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The Rate of Penetration of Photographic Chemicals into Gelatin Layers. I. Diffusion Rate of Developing Materials

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The rate of diffusion of various kinds of developing materials through coated gelatin layers was determined by using silver halide as a detector. *p*-Phenylenediamines have the biggest diffusion constants among materials tested. They have no pH-dependency nor concentration-dependency. *p*-Aminophenols have slightly lower diffusion constants than the corresponding *p*-phenylenediamines. The constants increase with increase in molecular sizes and also with pH. Hydroquinones have relatively low diffusion constants. They are considerably affected by variation of pH, concentration and ionic strength. These characteristics are discussed in connection with the chemical structures of developing materials.

The penetration of photographic chemicals into gelatin layers is a fundamental problem for rapid development process.

Since the measurement of dye-diffusion by Herzog and Polotzky,[1] many investigations have been reported about the diffusion of dyes and photographic chemicals in gelatin gel. Ostwald and Quast,[2] Pontius and his colaborators[3] and other investigators[4,5] determined the rate of diffusion of various dyes. Blyumberg and Davidkin[6] and Bagdanov and Polyakova[7] measured the diffusion rate of developing materials, halides and alkaline substances. Adair[8] and other investigators[9] adopted a capillary tube method to determine the diffusion rate of bromide ion in gelatin gel.

The diffusion rate in gelatin gel is different from that in a coated gelatin layer. Reckziegel[10] is the first who investigated the diffusion in coated layers.

The author made a series of investigations using gelatin coatings, and this paper deals particularly with the effect of molecular size, pH, ionic strength and temperature on the diffusion rate of various developing materials.

Experimental Procedure

The method of measurement was similar to that by Reckziegel.[10]

Test Samples. Various thickness of gelatin layers (0 to 26 μ) were coated on a silver bromo-iodide emulsion layer applied on a film support with 2.7 μ thickness which acted as a detector layer (Fig. 1).

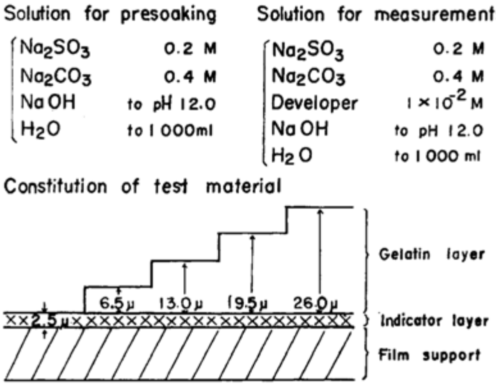

Fig. 1. Explanation of experimental procedure.

Measurement. Pre-swollen samples were dipped into a bromide-free solution containing a developing material. The developing material diffuses through gelatin to the emulsion layer at the bottom and then reduces silver halide instantaneously. The blackening indicates the time required for penetration. The solu-

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[1] R. O. Herzog and Polotzky, *Z. Elektrochem.*, **17**, 679 (1911); *Z. Phys. Chem.*, **87**, 449 (1914).

[2] a) W. Ostwaldt and A. Quast, *Kolloid Z.*, **51**, 273 (1930); b) *ibid.*, **51**, 361 (1930); c) *ibid.*, **48**, 83 (1929).

[3] a) R. B. Pontius, M. L. Kaplan and R. M. Husney, *J. Phys. Chem.*, **61**, 9 (1956); b) R. B. Pontius and J. A. Wenrich, *Phot. Sci. Engineering*, **2**, 131 (1958).

[4] W. Luck, *Ber. Bunsenges. Phys. Chem.*, **69**, 255 (1965).

[5] B. Vlcek and S. Vlcekova, *Zhur. Nauch. i Priklad. Foto. i Kinema.*, **5**, 187 (1960).

[6] a) J. B. Blyumberg and I. M. Davidkin, *ibid.*, **8**, 3 (1963); b) *ibid.*, **8**, 81 (1963).

[7] S. G. Bagdanov and N. V. Polyakova, *ibid.*, **2**, 187 (1957).

[8] G. S. Adair, *Biochem. J.*, **14**, 762 (1920).

[9] J. P. Stonham and A. M. Kragh, *J. Phot. Sci.*, **14**, 97 (1966).

[10] R. Reckziegel, *Mitteilungen aus den Forschungslab. Agfa.*, **1**, 239 (1955).

tion used for pre-soaking to eliminate the effect of swelling had the same composition as the developer solution except that it did not contain the developing material.

Accuracy. The relative errors for measurement of layer thickness fell within ±2% by Tsugami Precision Microcator under 95% confidence limit, and that of diffusion time fell within ±5% under 95% confidence limit.

