Photo-dichroism of Printed-out Silver. III. Absorption Spectra and Dichroism

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According to the theory which has been developed by the author, the phenomenon of photo-dichroism is probably an anisotropic Herschel effect and when the film of printed-out silver is exposed to linear polarized red light of energy 1.8 eV. for t minutes at T° K, the value of dichroism is given by the following equation,

$$D=n_0K(\lambda_{\parallel}-\lambda_{\perp})\{\exp(0.002\,t)-\exp(-0.026\,t)\}\exp(-U/RT) \qquad (1)$$

where $\lambda_{\parallel}$ and $\lambda_{\perp}$ are the absorption coefficients of the lightof which the electric vectors are in the plane of incidence and perpendicular to the plane. (This plane is constructed with the incident ray and the normal to the surface of colloidal silver). U is activation energy, R is gas constant and n_0K is constant.

When T is constant, with suitable values of parameter $n_0Ke^{-U/RT}(\lambda_{\parallel}-\lambda_{\perp})$, (1) gives curves of D against the time of exposure closely resembling the experimental results, as has been shown in a previous paper[1]. The method of calculating D with the parameter has been called the parameter method.

This parameter method, however. was not acceptable to calculate the values observed with the light of which wave lengths are in the region between 580 mμ and 550 mμ.

This is probably due to the fact that $(\lambda_{\parallel}-\lambda_{\perp})$ is no longer taken to be independent of the time of exposure in this case.

Moreover, the treatment using this method did not say anything about the complicated phenomena such as *Color-adaptation* and *Inversion effect*, for, in order to explain these phenomena, the variation of $(\lambda_{\parallel}-\gamma_{\perp})$ under the action of exposing light must be considered.

From this point of view, the author has investigated the question if the variation of absorption spectrum of the film of printed-out silver is found when exposed to red or orenge light.

Actually, there appeared a new absorption spectrum in the film after prolonged exposure to red or orange light.

A possible explanation of this appearance of the new absorption spectrum could

1) I. Kamiya, This Bulletin, **30**, 294 (1957).

be given when it is assumed that the process would be an anisotropic Herschel effect.

It has been also found that the absorption difference curve by subtracting the absorption curve of an exposed film from of an unexposed one is very similar to the obsorved spectral dispersion curve of dichoroism. Then the author has been able to explain the processes of *Color-adaptation* and *Inversion effect* as well as of the peculiar behavior of the values of dichroism observed with the light of which the wave lengths are in the region between 580 mμ and 550 mμ, which is his main purpose in this paper, assuming that the phenomenon of photo-dichroism would be a results of difference in absorption of two systems, one is that before exposure and the other is that after exposure.

Experimental

The films of Valenta's emulsion were prepared by the same method as described by Weigert[2].

One of these was washed by water so that it was almost free from all soluble silver salts (such as silver nitrate and organic silver compounds), let this plate be called " washed plate ". The other was unwashed: called " unwashed plate ".

Then, the absorption curves were measured by use of Beckmann-type spectrophotometer under various conditions as the following:

1. The absorption curve of washed plate of printed-out silver which had been illuminated with ultra-violet light of Hg-lamp was measured, and after that time that of the washed plate after being exposed to strong natural red light (630 mμ) was measured. The measurements are shown in Fig. 1, where the continuous line (a)

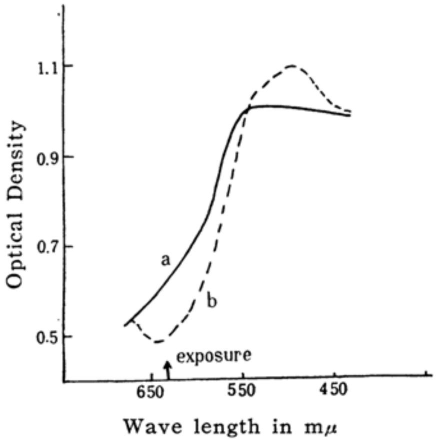

Fig. 1. Absorption curves of washed plate.
a: before exposure,
b: after exposure to 630 mμ.

2) F. Weigert, *Ann. Physik*, **63**, 685 (1920).

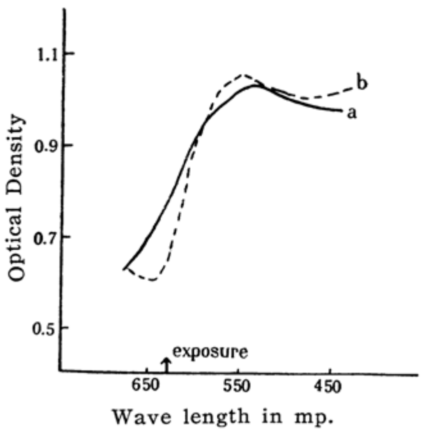

Fig. 2. Absorption curves of unwashed plate.
a: before exposure,
b: after exposure to 630 mμ.

and broken one (b) denote the absorption curves before and after exposure respectivery.

