Photo-dichroism of Printed-out Silver. I. Some Experimental Evidences in Favor of the View that the Photo-dichroism of Printed-out Silver is an Anisotropic Herschel Effect

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Introduction

A film of a partially printed-out emulsion which has been isotropic becomes anisotropic in its optical nature when exposed to linear polarized red light for a considerable period. This phenomenon which was discovered by Weigert[1] in 1919, is called either the "Weigert effect" or photo-dichroism.

Many discussions on this subject have been carried out by many authors[2].

1) F. Weigert, *Ver. Phys. Ges.*, **21**, 479 (1919).

2) For example, F. Weigert, *Ann. Phys.*, **63**, 681(1920); F. Weigert and J. Shidei, *Z. Phys. Chem.*, **B9**, 344(1930); S. V. Chrdynlsev, *J. Phys. Chem.(USSR)*, **15**, 441(1941); J. Shidei, D. Yamamoto and I. Kamiya, *J. Chem. Soc. Japan*, **72**, 171 (1951); A. Narath and K. Warserroth, *Science et inds. phot.*, **23A**, 38 (1952); I. Kamiya, *J. Chem. Soc. Japan*, **76**, 576 (1955).

Weigert and Stiebel[3] postulated a theory that the colloidal particles of metallic silver in photographic emulsion (such as printed-out silver or latent image) would undergo a change to a vibrating of their structure, as they termed it "*Form-faktor*", in planes parallel to the electric vector of the light when exposed to polarized red light.

Cameron and Taylor advanced[4] the above theory and proposed a mechanism in a somewhat concrete way as follows.

Pointing out the fact that the colloidal particles such as printed-out silver are unlikely spherical but will have their long axes along planes of weakness in crystal of silver halide, they assumed that the particles which resonate to any particular wave-length would be destroyed by prolonged exposure, and that if the long axis of a particle is parallel to the electric vector of the exposed light, the destruction of this resonator would be the greatest.

These discussions are said to be unsatisfactory because of being based on such a metaphysical interpretation as *Form-faktor* or *destruction of resonator*. Moreover, it will be perhaps questionable as to whether such particles can operate in this manner.

The work reported here was undertaken in the hope that a more satisfactory theory of the phenomenon might be formulated.

The present author would prefer to propose the following explanation.

The phenomenon might be some specific effect related to Herschel effect; that is; this might be an anisotropic Herschel effect.

In the next paper, the author will discuss the mechanism, based on Herschel effect, by which the anisotropic nature is formed.

In the present paper, some experimental evidences in favor of this view are reported.

Experimental Evidences

The first part of the work consisted in search for necessary and sufficient conditions for the production of the phenomenon.

The colloidal silver and selenium were prepared by the following method.

Adding the dilute solution of ammonium hydroxide to one per cent of a solution of silver nitrate until the white precipitation became soluble, and adding 5-6 drops of tannin solution; dark reddish colloidal silver was produced. Pouring 2 l. of warm water to 1 g. of selenium oxide, 15-16 drops of the solution of hydrazin hydrate, were added; it was then heated; dark reddish colloidal selenium was produced.

Each colloidal solution was added to gelatin emulsion to prepare the films. The absorption spectra of these films were analogous to that of the film of printed-out silver (printed-out Valenta's emulsion[5]).

These films were exposed to linear polarized red light, so that they could be examined to see if the phenomenon would be produced in them. There was found no phenomenon in the films, which means that silver chloride will be necessary to the phenomenon.

To decide this, another experiment was undertaken.

In the first place, a film of printed-out silver which had been previously fixed in the solution of alkaline hypo to avoid the dissolving silver chloride was exposed to polarized red light. In the second place, the film which had been exposed to the light for a short time was fixed, and then it was exposed again. In the third, it was never fixed. The values of dichroism observed in the three cases are shown in Table I, where, for simplicity, the angle of maximum rotation (2α)* is directly taken to express the degree, as proposed by Weigert.

TABLE I

PHOTO-DICHROISM IN FIXED AND IN UNFIXED FILMS

	Time of Exposure (min.)				
	1	5	10	20	30
No. I	0.00	0.00	0.01	0.02	0.03
No. II	1.52	4.78	5.88	5.90	5.90
No. III	1.00	2.72	3.12	4.44	6.76

It can be seen as the results of these experiments that silver chloride would be necessary to produce the phenomenon.

On the other hand, Zocher and Coper[6] have found the phenomenon in a silver mirror treated with chlorine gas to produce silver chloride on its surface (Chlorierten Silber Spiegeln) when exposed to polarized light, and Cameron and Taylor[4] have also observed it in a single crystal of blue silver chloride (containing printed-out silver).

From this point of view, it can be said that the phenomenon is to be observed in the systems in which the solid medium (such as gelatin or collodion) is absent.

Next, the author has examined the reversible effect in the partially printed-out Valenta's emulsion.

