Photo-dichroism of Printed-out Silver. II. Theoretical Consideration of the Mechanism from the point of View that the Phenomenon of Photo-dichroism would be an Anisotropic Herschel effect

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In the previous paper[1], the author has reported some experimental evidences in favor of the view that the phenomenon of photo-dichroism of printed-out silver is an anisotropic Herschel effect.

In the present paper, the author carries out the theoretical consideration of the same subject and proposes the mechanism by which the films of printed out silver being exposed to polarized light become anisotroric in their optical nature.

According to the theory, the value of photo-dichroism would be given by the formula which is the function of the time of exposure, energy of exposing light, temperature and the wave length of observed light. Thus, the quantitative expression of the phenomenon, which has not been reported up to the present, can be undertaken.

Consideration

Mott and Gurney[2] have proposed the following explanation of the mechaism of of Herschel effect.

When a previously illuminated film (in which the latent image is contained) is exposed to red light, the action of the light will remove electrons from the latent image (paticles of metallic silver) into conduction band of silver halide. The silver speck then carries a positive charge. This will cause an electrolytic current, consisting of silver ions, to flow from the latent image into the silver halide crystals. The silver speck thus will be gradually destroyed.

When a surface of metallic silver is exposed obliquely, as shown in Fig. 1, to polalized light of which the electric vector is in the plane of incidence, the number of inner-photo-electrons (say $J_{\parallel}$) is given by the following formula[3],

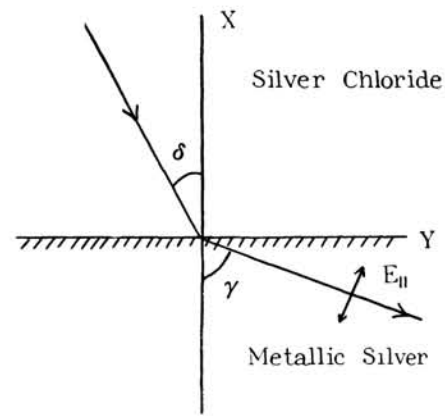

Fig. 1.

$$J_{\parallel}=\frac{R_0}{h\nu}\frac{\sin^2\gamma\sin^2\delta}{\sin^2(\gamma+\delta)\cos^2(\delta-\gamma)}\times\left(1-\sqrt{(\phi-\chi)/h\nu}\right)\left[1+\frac{3}{2}\times(2-\cos^2\gamma)\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}\right] \quad (1)$$

by the light of which the electric vector is perpendicular to the plane ($J_{\perp}$),

$$J_{\perp}=\frac{R_0}{h\nu}\frac{\sin^2\gamma\cos^2\delta}{\sin^2(\gamma+\delta)}\left(1-\sqrt{(\phi-\chi)/h\nu}\right)\times\left[1-\frac{1}{2}\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}\right] \quad (2)$$

where ϕ is the work function of metallic silver, χ is the electron affinity of silver chloride, $h\nu$ is the energy of exposiog light and δ and γ are the angles of incidence and refraction. R_0 is to be given as,

$$R_0=A(\varepsilon+A)\,[1-\exp\{-(\varepsilon+A)d\}]$$

where A is the fraction of absorbed quanta contributing to remove the electrons and ε is that on other processes and d is the thickness of the metal.

In fact, there would be a great many such surfaces of metallic silver in the film of printed-out silver and the normals

1) I. Kamiya, This Bulletin, **30**, 6 (1957).
2) N. F. Mott and R. F. Gurney, "Electronic. Processes in Ionic Crystals," Oxford Press (1950), p. 243.
3) I. Kamiya, *J. Chem. Soc. Japan*, **76**, 960 (1955).

of these surfaces would orientate in all directions.

The number of inner-photo-electrons for arbitrary surfaces can be calculated in the following ways.

Let x be the direction of incident parallel beam of which the electric vector is in xy-plane (y being perpendicular to x) and z be the direction being perpendicular to x and y.