Theoretical Treatment of Diffusion Process

One dimensional expression of Fick's diffusion law may be applied to the penetration of developing materials through the gelatin layer;

$$\partial c/\partial t = K\partial^2 c/\partial x^2 \tag{1}$$

were c is the concentration of the developing material, t the time required for the developer to diffuse through the layer with thickness x and K the diffusion constant. Following Lederer,[11] Eq. (1) can be solved as follows:

$$\begin{aligned} C_i = C_a[1-(4/\pi)\cos(\pi l/2x)\exp(-ft) \\ -(4/3\pi)\cos(2\pi l/2x)\exp(-9ft)+\cdots] \end{aligned} \tag{2}$$

where $f = \pi^2 K/4x^2$

C_i: Concentration of the developing material at x from surface of gelatin layer.

C_a: Concentration of the developing material in bulk solution.

Supposing that the blackening of the detector layer occurs instantly when the first portion of the developing material (m) has reached through gelatin layer (x) to the detector layer, the following relation can be obtained between m and x by integrating Eq. (2).

$$m = C_a[a-(8/\pi^2)(x+a)\sin\{\pi a/(x+a)\}\exp(-ft)+\cdots] \tag{3}$$

Here, a means a hypothetical diffused length of the developing material into the detector layer to induce the first blackening.

If $h + a \gg 2a$, Eq. (3) can be simplified by approximation.

$$m = C_a a\{1-(4/\pi)\exp(-\pi^2 Kt/4x)\} \tag{4}$$

By considering the condition,

$$\lim_{x\to\infty}\{\log(C_a a/C_a a-m)\} = 0 \tag{5}$$

we can derive from simplification of Eq. (4)

$$t = (4x^2/\pi^2 K)\ln(4/\pi) \tag{6}$$

or

$$x = K' t^{1/2} \tag{7}$$

where $K' = \pi K^{1/2}/2\{\ln(4/\pi)\}^{1/2}$

Equation (6) or (7) means that, if penetration of the developing materials proceeds by Fick's diffusion process, the time required to penetrate through the layer will be proportional to the square of layer thickness.

Experimental Results

1. Diffusion of Various Types of Developers. The rate of diffusion was determined by a solution containing 10 mmol/l of the developing material, 0.2 mol/l of Na_2SO_3, 0.4 mol/l of Na_2CO_3 and NaOH or H_2SO_4 to adjust pH. Plots of layer thickness *vs.* square root of penetration time showed linear relation for almost all developers examined (Fig. 2). This means that the diffusion process satisfies Fick's law, so far as the equation is con-

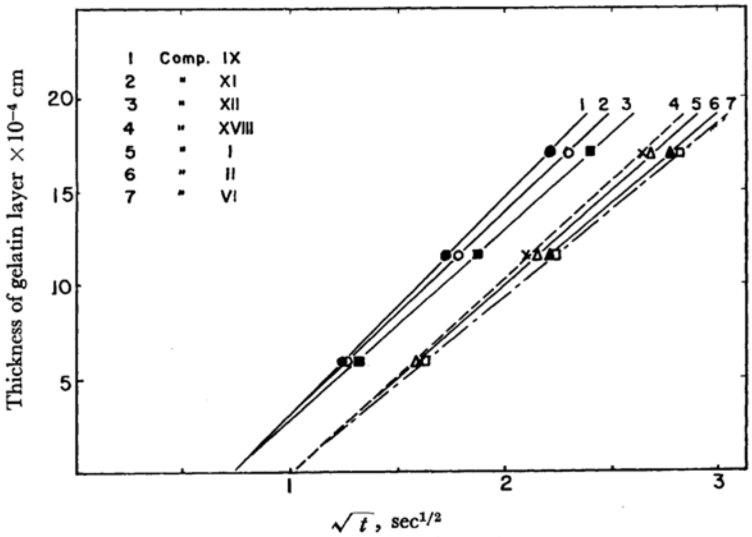

Fig. 2. Distance - time relation during diffusion process.

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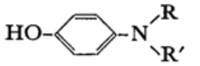
[11] E. L. Lederer, *Kolloid Z.*, **44**, 108 (1928).

cerned. Therefore, the diffusion constant can be obtained from the tangent(K) of Fig. 2 by using Eq. (7).

The diffusion constants of various types of developers thus obtained are listed in Tables 1—3. The results showed: (1) In the series of *p*-aminophenols and *p*-phenylenediamines, diffusion constants decreased with the increase in size of substituted groups, but no distinct rule could be observed about hydroquinone derivatives. (2) The diffusion constants of *p*-phenylenediamines were generally greater than those of corresponding *p*-aminophenols and the latter were greater than those of hydroquinones.