A five ampere carbon are and glass filter of 620–640 mμ spectral region (Shimazu, No. 63) were used as exposing red light source.

2. The curves of the unwashed plate were also measured under the same conditions as that of the washed plate by the same way as described above, which are shown in Fig. 2, where the descriptions are the same as those in Fig. 1. As shown in Fig. 1 and Fig. 2. there can be seen the remarkable *Color-adaptation*, that is, the plates which have been exposed to red light are transparent in red light.

The curves obtained under other conditions (such as under exposure to orange light) are to be shown in the next section.

Discussion

After per-illumination with ultra-violet light, the film of Valenta's emulsion which bad been almost transparent turned brown at first, then became dark red.

This coloring metter, a new absorption band appearing in visible region, is attributed to the formation of colloidal particles of metallic silver[3].

According to Freundlich[4], the absorption spectra of colloidal particles of metallic siver depend on the dimensions of these particles and the maxima of the spectra shift to the shorter wave length side as the dimension become smaller. In Table I, the relation between diameters of the perticles and transmitted light is illustrated.

As seen in Fig. 1 and 2, the transparency of red light increases after exposed to red light (*Color-adaptation*).

3) R. Hilsch and R. W. Pohol, *Z. Phys.*, **77**, 42 (1933).
4) H. Freundlich, "Kapillarchemie", **I**, Leipzig (1932). P.P. 32.

TABLE I
RELATION BETWEEN DIAMETER AND TRANSMITTED LIGHT OF COLLOIDAL SILVER PARTICLES

Diameter of colloidal silver particles in mμ	Transmitted light
25—35	red
35—45	red—violet
50—60	blue—violet
70—80	blue

This may be due to the following mechanism.

When the particles of metallic silver are exposed to red light, the comparative large particles which are sensitive to red light will absorb the light and be destroyed causing Herschel effect so that the transparency in red light increases[1].

Tallert[5], in the study of Herschel effect, has concluded that colloidal particles of metallic silver do nothing but break up into smaller and more numerous parts by Herschel effect. On account of this, the opacity of the film increases in green region by such re-distributed particles which are the most sensitive to green light.

Next, if the absorption difference curve by substructing the absorption curve of exposed film from that of non-exposed one is made, i.e. the curve of (b)—(a) in Fig. 1 or 2, this is almost similar to the spectrometric dichroism curve.

In Figs. 3 and 4, the difference curves and observed dichroism curves of the washed plate and the unwashed plate are shown, where the upper curve donotes the dichroism curve and the lower the

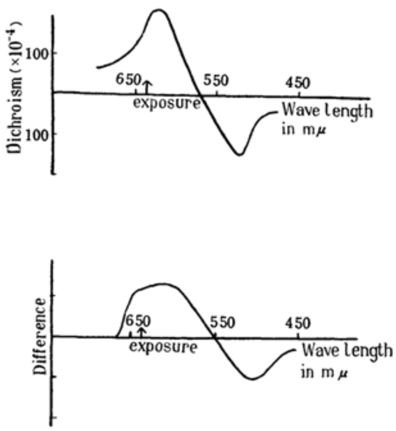

Fig. 3. Absorption difference curve and dichroism curve of washed plate when exposed to 630 mμ.

5) H. Tallert, *Z. phys. Chem.*, **140**, 355 (1929).

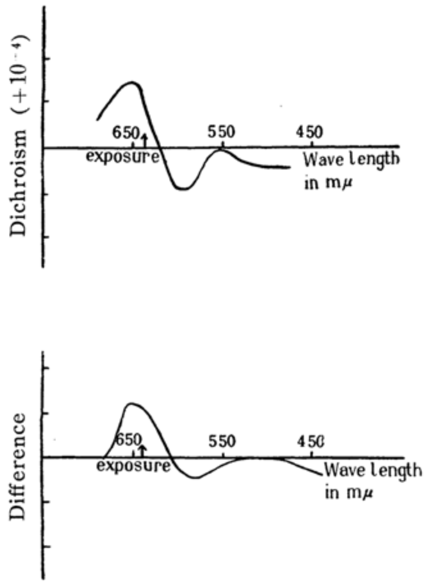

Fig. 4. Absorption difference curve and dichroism curve of unwashed plate when exposed to 630 mμ.

difference curve. The dichroism and difference curves of unwashed plate are almost similar to those of washed plate, but are displaced somewhat in the direction of the long wave length side.