Then, if the direction cosines of the normal to this surface are $\cos\alpha$, $\sin\alpha\cos\beta$, and $\sin\alpha\sin\beta$ with respect to x, y and z, and y and z axes are rotated by β on yz-plane, let two new axes be called to y' and z' axes, then the xy'-plane will be the plane of incidence and xz'-plane will be the plane being perpendicular to the plane of incidence (Fig. 2).

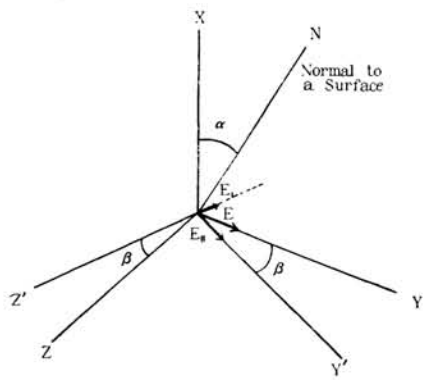

Fig. 1.

The electric vector of exposing light is divided into two components, one of which is in xy'plane (say $\boldsymbol{E}_{\parallel}$), and the other in xz'-plane (say $\boldsymbol{E}_{\perp}$).

Thus, the number of inner-photo-electrons due to $\boldsymbol{E}_{\parallel}$ can be obtained by the same method as before, that is,

$$J_{\parallel}' = \frac{R_0}{h\nu}\frac{\sin^2(\alpha+\alpha')\cos^2(\alpha-\alpha')}{\sin^2\alpha\sin^2\alpha'}\times\left(1-\sqrt{(\phi-\chi)/h\nu}\right)\times\left[1+\frac{3}{2}(2-\cos^2\alpha')\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}\right]\boldsymbol{E}_{\parallel}^2 \quad (3)$$

and to $\boldsymbol{E}_{\perp}$,

$$J_{\perp}' = \frac{R_0}{h\nu}\frac{\sin^2\alpha\cos^2\alpha'}{\sin^2(\alpha+\alpha')}\left(1-\sqrt{(\phi-\chi)/h\nu}\right)\times\left[1-\frac{1}{2}\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}\right]\boldsymbol{E}_{\perp}^2 \quad (4)$$

where α and α' are the angles of incidence and refraction. The relation between α and α' will be given as,

$$n_1\sin\alpha = n_2\sin\alpha'$$

in which n_1 is refractive index of silver chloride and n_2 is that of metallic silver.

Then, the total number of such electrons for all particles due to each component are given by the following formula,

To $\boldsymbol{E}_{\parallel}$,

$$J_{\parallel\,\mathrm{Tol}} = \int_0^{\pi}\int_0^{\pi/2}\frac{R_0}{h\nu}\left(1-\sqrt{(\phi-\chi)/h\nu}\right)\times\frac{\sin^2\alpha\sin^2\alpha'}{\sin^2(\alpha+\alpha')\cos^2(\alpha-\alpha')}\times\left[1+\frac{3}{2}(2-\cos^2\alpha')\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}\right]\cos^2\beta\,\mathrm{d}\alpha'\mathrm{d}\beta \quad (5)$$

and to $\boldsymbol{E}_{\perp}$,

$$J_{\perp\,\mathrm{Tol}} = \int_0^{\pi}\int_0^{\pi/2}\frac{R_0}{h\nu}\left(1-\sqrt{(\phi-\chi)/h\nu}\right)\times\frac{\sin^2\alpha\cos^2\alpha'}{\sin^2(\alpha+\alpha')}\times\left[1-\frac{1}{2}\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}\right]\sin^2\beta\,\mathrm{d}\alpha'\mathrm{d}\beta \quad (6)$$

where, for simplicity, the electric vector is taken to be a unit, so that $\boldsymbol{E}_{\parallel}=\cos\beta$ and $\boldsymbol{E}_{\perp}=\sin\beta$. Then, it is furthr put that n_2 is equal to $n_1/10$*, R_0 is independent on α'.

