Photo-dichroism of Printed-out Silver. IV. An Explanation of the Relation between Dichroism Curve and Absorption Difference Curve and the Effect of After-, and Pre-illumination in Terms of the Theory of Anisotropic Herschel Effect

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In the previous paper[1], the author has reported that the absorption difference curve of printed-out silver between before and after exposure to natural red (or orange) light is very analogous to spectral dispersion curve of photo-dichroism of printed-out silver which is produced after being exposed to polarized red (or orange) light, and that, if it is assumed that the absorption difference curve would be taken approximately as the dichroism curve, the author has been able to explain the mechanism of "Color adaptation" and "Inversion effect"[2], as well as of the peculiar behavior of dichroism being observed with the light of which the wave lengths are in the region between 580 and 550 mμ.

However, the question why the difference curve is analogous to the dichroism curve has not been answered.

In the present paper, the author has first given a theoretical expression of this relation from the point of view that the phenomenon of photo-dichroism would be anisotropic Herschel effect.

It has been known that the values of photo-dichroism produced after being exposed to polarized red light are to be decreased by subsequent illumination with natural red light, which is called "the effect of after-illumination", and it is also known that the value of dichroism of the film which was previously illuminated with natural red light is smaller than that of non-pre-illuminated film[3].

The author has also considered the mechanism of these effects and given a quantitative explanation, which is in good agreement with experimental results, using the theory of anisotropic Herschel effect[4].

1) I. Kamiya, This Bulletin **30**, 298 (1957).
2) F. Weigert, *Z. phys. Chem.*, **B3**, 377 (1929).
3) E. Elvegård, "Über den Weigert-Effect," Univ. Leipzig (1929), p. 32.
4) I. Kamiya, This Bulletin, **30**, 294 (1957).

Explanation of the Relation between Dichroism Curve and Absorption Difference Curve

In the previous paper, it has been shown that, if $J_{\parallel}$ and $J_{\perp}$ are the numbers of inner-photo-electrons raised from the surfaces of colloidal particles of metallic silver to conduction band of the crystals of silver chloride when exposed to polarized red light of which the electric vectors are in the plane of incidence ($L_{\parallel}$), and perpendicular to the plane ($L_{\perp}$), the plane of incidence is formed with the line of exposing ray and the normal to the surface of colloidal particle of metallic silver, and n_0 is the number of the colloidal particles before exposure, the number of remaining particles which have not been destroyed after t minutes' exposure are given as,

$$n_{\parallel}=n_0[1-\{1-K(1-\exp(-J_{\parallel}t))\}] \quad \text{for } L_{\parallel} \tag{1}$$

$$n_{\perp}=n_0[1-\{1-K(1-\exp(-J_{\perp}t))\}] \quad \text{for } L_{\perp} \tag{2}$$

where K is constant if the temperature is constant.

Then, the value of photo-dichroism (D) produced after t minutes' exposure is given,

$$D=(n_{\perp}-n_{\parallel})(\lambda_{\parallel}-\lambda_{\perp}) \tag{3}$$

where $\lambda_{\parallel}$ and $\lambda_{\perp}$ are the absorption coefficients of observed light of which the electric vectors are in the plane of incidence and perpendicular to the plane.

In eq. (3), it may be assumed that $\lambda_{\parallel}$ is much greater than $\lambda_{\perp}$, as is probable, (3) is approximately taken as,

$$D=\lambda_{\parallel}n_{\perp}-\lambda_{\parallel}n_{\parallel} \tag{4}$$

When the above consideration is permissible, the first term in (4), $\lambda_{\parallel}n_{\perp}$, will approximately show the absorption curve analogous to that before exposure, because the value of $J_{\perp}$ might, in fact, be very small, and the second term, $\lambda_{\parallel}n_{\parallel}$, will be shown as the absorption curve after exposure, which is shown as curve-a and curve-*c* in Fig. 1. This is the reason why the dichroism curve is analogous to absorption difference curve between, before and after exposure to natural red (or orange) light.