After exposure to the polarized red light for about forty minutes, the plane of polarization of the light was turned by 90°, so that the degree of dichroism began to diminish and soon had

3) F. Weigert and F. Stiebel, *Z. Phys. Chem.*, **B13**, 279 (1931).

4) A. E. Cameron and A. M. Taylor, *J. Opti. Soc. Am.*, **24**, 316 (1934).

5) Valenta in Eder, *Jahrb. Photogr.*, **76**, 960 (1898).

* $D=2\log\tan(45\pm\alpha)$, D : dichroism

6) H. Zocher and M. Coper, *Z. Phys. Chem.*, **132**, 303 (1928).

entirely disappeared. Now, if the exposure was still continued, the phenomenon appeared again in the reversed direction as at first. This has beed termed *reversible effect*[7]. The experimental results are shown in Fig. 1, where it can clearly be seen that the degree of dichroism tends to diminish as repeating the reversed exposure. This tendency depends on the time of pre-illumination to print out the film, i.e. when the film is pre-illuminated for a long time, it is not so remarkable even though the degree is comparatively small, while it is remarkable for a short-time pre-illumination.

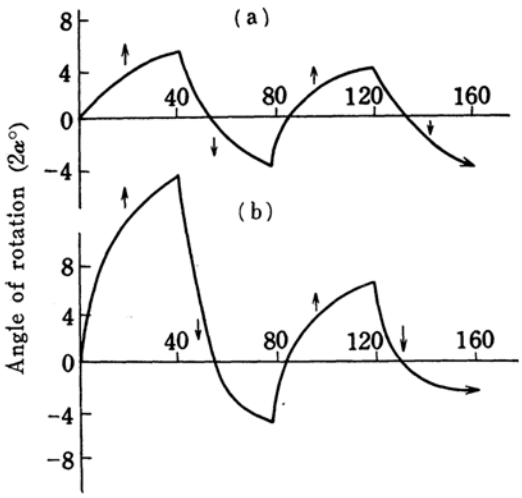

Fig. 1. Reversible effect of Photo-dichroism.
(a) and (b) show the results after 30 and 10 minutes' pre-illumination.

As the result of this, it is found that the production of photo-dichroism would be due to the partial bleaching of colloidal silver.

Finally, it is concluded that silver and silver chloride are the necessary and sufficient conditions to produce the phenomenon.

The phenomenon of photo-dichroism has been observed in the films of some gelatin-dye system as well as in the film of printed-out silver.

According to Ungar, Nikitine, and Yamamoto[8], the phenomenon observed in the films of gelatin-dye is due to an anisotropic bleaching of dye molecule; in other words, the molecules of dye-stuff of which the absorption axes orientate to the direction parallel to the electric vector of the light would be bleached, so that there remain unbleached molecules being arranged in the film after exposure to polarized light.

From this point of view, it will be emphasized that the degree of dichroism of gelatin-dye systems will decrease with increasing temperature owing to disturbance in such an arrangement.

The experimental evidence in favor of the conclusion has not been reported.

For this reason, the author has studied the temperature dependence of the phenomenon in gelatin-dye systems in just the same manner as reported by J. Shidei, M. Hosohara and D. Yamamoto[9].

The experimental results obtained in several kinds of dye-stuff are shown in Table II, where the degree of dichroism was measured with white light using 100 watt tungsten lamp, and is denoted as 2α as before. It can be seen that the degree decreases with increasing temperature as has been expected.

TABLE II

TEMPERATURE DEPENDENCE OF DEGREE OF PHOTO-DICHROISM IN GELATIN-DYE FILMS

(a) Pinacyanol-gelatin Film (observed in white light)

	Time of Exposure (min.)						
	0	1	2	5	10	20	40
6°C	0.00	0.03	0.05	0.08	0.13	0.24	0.41
Temp. 15°C	0.00	0.00	0.02	0.03	0.04	0.07	0.15
40°C	0.00	0.00	0.00	0.00	0.00	0.03	0.03

(b) Pinachrome-gelatin Film. (Observed in white light)

	Time of Exposure (min.)						
	0	1	2	5	10	20	40
6°C	0.00	0.01	0.02	0.04	0.05	0.11	0.16
Temp. 15°C	0.00	0.00	0.01	0.03	0.04	0.07	0.11
40°C	0.00	0.00	0.00	0.00	0.01	0.01	0.02

On the contrary, it has been reported[9] that the degree of dichroism of printed-out silver is increased with increasing temperature. To make this sure, the decisive test was undertaken using partially printed-out Valenta's emulsion in more detail in the same manner as with the method reported by above authors[9]. These results are shown in Table III. From these evidences, it would be concluded that the mechanism of the phenomenon in printed-out silver is different essentially from that of in gelatin-dye systems.