To these approximations, $J_{\parallel\,\mathrm{Tol}}$ and $J_{\perp\,\mathrm{Tol}}$ cnn be calculated by means of approximation integration using trapezoidal rule,

$$J_{\parallel\,\mathrm{Tol}} \fallingdotseq \frac{1-\sqrt{(\phi-\chi)/h\nu}}{h\nu}[0.13+0.27\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}]R_0 \quad (7)$$

$$J_{\perp\,\mathrm{Tol}} \fallingdotseq \frac{1-\sqrt{(\phi-\chi)/h\nu}}{h\nu}[0.09-0.05\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}]R_0 \quad (8)$$

After the absorption process, the silver specks will be gradually destroyed by the mechaism proposed by Mott and Gurney.

* The refractive indexes of metallic silver, silver chloride and silver bromide for $\lambda=656\,\mathrm{m}\mu$ are given as 0.25, 2.05 and 2.23 respectively. J. W. Mellor, "A Comprehensive Trea- tise on Inorg. and Theor. Chem." Vol. III (1930), pp. 331, 396 and 421.

In order to calculated the rate of destruction of silver specks, it is assumed that the rate will depend on the concentration gradient of silver ions.

When the film in which n_0 particles of metallic silver have been contained is exposed to polarized red light, the number of silver ions produded in t minutes is given by the following formula, since the number of such ions is equal to that of inner-photo-electrons,

$$\left.\begin{aligned} n_{\parallel}' &= n_0\{1-\exp(-J_{\parallel \mathrm{Tol}}\cdot t)\} \quad \text{to } \boldsymbol{E}_{\parallel}, \\ n_{\perp}' &= n_0\{1-\exp(-J_{\perp \mathrm{Tol}}\cdot t)\} \quad \text{to } \boldsymbol{E}_{\perp}. \end{aligned}\right\} \quad (9)$$

Now, let dn be the amount of silver ions self-diffusing into silver chloride in time of dt, then this is shown as,

$$\mathrm{d}n = D\cdot S\cdot \Delta C \mathrm{d}t \quad (10)$$

where, S the contact area between silver ion and silver chloride, ΔC is the concentration gradient of these ions and D is diffusion constant.

In (10), it is further assumed that, S is independent on exposing time and ΔC is propotional to the number of producing ions by the assumption made before, then,

$$\Delta C = k\mathrm{d}[n_0\{1-\exp(-J_{\mathrm{Tol}}\cdot t)\}]/\mathrm{d}t$$
k: constant.

With this consideration, the remainded number of colloidal particles of metallic silver after t minutes' exposure is given,

$$n_{\parallel \mathrm{R}} = n_0 - \int_0^t DSk\mathrm{d}\{1-\exp(-J_{\parallel \mathrm{Tol}}\cdot t)\}/\mathrm{d}t\cdot \mathrm{d}t = n_0[1-DSk\{1-\exp(-J_{\parallel \mathrm{Tol}}\cdot t)\}] \quad \text{to } \boldsymbol{E}_{\parallel}, \quad (11)$$

$$n_{\perp \mathrm{R}} = n_0[1-DSk\{1-\exp(-J_{\perp \mathrm{Tol}}\cdot t)\}] \quad \text{to } \boldsymbol{E}_{\perp}. \quad (12)$$

Now, it may be taken that,

$$D = D_0\exp(-U/RT)$$

where, U is the diffusion energy of silver ion at the temperature of $T°$ K, R is gas constant and D_0 is a constant, so that (11) and (12) will be, putting $K = D_0Sk$,

$$n_{\parallel \mathrm{R}} = n_0[1-K\{1-\exp(-J_{\parallel \mathrm{Tol}}\cdot t)\}\times\exp(-U/RT)] \quad (13)$$

$$n_{\perp \mathrm{R}} = n_0[1-K\{1-\exp(-J_{\perp \mathrm{Tol}}\cdot t)\}\times\exp(-U/RT)] \quad (14)$$

Now, if we measure the absorption of of the film, which has been exposed to polarized red light, with the light of which the electric vector is the same direction as that of exposed light, the intensity of the light after passing through the film is,

$$I_{\parallel} = I_0\exp\{-(\lambda_{\parallel} n_{\parallel \mathrm{R}} + \lambda_{\perp} n_{\perp \mathrm{R}})\} \quad (15)$$

with the light of which the electric vector is perpendicular to that of exposed light,

$$I_{\perp} = I_0\exp\{-(\lambda_{\perp} n_{\parallel \mathrm{R}} + \lambda_{\parallel} n_{\perp \mathrm{R}})\} \quad (16)$$

where, $\lambda_{\parallel}$ is the absorption coefficient when the electric vector of observed light is in the plane of incidence and $\lambda_{\perp}$ is that when the electric vector is perpendicular to the plane.

