, the inverse of the matrix is nonnegative.([3]) If we can prove the nonnegativeness of the inhomogeneous term in the system (23) and (3.10), the nonnegativeness of $T^{\frac{1}{2}}_{m,l}$ follows. By our hypothesis, $\frac{2\mu}{D} - 2 - \frac{\kappa k\mu}{2D}C^1_{m,l}$ is nonnegative. Hence we obtain the nonnegative inhomogeneous term. That leads to the nonnegativeness of $T^{\frac{1}{2}}_{m,l}$. By the same argument, we can prove the nonnegativeness of $T^1_{m,l}$.

Suppose that $C^n_{m,l}$ and $T^n_{m,l}$ are nonnegative. Trivially,

$$C^{n+1}_{m,l} = \frac{1}{1 + k\kappa T^n_{m,l}} C^n_{m,l} \ge 0. \tag{25}$$

We must prove the nonnegativeness of $T^{n+1}_{m,l}$. But the proof is exactly the same as the one for the case $n = 1$. This proves our claim. □

From theorem 3, we easily deduce the following useful consequence.

Corollary 1. *With the same hypothesis as in theorem 3,* $C^n_{m,l}$ *is bounded for all* n.

Proof : By the equality in (25) and the non negativity of $T^n_{m,l}$, the following inequallities are hold for all m and l:

$$0 \leq \cdots \leq C^{n+1}_{m,l} \leq C^n_{m,l} \leq \cdots \leq C^1_{m,l} \leq C^0_{m,l}. \tag{26}$$

This proves the theorem. □

We can naturally calculate the discritized dye function $Y^n_{m,l}$ by the following equation with aid of the equation (14) in the last part of section 2:

$$Y^n_{m,l} = C^0_{m,l} - C^n_{m,l}. \tag{27}$$

Hence the equation (26) in Corollay 1 simply lead the nonnegativeness of dye function with our algorithm.

Next, we shall consider the stability for this scheme. We need some calculation for this.

Lemma 1. *With the same hypothesis as in theorem 3, the following inequality holds. For all real ζ and η, with all positive constants μ, κ, k and D,*

$$\left| \frac{\left(4\mu - \left(\kappa k\mu C^n_{m,l} + 8Dsin^2\frac{\zeta}{2}\right)\right)\left(4\mu - \left(\kappa k\mu C^n_{m,l} + 8Dsin^2\frac{\eta}{2}\right)\right)}{\left(4\mu + \left(\kappa k\mu C^n_{m,l} + 8Dsin^2\frac{\zeta}{2}\right)\right)\left(4\mu + \left(\kappa k\mu C^n_{m,l} + 8Dsin^2\frac{\eta}{2}\right)\right)} \right| \leq 1. \tag{28}$$

Proof. We first consider that the quotient in (28) is less than or equal to 1. But it's easily obtained since the terms $\kappa k\mu C^{n+1}_{m,l} + 8Dsin^2\frac{\zeta}{2}$ and $\kappa k\mu C^{n+1}_{m,l} + 8Dsin^2\frac{\eta}{2}$ are positive.

Let us denote the quotient in (28) by g_n. We only prove that $g_n \geq -1$. Expanding the inequality $g_n \geq -1$, we obtain the following inequality:

$$\kappa^2k^2\mu^2\left(C^n_{m,l}\right)^2 + 8\kappa k\mu D\left(sin^2\frac{\zeta}{2} + sin^2\frac{\eta}{2}\right)C^n_{m,l} + 16\mu^2 + 64D^2sin^2\frac{\zeta}{2}sin^2\frac{\eta}{2} \geq 0.$$

Using again the nonnegativity of $C^n_{m,l}$, the above inequality clearly holds. This is the desired proof. □

As in the proof of Lemma 1, we denote the quotient in the absolute value at the left hand side of inequality (28) simply by $g_n(h\zeta, h\eta)$.

Using $g_n(h\zeta, h\eta)$ as the amplification factor, we obtain the following estimate.

Theorem 4. *With the hypothesis of theorem 3, the following inequality holds:*

$$\|T^n\|^2 \leq C_{T^n}\left(\|T^0\|^2 + k\|E\|^2\right)$$

where C_{T^n} is a positive constant and $\|T^n\|^2 = \sum_{m,l\in Z} |T^n_{m,l}|^2 h$.