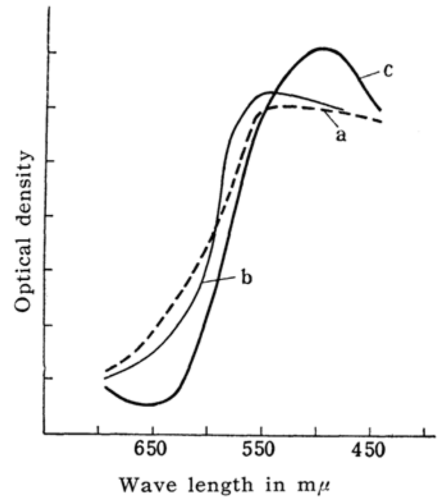

Fig. 1. Schematic representation of the absorption spectra of printed-out Valenta's film. curve-*a*: before exposure, curve-*b*: after a short exposure, curve-*c*: after a long exposure to natural red light.

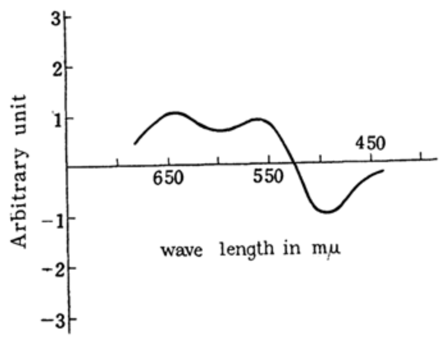

Fig. 2. Absorption difference curve between curve-*b* and curve-*c* in Fig. 1.

For long-exposure, $n_\perp$ will be no longer n_0, and hence the curve of $\lambda_\parallel n_\perp$ will not be shown as curve-*a* but will be shown as curve-*b* in Fig. 1, since $n_\perp$ is decreased a little for a long-time exposure, so that the curve is to be taken as that analogous to the absorption curve after short-time exposure having been shown as curve-*b* in the previous paper[1]. Thus, the values of photo-dichroism being taken as *c*—*b*, it may be found that the spectral dispersion curve of *D* might have two maxima in certain special cases as illustrated in Fig. 2.

In reality, these two maximum points have been observed for long-time exposure by several authors[5] (Fig. 3).

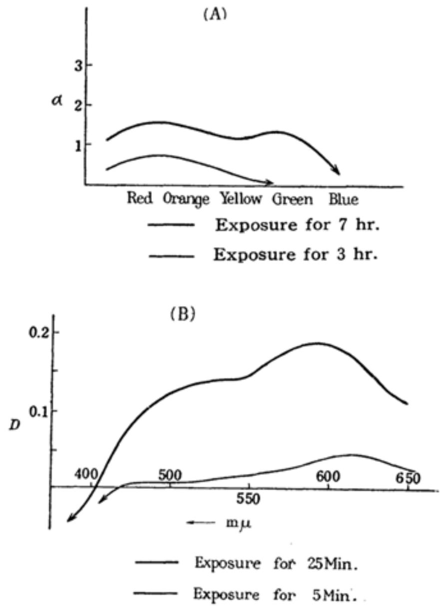

Fig. 3. Spectral dispersion curves of photo-dichroism observed by Horiba, Kondo (A), and Narath, Wasserroth (B).

The Effect of After-illumination

It has been known that the values of photo-dichroism produced after exposure to polarized red light is to be decreased by subsequent illumination with natural red light. This is called, "The effect of after-illumination".

The author has carried out the experiments on the effect using the films of Valenta's emulsion by the way as follows.

The values of dichroism of the films which had been exposed to polarized red light for various periods were measured with red light after being illuminated for 10, 20, 30, 40 and 50 minutes with strong natural red light. The source of illuminating light was the same as described in the previous paper[6]. These results are shown in Table I.

From these, it is seen that; (i). the rate of decreasing during this after-illumination is fast in the initial stages and then becomes slower and slower, (ii). if D and D' are the values of dichroism before and after illumination, the values of $(D-D')/D$,

5) S. Horiba, and T. Kondo, *The Sexagint* (Osaka Fest.) Kyoto Univ., **1927**, p. 68.
A. Narath and K. Wasserroth, *Sc. et Industr. phot.*, **23A**, 39 (1952).
6) I. Kamiya, This Bulletin, **30**, 6 (1957).