The value of photo-dichroism ($\boldsymbol{D}$) is defined[4] as,

$$\boldsymbol{D} = \ln I_{\parallel} - \ln I_{\perp} \quad (17)$$

hence, putting (15) and (16) into (17), we obtain as,

$$\boldsymbol{D} = (\lambda_{\parallel} - \lambda_{\perp})(n_{\perp \mathrm{R}} - n_{\parallel \mathrm{R}}) \quad (18)$$

Then, from (8), (9), (13) and (14), (18) is written as,

$$\boldsymbol{D} = n_0K(\lambda_{\parallel} - \lambda_{\perp}) \times [e^{-(1-\sqrt{(\phi-\chi)/h\nu})/h\nu\,[0.09-0.05\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}]R_0t} - e^{-(1-\sqrt{(\phi-\chi)/h\nu})/h\nu\,[0.13+0.27\{\sqrt{(\phi-\chi)/h\nu}+(\phi-\chi)/h\nu\}]R_0t}] \times \exp(-U/RT) \quad (19)$$

TABLE I

THEORETICAL AND EXPERIMENTAL VALUES OF DICHROISM AGAINST THE TIME OF EXPOSURE

Wave length of measuring light (mμ)	Time of exposure (Min.) Parameters $n_0K(\lambda_{\parallel}-\lambda_{\perp})\exp(U/RT)$.	5		15		30		60	
		obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	cald.
680	135.4	18	15.2	38	39.7	62	65.4	83	91.4
640	353.5	45	39.6	114	103.7	159	170.8	205	238.4
620	444.9	62	65.4	136	145.2	227	239.1	334	333.9
540	−309.8	—	−37.8	—	−80.8	−152	−148.6	−206	−210.7
520	−227.2	−26	−25.5	—	−66.6	−103	−109.7	−162	−153.3

4) F, Weigert, *Z. Phys. Chem.*, **B3**, 389 (1929).

As seen from (19), D depends on the time of exposure (t), energy of exposing light ($h\nu$), temperature (T) and the wave length of measuring light. ($\lambda_{\parallel}-\lambda_{\perp}$).

With the experimental condition, we put $h\nu=1.8$ eV. and assume that $\phi-\chi$ is 1 eV[2]. and R_0 is equal to 1/2**, then (19) is deduced to be,

$$D=n_0K(\lambda_{\parallel}-\lambda_{\perp})\{\exp(-0.026\,t)-\exp(-0.002\,t)\}\exp(-U/RT) \quad (20)$$

In (20), if T is constant, D is the function of t and ($\lambda_{\parallel}-\lambda_{\perp}$). Thus, by taking ($\lambda_{\parallel}-\lambda_{\perp}$) to be the suitable parameter which is the function of the wave length of observed light, D can be plotted against t. These results are shown in Table I, where, it is found that the theoretical is in fairly good agreement with the experimental.

Furthermore, according to the author's theory, the activation energy of this dichroric change is explained as the diffusion energy of silver chloride, which has been known to be about 7000 cal/mol[5]. In the previous paper, the activation energy has been found to be of the order 7000 cal/mol[1].

From these evidences, it would be said that the author's theory might be permissible.

As has been shown, the parameter method can explain the behavior of dichroism against the time of exposure. This method, however, is not pemissible to solve the values observed with the light of which the wave lengths are in the region between 550 and 580 mμ. As illustrated in Fig. 3, the continuous curves obtained by means of the parameter method are in good agreement with experimental results in the region more than 580 mμ and less than 550 mμ. (being shown as triangle points). This agreement, however, is not satisfactory in the region between 550 and 580 mμ as seen in Fig. 3 (dotted lines).