Proof. Consider the following inversion formula for the discrete Fourier transform:

$$T^n_{m,l} = \frac{1}{2\pi}\int_{[-\frac{\pi}{h},\frac{\pi}{h}]^2} e^{ih(m,l)\cdot(\zeta,\eta)}\widehat{T}^n(\zeta,\eta)d\zeta d\eta.$$

Substituting this formula difference equation (23) and (24), using the uniqueness of the Fourier Transform, and eliminating $\widehat{T}_{m,l}^{n+\frac{1}{2}}$, we obtain the following equation. For all n

$$\widehat{T}^{n+1} = g_{n+1}(h\zeta, h\eta)\widehat{T}^{n} + K_{n+1}k\widehat{E},$$

where

$$K_n = \frac{4\mu\gamma h^2}{\left(4\mu + 4D + \kappa k\mu C_{m,l}^{n} - 4cos(h\zeta)\right)\left(4\mu + 4D + \kappa k\mu C_{m,l}^{n} - 4cos(h\eta)\right)}.$$

Hence, simply replacing $g_n(h\zeta, h\eta)$ by g_n,

$$\widehat{T}^{n+1} = g_{n+1}g_n \cdots g_1\widehat{T}^{0} + (g_{n+1}g_n \cdots g_1K_1 + \cdots + g_{n+1}K_n + K_{n+1})\, k\widehat{E}.$$

Taking the L_2 norm $\widehat{T}$ and using Parseval's equality and Lemma 1,

$$\|T^{n+1}\|^2 \leq \|T^{0}\|^2 + \Big(|K_1| + \cdots + |K_{n+1}|\Big)k\|E\|^2.$$

Denoting $C_{T^{n+1}}$ by $max\Big\{1, |K_1| + \cdots + |K_{n+1}|\Big\}$, this proves our theorem. □

This means our desired stability.

4. Experimental results

Consider the system (15) and (16) with the initial condition

$$C_0(x, y) = 1.125 \times 10^{-11} moles/microns$$

and specified constants

$$D = 100\, microns^2/sec, \quad \gamma = 7.5 \times 10^{-12} moles/microns\, sec,$$
$$\kappa = 6.6 \times 10^{12} microns/moles\, sec, \quad L = 1.5 \times 10^{5} microns.$$

We use the picture in Fig. 1. as an exposure function. Inputting the initial data as an exposure function is done by reading the raw data from the picture and converting the data to matrix array by using MatLab. The MatLab algorithm is as follows.

```
inIMG=imread('c:\001.jpg');
outDAT=fopen('c:\001149.dat','w')
 for I=1:149,
       for J=1:149,
         fprintf(outDAT,'%14.12f',double(inIMG(I,J))/255);
       end
    fprintf(outDAT,'\n');
```