TABLE III

TEMPERATURE DEPENDENCE OF THE DEGREE OF PHOTO-DICHROISM IN VALENTA'S FILM (OBSERVED IN RED LIGHT OF 630 mμ)

	Time of Exposure (min.)			
	5	10	20	40
10°C	1.32	1.54	1.95	2.74
Temp. 30°C	2.72	3.12	4.04	5.86
45°C	4.34	5.88	7.30	9.92
60°C	5.36	6.02	7.06	8.90

7) S. Horiba and R. Kondo, "The Sexagint (Osaka-Fest.)" Kyoto Univ , p. 61.
8) G. Ungar, *Z. phys. Chem.*, **B38**, 427 (1938); S. Nikitine, *Ann. Phys.*, **15**, 284 (1941); D. Yamamoto, *J. Chem. Soc. Japan*, **72**, 948 (1951).
9) J. Shidei, M. Hosohara and D. Yamamoto, *J. Chem. Soc. Japan*, **73**, 184 (1952).

Now, if D_T is the value of dichroism at T°K of temperature, and $\log D_T$ is plotted against $1/T$, then an almost approximate line is to be obtained as is shown in Fig. 2. This means that the relation between D_T and T must be given as,

$$\log D_T = a + b/T \qquad (1)$$

where, a and b are constant.

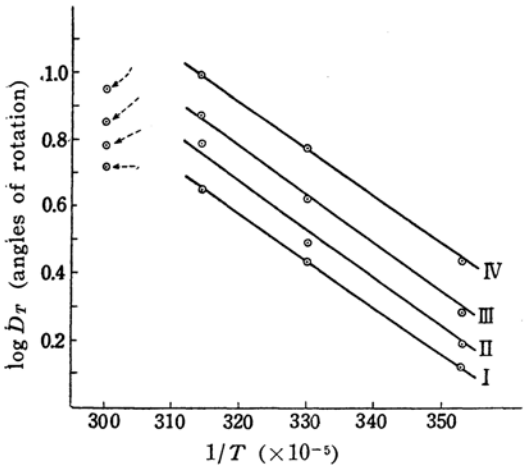

Fig. 2. Log D_T vs. $1/T$.
I, II, III and IV show the results after 5, 10, 20 and 40 minutes excitation.

These results support the author's theory, which will be reported in the next paper, that the D_T is to be shown as,

$$\log D_T = \log D_0 - U/2.3RT \qquad (2)$$

where, R is gas constant, D_0 is a constant and U is activation energy.

The probable value of U obtained from (1), are shown in Table IV.

TABLE IV
ACTIVATION ENERGY OF PHOTO-DICHROIC CHANGE IN VALENTA'S FILM

Time of Exposure (min.)	5	10	20	40
Activation energy (cal./mol.)	6941	7066	7091	7120

Note: On this caluclation, the values observed at 60°C were neglected, probably because of deviation on account of distortion of gelatin molecules.

In the course of these experiments, the source of pre-illuminating light was a Hg-lamp, filtrated with a UVD_1 filter glass, (Matsuda), and that of exposing polarized red light was a five ampare carbon arc filtrated with a filter consisting of a glass tank filled with the scarlet solution transmitting the spectrum region between 630–650 mμ, and a Nicol's prism. These values were measured with the 100 watt tungsten lamp, filtrated with S-63 glass filter (Shimazu).

Discussion

It was shown in the first part of the experimental results that silver and silver chloride are the necessary and sufficient conditions to produce the phenomenon.

It has already been known that the wave length of exposed light which is the most effective is in the region between 600 mμ and 650 mμ, and that the exposing for a long period is necessary to produce the phenomenon. All these facts are very similar to that in Herschel effect. Cameron and Taylor[4] have reported that the phenomenon is not produced in the film, which has been previously printed out, at the temperature of liquid nitrogen. The same behavior has also been observed by Evans and Webb[10] in the experiment on Herschel effect.

Moreover, we have just seen that the activation energy for dichroic change is obtained as about 7000 cal./mol., which is almost the same value as that of diffusion of interstitial silver ions in silver chlroride. According to the mechanism proposed by Mott and Gurney[10] the activation energy to produce the Herschel effect will be explained by the same mechanism (i.e. be diffusion energy of interstitial ions).

There is a suggestion, in opposition to the author's conclusion, that the phenomenon would be due to a solarisation. This suggestion, however, would seem not to be permissible by the following evidences.

If the solarization is, as explained by Eder[11] and Mott[10], due to the formation of a layer of silver chloride covering the metallic silver which has been attacked by the chlorine liberated in the photochemical reaction, it is not possible to explain the following fact that there is no change in the total amount of photo-silver during exposure to polarised light, which has been reported by Cameron and Taylor[4] and Weigert. Moreover, if the mechanism based on such solarization were true, the chlorine atom liberated by exposing light would be able to attack the particle of metallic silver, so that there could be found the phenomenon at liquid air temperature.

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10) N. F. Mott, R. W. Gurney, "Electronic Processes in Ionic Crystals," Oxford Press(1950), p. 243; J. H. Webb and C. H. Evans, *J. Opti. Soc. Am.*, **28**, 294 (1938).
11) J. M. Eder, *Z. Phys. Chem.*, **117**, 293 (1925).