This will probably be due to the fact that the values of ($\lambda_{\parallel}-\lambda_{\perp}$) are not independent to the time of exposure. This is to be discussed in the next paper.

It has been found that, when the film is exposed to the light of which the wave length is 630 mμ, the value which is observed with this wave length is larger than that with any other wave length, and if exposed to green light, the value

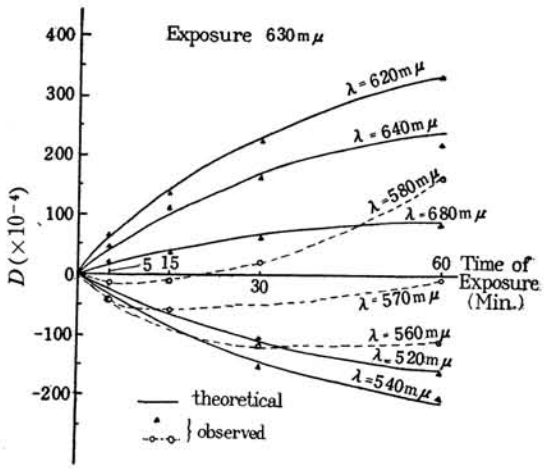

Fig. 3. The curves of theoretical and experimental values of D against the time of exposure.

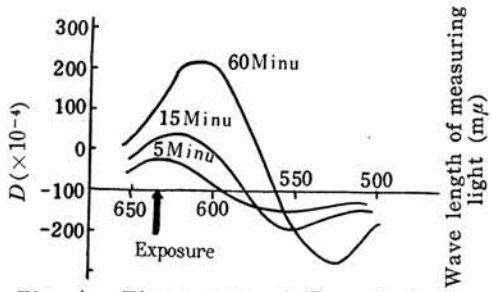

Fig. 4. The curves of D against the wave length of measuring light for exposure to 630 mμ.

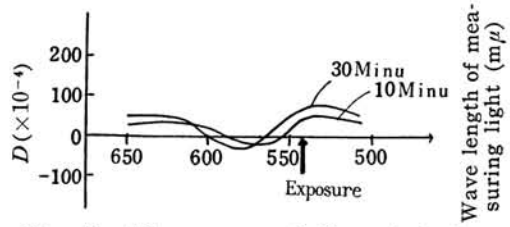

Fig. 5. The curves of D against the wave length of measuring light for exposure to 540 mμ.

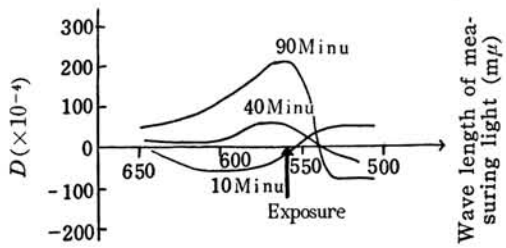

Fig. 6. The curves of D against the wave length of measuring light for exposure to 560 mμ.

5) Ref, (2) p. 47.

** Being A equal to ε, R_0 is to be 1/2 for larger value of α.

observed with green light is maximum and so on. In Figs. 4, 5 and 6, the observed values of dichroism with various wave lengths are shown for the films which are exposed to 630, 540 and 500 mμ respectively, in which the ordinates denote the degree of dichroism and the abscissa the wave length of observed light.

This phenomenon is termed "Color adaptation of photo-dichroism.

The phenomenon of photo-dichroism shows further peculiar behavior. The maximum point, corresponding to color adaptation, is shifted to a shorter wave length region by increasing the exposure. The values in the green region become negative for the film which is exposed to red light, whereas the values in red region become negative for one exposed to green light. These are shown in Figs. 4 and 5. This is called "Inversion effect of photo-dichroism."

Every kind of behavior can not be solved by means of the parameter method. That is, it is recessary to study the variation of $(\lambda_{\parallel}-\lambda_{\perp})$ in order to investigate these complicated kinds of behavior.

From the above point of view, the author is going to investigate the absorption spectra of the films of printed-out silver in various conditions so that these kinds of behavior may be explained by the changing of absorption coefficients.

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