Table 1. Diffusion constants of *p*-aminophenols



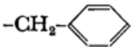
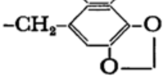
Comp.	R	R′	$D\times10^{-7}$ cm²/sec
I	-H	-H	1.69
II	-H	$-CH_3$	1.58
III	-H	$-C_2H_5$	1.20
IV	-H	$-s\text{-}C_4H_9$	1.05
V	-H	$-n\text{-}C_4H_9$	1.05
VI	-H		0.923
VII	-H		0.695
VIII	$-C_2H_5$	$-C_2H_5$	0.962

Table 2. Diffusion constants of *p*-phenylenediamines

Comp.		$D\times10^{-7}$cm²/sec
IX	*N*,*N*-Diethyl-*p*-phenylenediamine	1.85
X	3-Methyl-4-amino-*N*,*N*-diethylaniline	1.56
XI	4-Amino-*N*-ethyl-*N*-hydroxyethylaniline	1.77
XII	3-Methyl-4-amino-*N*-ethyl-*N*-hydroxyethylaniline	1.46

Table 3. Diffusion constants of hydroquinones and other developing materials

Hydroquinone and other developing material		$D\times10^{-7}$ cm²/sec
XIII	Hydroquinone	0.695
XIV	Methylhydroquinone	0.324
XV	2,5-Dihydroxyphenylamylketone	0.527
XVI	2,5-Dihydroxyphenylcetylketone	0.057
XVII	Phenylhydroquinone	0.645
XVIII	1-Phenyl-3-pyrazolidone	1.27
XIX	Amidol	1.42
XX	Pyrogallol	0.424

2. Effect of pH. The pH-dependency of the diffusion of three types of developing materials differed from each other.

A typical *p*-phenylenediamine (compound XII) showed no pH-dependency over a pH-range from 9.4 to 12.0, as shown in Fig. 3. On the other hand, *p*-aminophenols had some pH-dependency. This dependency became smaller with increase in pH. In fact, it almost disappeared over pH 10.7 in the case of metol.

In contrast to the results of *p*-aminophenols, the rate of diffusion of hydroquinones decreased with increase in pH.

3. Effect of Temperature. The temperature dependency of three types of developers also showed some difference from one another (Fig. 4).

The plots of rate *vs.* $1/T$ consists of two straight lines in case of hydroquinone. Activation energies

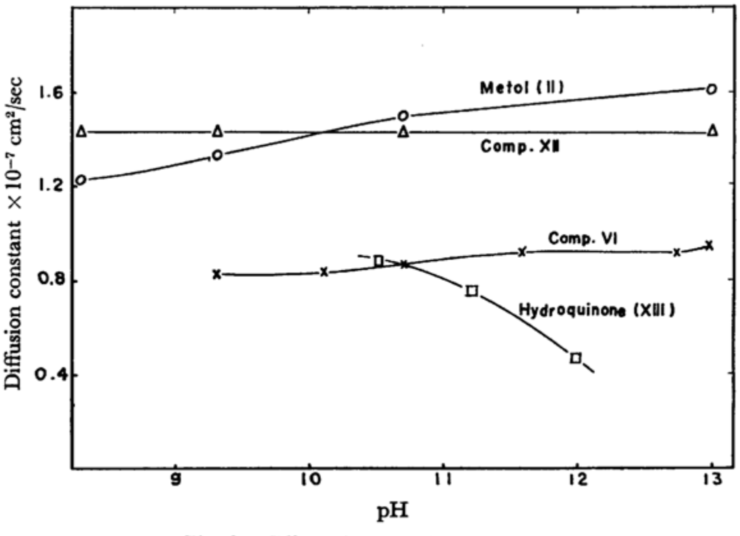


Fig. 3. Effect of pH on diffusion constant.