This might be due to the difference of absorption spectra between washed and unwashed plates.

This similarity is also found when the film is exposed to strong orange light (580 mμ). The absorption curves after and before exposure are shown in Fig. 5, where

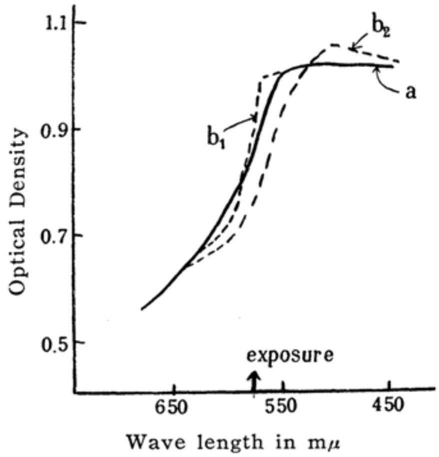

Fig. 5. Absorption curves of washed plates.
a: before exposure-
b_1: after 20 minutes' exposure,
b_2: after 90 minutes' exposure to 580 mμ.

(a) is the absorption curve of the washed plate before exposure, (b_1) and (b_2) are those after exposure for 20 and 90 minutes. Thus the absorption difference curves for 20 and 90 minutes' exposure were obtained as before.

In Fig. 5, these difference curves are shown. It is found that these curves are fairly analogous to dichroism curves (when exposed to linear polarized orange light), which are shown in Fig. 6.

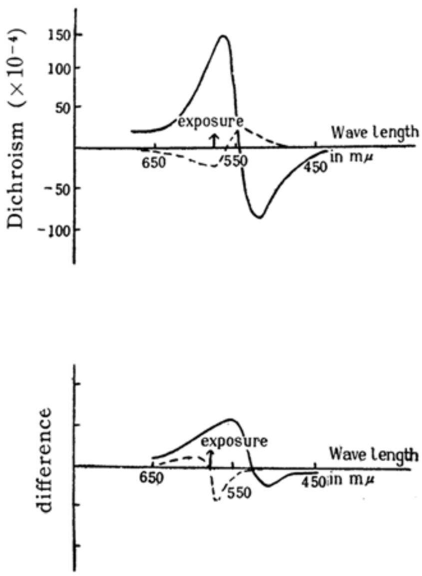

Fig. 6. Absorption difference curve and dichroism curve of washed plate when exposed to 580 mμ.
- - -: after 20 minutes' exposure,
——: after 90 minutes' exposure.

A five ampere carbon arc and a glass filter of 580 mμ and 600 mμ spectral region were used as orange light source.

It should be noticed here that the absorption difference curve is not color-adaptable in the beginning of exposure as the dichroism curve also is.

These results should be kept in mind for it proves to be explained that the photo-dichroism may be a results of difference in absorption between, after and before exposure.

From such a point of view, it is to be assumed that the absorption coefficients of the film before and after exposure might be similar to $a_{\perp}$ and a respectively if the vectrial absorption coefficient having component $a_{\perp}$ and a is perpendicular and parallel to the electric vector of exposing light.

In the previous paper[2], the author has described the phenomenon that the values of dichroism observed using the light of which the wave lengths are in the region between 580 mμ and 550 mμ can not be explained by the parameter method.

By the above assumption, the question, what causes this behavior, can be answered by considering the following mechanism.

The absorption curve of Valenta's plate is to be taken as (a) in Fig. 1 and if the same plate is exposed to red light, the colloidal perticles of metallic silver which are sensitive to red light are re-distributed causing Herschel effect; at the first step of the process the destruction would occur a little as shown as (b_1) in Fig. 7. By increasing exposure, the absorption will change from (b_1) to (b_2) and then to (b_3) in Fig. 7 owing to the fact that further destruction takes place.

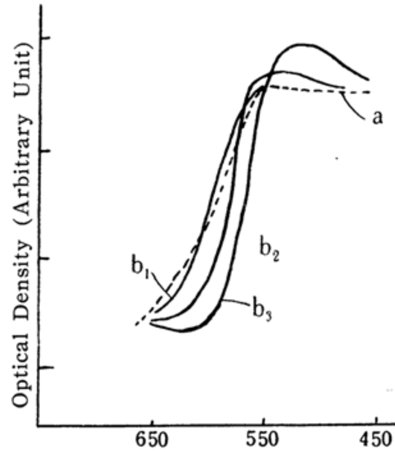

Fig. 7. Schematic changes of absorption curve by increasing exposure to red light.
a: before exposure
b_1, b_2, b_3: after exposure.
The curve will be changed b_1, b_2 and b_3 by exposing.