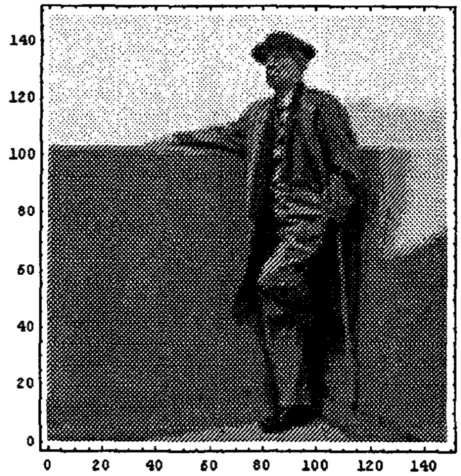

FIGURE 1. The exposure function expressed by density plot

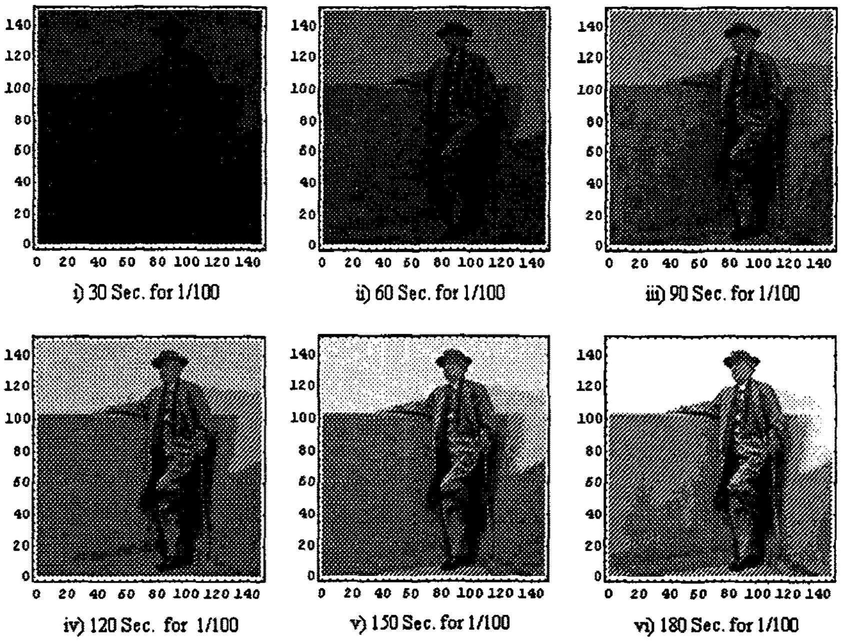

FIGURE 2. Dyeing results during the first three minutes

```
  end
fclose(outDAT)
```

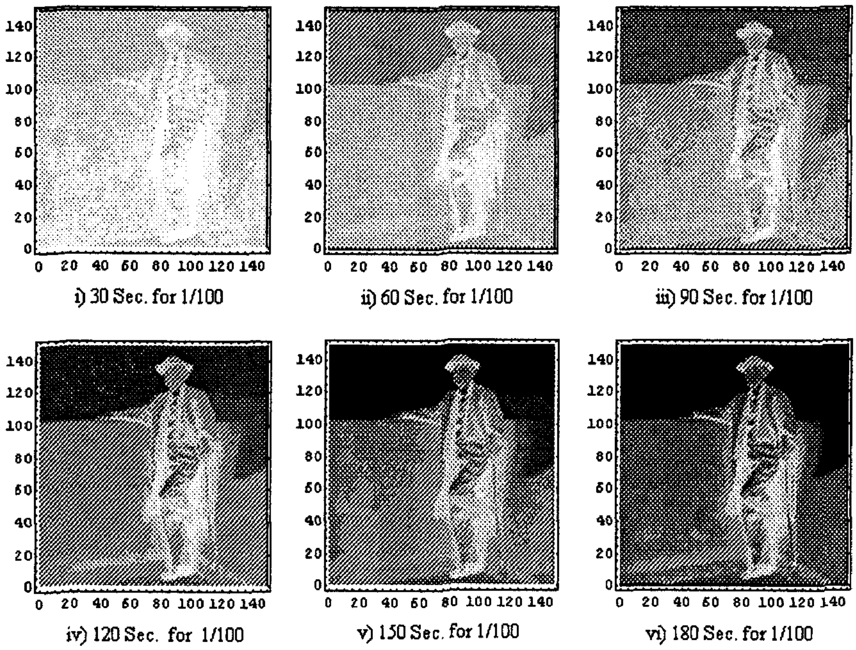

FIGURE 3. Dyeing results for Negative during the first three minutes

Now we examine how to fix our data to the hypothesis in our theorems. Substitute the specified constants κ and D in the hypothesis of the theorem 3. Then

$$k \le \frac{h^2}{100 + (1.65 \times 10^{12})h^2 C^n_{m,l}}.$$

But $C^n_{m.l} \le 1.125 \times 10^{-11}$, since $C^n_{m,l}$ decreases monotonically because of the nonnegativeness of $T^n_{m,l}$, we only check that $k \le \dfrac{h^2}{100 + (18.5625)h^2}$. For example, if we take $h = 1000\mu m$, then $k \le 0.0538718$. We must take k less than or equal to $1/20sec$. The Fig. 2 and 3 are results of our computation with $k = 1/100sec$ and $h = 1000\mu m$.

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