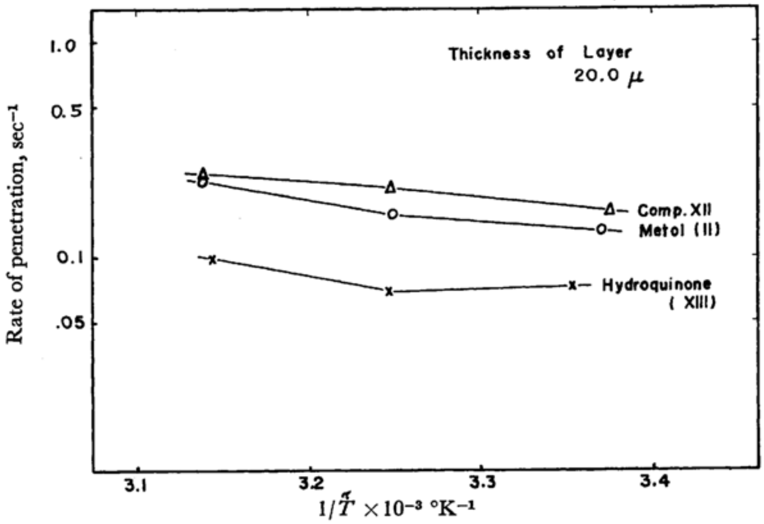


Fig. 4. Effect of temperature on penetration rate.

of diffusion obtained from the slope of the curves for the three types of developing materials are listed in Table 4.

TABLE 4. ACTIVATION ENERGY OF DIFFUSION

Compound	Temperature	$E_{act.}$
II	23—35°C	2.9 kcal/mol
	35—45°C	6.5 kcal/mol
XII	23—45°C	3.1 kcal/mol
XIII	35—45°C	7.2 kcal/mol

4. Effect of Concentration of Developing Materials. The diffusion constants of *p*-aminophenols and *p*-phenylenediamines did not show any dependence on concentration except the case of extremely low concentration, but that of hydroquinone showed relatively large dependence up to the concentration of 8×10^{-2} mol/*l* (Fig. 5). The fact that the diffusion constant of metol is independent of concentration means that this process is pure physical diffusion which can be expressed by Fick's law.

5. Penetration of Developing Materials into Unswollen Layer. Measurement of penetration into the gelatin layer which had not been preswollen also gave a linear relation between the depth of penetration and the square root of penetration time (Fig. 6). Therefore, this penetration process can be simulated to diffusion, although it contains many complicated processes such as absorption of water by gelatin, swelling and hydration.

The apparent rate of penetration was independent of the types of developing materials, if the applied

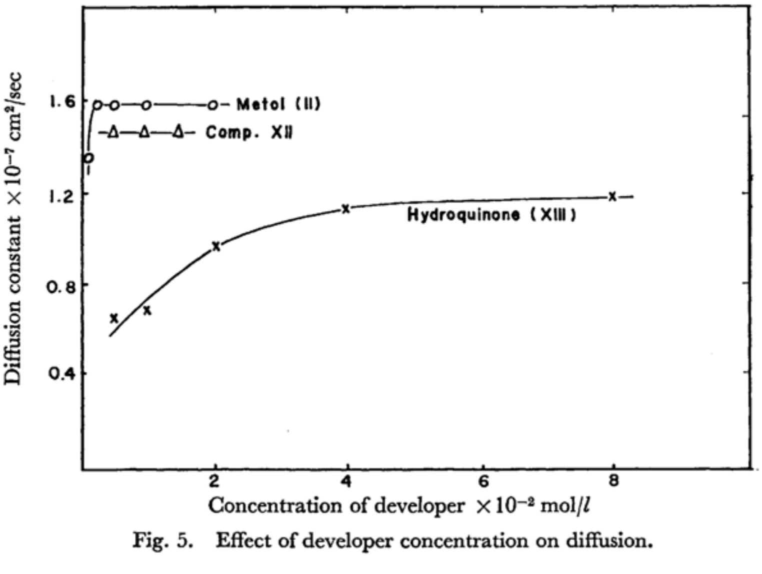


Fig. 5. Effect of developer concentration on diffusion.

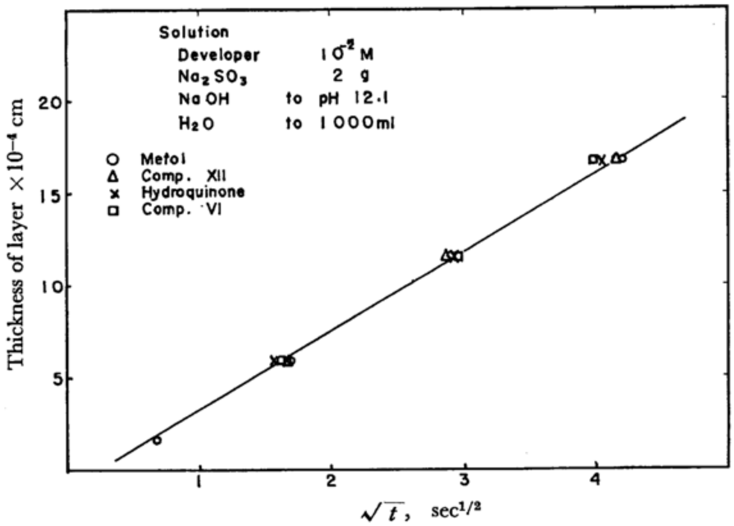


Fig. 6. Penetration of developer into unswollen layer.