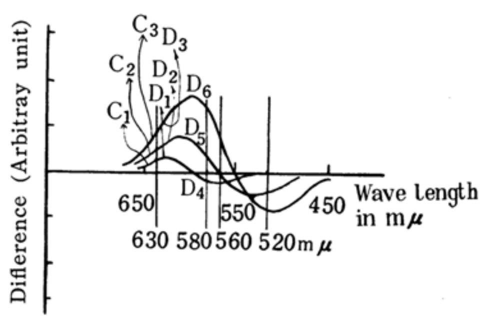

Fig. 8. Schematic absorption difference curve under various time of exposure to red light.
The curve will be changed as c_1, c_2 and c_3 by exposing.

From (a) and (b_1), (b_2), (b_3), the absorption difference curves in each case can be obtained, which are shown as (c_1), (c_2) and (c_3) in Fig. 8.

If the absorption difference curves are treated as dichroism curves, the theoretical values of dichroism against the time of exposure can be obtained by the following method.

When the lines perpendicular to abscissa at the points of 630 mμ, 570 mμ, 560 mμ and 520 mμ are drawn, and the crossing points of these lines to the absorption difference curves in Fig. 8 are denoted as D_1, D_2, D_3, D_4……, these points will be taken as the values of dichroism against the time of exposure and thus semi-quantitative curves observed with 630 mμ, 570 mμ, 560 mμ and 520 mμ can be obtained, which are illustrated in Fig. 9.

The experimental dichroism curves against the time of exposure measured with 630 mμ, 570 mμ, 560 mμ and 520 mμ are also shown in Fig. 10.

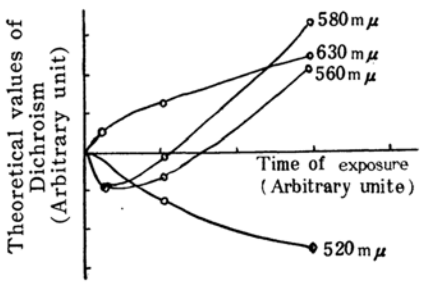

Fig. 9. Schematic change of absorption difference values against the time of exposure under various wave length of measuring light.

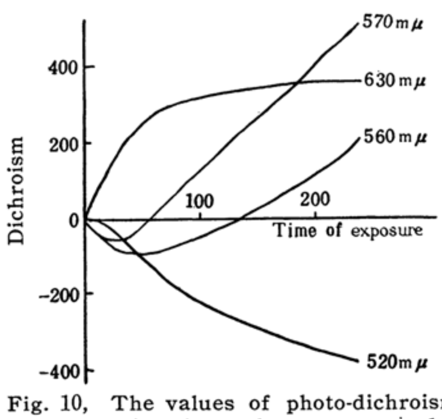

Fig. 10, The values of photo-dichroism against the time of exposure under various wave length of measuring light.

It will be seen that the experimental curves correspond to th theoretical. Thus, it can be concluded that when the film of Valenta's emulsion is exposed to 630 mμ, the comparative large particles which are sensitive to the light will be destoyed and broken up into smaller particles which are sensitive to green light, so that the absorption of the film after exposure to the light will be decreased in the red and increased in the green region, and thus the parameter method is useful.

On the other hand, the amount of colloidal silver which is sensitive to orange light will be increased at the beginning of exposure to 630 mμ because some of collidal particles which are sensitive to red light will change to somewhat smaller particles, so that the values of dichroism are negative when observed with orange light at first, where-by for a long-time exposure the number of the particles which are sensitive to orange light will be descreased because these particles would be sensitive and destroyed more or less when exposed to red light, so that the values turned to positive for a long time.

This is the answer to the question why the parameter method is not useful to explain the behavior of the values observed with the light of which the wave lengths are in the region between 580 mμ and 550 mμ.

From these evidences, the conclusion that the phenomenon of photo-dichoroism of printed-out silver would be produced by the same mechanism as that of Herschel effect might be permissible.

However, the question why the difference curve is analogous to that of dichroism has not been discussed.

Unfortunately, the absorption difference curve obtained by exposure with blue light was too different from the dichroism curve to make such a simple assumption.

This is probably due to the following possible events.

When the film is exposed to blue light, the photolytic process may take place to produce the colloidal particles of metallic silver or *Induced photo-dichoroism* may be caused in the system.

On this reason, the discussion has to be limited to the case when the film is exposed to red or orange light by which the photolysis or *Induced photo-dichoroism* does not occur.

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