TABLE I

VALUES OF DICHROISM FOR VARIOUS PERIODS OF AFTER-ILLUMINATION WITH NATURAL RED LIGHT (D')

Film No.	Time of after illumination with natural red light, (Min.)	0	10	20	30	40	60
I	$D'(2\alpha)$	2.31 ($=D$)	1.61	1.46	1.30	1.16	1.12
	$(D-D')/D$	—	0.30	0.37	0.43	0.50	0.50
II	$D'(2\alpha)$	3.30 ($=D$)	2.26	2.06	1.86	1.67	1.64
	$(D-D')/D$	—	0.31	0.37	0.43	0.49	0.50

D: Values of dichroism before illuminations.

that is the percentages of decreasing values, seem to be independent of D. These values are also illustrated in Table I.

The author has considered the mechanism of this effect and proposed a theory, which enables him to understand why these characters described above are found, from the point of view that the phenomenon of photo-dichroism would be an anisotropic Herschel effect.

As has been shown by the author, the values of dichroism D is given as,

$$D=(n_{\perp}-n_{\parallel})(\lambda_{\parallel}-\lambda_{\perp})$$

It is reasonable to assume that the remaining numbers of $n_{\perp}$ and $n_{\parallel}$ are destroyed by after-illumination with natural red light having the same mechanism as Herschel effect. The light of illumination being divided into two components: one is the most effective to destroy $n_{\perp}$ and the other $n_{\parallel}$ since the destruction of these colloidal particles are the most effective to be destroyed when the electric vector of illuminating light is in the plane of incidence, the numbers of destroyed particles, $\Delta n_{\perp}$, and $\Delta n_{\parallel}$ in each case are calculated from the same point of view as in the previous treatments[4].

$$\left.\begin{aligned}\Delta n_{\perp}&=n_{\perp}[1-\exp(-J_{\parallel}t)]ke^{-\frac{U}{RT}}\\ \Delta n_{\parallel}&=n_{\parallel}[1-\exp(-J_{\parallel}t)]ke^{-\frac{U}{RT}}\end{aligned}\right\}\quad(5)$$

where $J_{\parallel}t$ is the number of inner-photo-electrons after t minutes' exposure, k is constant and U/RT is constant at a constant temperature. Hence, the value of dichroism after t minute's illumination can be obtained,

$$D'=\{(n_{\perp}-\Delta n_{\perp})-(n_{\parallel}-\Delta n_{\parallel})\}(\lambda_{\parallel}-\lambda_{\perp})\quad(6)$$

From (5), (6) becomes,

$$\begin{aligned}D'&=(n_{\perp}-n_{\parallel})(\lambda_{\parallel}-\lambda_{\perp})-(n_{\perp}-n_{\parallel})\\ &\quad\times[1-\exp(-J_{\parallel}t)]ke^{-\frac{U}{RT}}(\lambda_{\parallel}-\lambda_{\perp})\\ &=D-k\cdot D\cdot e^{-\frac{U}{RT}}[1-\exp(-J_{\parallel}t)]\quad(7a)\end{aligned}$$

where D' is the value of dichroism after t minutes' illumination and D that before illumination.

(6) is also written as,

$$(D-D')/D=ke^{-\frac{U}{RT}}[1-\exp(-J_{\parallel}t)]\quad(7b)$$

In order to be in agreement with experimental results, the constants $ke^{-\frac{U}{RT}}$ and $J_{\parallel}$ in (7) are put to 0.5 and 0.08 respectively.

The curve of $(D-D')/D$ against t using the formula of 0.5 $(1-e^{-0.08t})$ and the experimental values are illustrated in Fig. 4. These are in good agreement with each other.

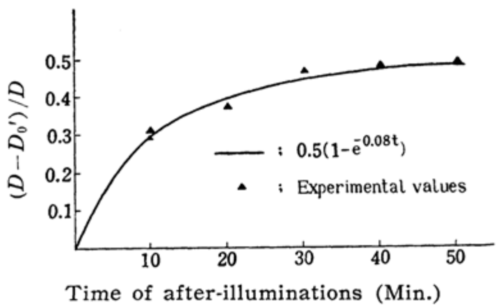

Fig. 4. Theoretical curve and experimental values of the percentages of decreasing dichroism against the time of after-illumination with natural red light.

The value of $J_{\parallel}$ ($=0.08$) used here is somewhat larger than that before ($=0.026$). This deviation will be probably due to the fact that the later is the value when the illuminating light was passed through a Nikol's prism whereas the former is that which was not passed through.