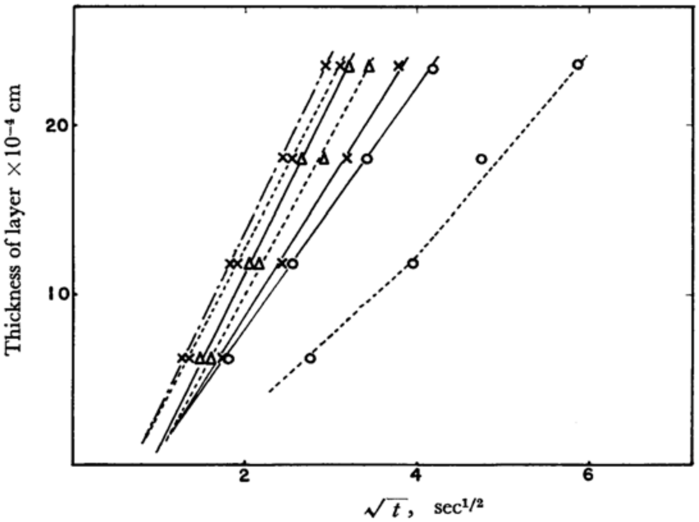


Fig. 7. Effect of salt on penetration.
△ Comp. II, × Comp. XII, ○ Comp. XIII
—— with Na_2SO_4, ---- without Na_2SO_4, —·— Na_2SO_4 soln. was applied only in pre-swelling

solution had low ionic strength or relatively low pH. This result is interpreted from the slow penetration rate of OH^- ion in these solutions which determines the initiation of blackening of detector layer. This explanation is supported by the fact that the initiation of blackening occurred about 1 sec after OH^- ion had reached the bottom layer (detector).

On the other hand, the rate of penetration from solutions of high alkalinity or of high ionic strength depended on the types of developing materials.

6. The Effect of Salt Concentration. The presence of salts such as Na_2SO_4 affected the diffusion rate in different ways according to the types of developing materials, as shown in Fig. 7. The presence of Na_2SO_4 accelerated the diffusion of hydroquinone and metol, but retarded that of a *p*-phenylenediamine derivative (compound XII). The accelerated diffusion of the compound XII, however, could also be observed, in the case Na_2SO_4 was present only in the swelling solution and not in the solution of the developing material.

Discussion

Three types of developing materials showed different characteristics with respect to diffusion.

p-Phenylenediamines have two amino groups and no hydroxy group. They have the biggest diffusion constants, no pH-dependence or concentration dependence. Their activation energies are constant over 23—45°C. Ionic strength slightly affects the diffusion.

Hydroquinone with two hydroxy groups has just the opposite property. Its diffusion constant is the smallest and had big pH- and concentration-dependence. It varies considerably with the change of ionic strength. The apparent activation energy varies with temperature. *p*-Aminophenols have one amino and one hydroxy group. They have the characteristics intermediate between the two mentioned above.

In alkaline medium, dissociated functional groups of gelatin will interact with charged developing materials, thus affecting the rate of diffusion. Therefore, it seems that hydroquinone which dissociates with $pK_1=9.9$ and $pK_2=11.4$ has relatively large dependency on pH, concentration and ionic strength, and that non-dissociating *p*-phenylenediamines do not have such dependency.

The constancy of diffusion coefficient over a wide range of concentration of a developing material means that (1) the penetration into pre-swollen layers can be treated as pure diffusion and that (2) the condition $C_a \times a \gg m$ is satisfied to calculate K by Eq. (6).

Hydroquinone does not have a constant rate of diffusion under 8×10^{-2} mol/*l*. This means again that it has some interaction with the medium or it has relatively large m value.

The decrease in diffusion constant with increase in molecular size of substituted group in *p*-aminophenol supports the suggestion by Alburger[12] who assumed that the property of duratol having a tendency to develop surface layer selectively is due to its molecular size. But the property is more closely related to the activity of the duratol rather than its poor diffusibility.

This investigation is concerned only with the first step of development processes. Many successive steps might affect the rate of development. The effect of pre-bathing and control of swelling by addendants to the solution or to gelatin are also important in photographic development.

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12) J. R. Alburger, *J. Soc. Motion Picture Engrs.*, **35**, 282 (1940).