The Effect of Pre-illumination

It is also known that the values of photo-dichroism of printed-out silver which had been pre-illuminated with natural red light is less than that of non-pre-illuminated silver, when exposed to polarized

TABLE II

VALUES OF DICHROISM FOR VARIOUS PERIODS OF PRE-ILLUMINATION WITH NATURAL RED LIGHT (D') (Observed by Elvegård)

Time of exposure to polarized red light (Min.)	Time of pre-illumination with natural red light (Min.)	0	4	16	64
2	D'	12 ($=D$)	8.6	5.6	5.3
	$(D-D')/D$	—	0.28	0.52	0.55
8	D'	29 ($=D$)	21	15	11
	$(D-D')/D$	—	0.28	0.48	0.62
16	D'	35 ($=D$)	29	22	16
	$(D-D')/D$	—	0.26	0.37	0.54

red light. This is called, "The effect of pre-illumination with natural red light" or "die Wirkung einer Vorbelichtung mit naturlichem lichte"[3].

Elvegård has investigated the effect. His results are shown in Table II.

The author has considered the mechanism in regard to the same points as before.

If the number of colloidal particles before being illuminated with natural red light is n_0, and that after t minutes' pre-illumination is n', n' is obtained as before; that is,

$$n' = n_0[1-k'\{1-\exp(-Jt)\}e^{-\frac{U}{RT}}] \quad (8)$$

where J is the number of inner-photoelectrons per minute when illuminated with natural red light.

Next, if the film is exposed to polarized red light for t minutes, the number of colloidal particles of metallic silver which remained undestroyed on exposure to the light of which the electric vector is in the plane of incidence, $n_{\parallel}'$ is

$$n_{\parallel}' = n'[1-k'\{1-\exp(-J_{\parallel}t)\}e^{-\frac{U}{RT}}] \quad (9a)$$

and that to the light of which the electric vector is perpendicular to the plane, $n_{\perp}'$ is

$$n_{\perp}' = n'[1-k'\{1-\exp(-J_{\perp}t)\}e^{-\frac{U}{RT}}] \quad (9b)$$

Thus, the value of dichroism is to be taken as,

$$D' = (n_{\perp}'-n_{\parallel}')(\lambda_{\parallel}-\lambda_{\perp}) \quad (10)$$

From (8) and (9), (10) becomes

$$\begin{aligned} D' &= (n_{\perp}-n_{\parallel})(\lambda_{\parallel}-\lambda_{\perp}) \\ &\quad \times [1-k'\{1-\exp(-Jt)\}e^{-\frac{U}{RT}}] \\ &= D[1-k'\{1-\exp(-Jt)\}e^{-\frac{U}{RT}}] \end{aligned}$$

so that

$$(D-D')/D = k'e^{-\frac{U}{RT}}\{1-\exp(-Jt)\} \quad (11)$$

where D' and D are the values of dichroism to be taken when the film is pre-illuminated for t minutes and if the same film was not illuminated.

In reality, D being unable to be determined by experiment, the following approximation is made.

D obtained with a film is the same as that with another film, though these values are actually slight by different from another.

From this approximation, the author has calculated the values of $(D-D')/D$ using the values of D and D' obrerved by Elvegård. These results are also shown in Table II.

In order to explain the experimental results with (11), the constants $k'e^{-\frac{U}{RT}}$ and J are to be taken as 0.55 and 0.16 respectively. In Fig. 5, the curve of $(D-D')/D$ against t and the experimental values observed by Elvegård are illustrated. It is seen that the theoretical is in fairly good agreement with the experimental for such approximation.

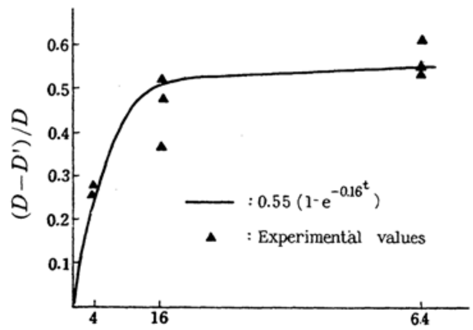

Fig. 5. Theoretical curve and experimental values of the percentages of decreasing dichroism against the time of pre-illumination with natural red light.

From these evidences described in this paper, it is also emphasized that the phenomenon of photo-dichroism would be an anisotropic Herschel effect.

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