# Studies on the Magnetic Dichroism of Dye-Gelatin Films. III. Magnetic Dichroism of Dye-Gelatin Films Excited by Light

By Daijiro YAMAMOTO

(Received May 4, 1951)

In the previous papers[1][2] the magnetic dichroism of dye-gelatin films and its theoretical consideration have been reported. The magnetic dichroism in this case was due to diamagnetic orientation of dye-molecules, and its relaxation phenomena seemed to be due to the visco-elastic properties of solid gelatin.

If dye molecules were paramagnetic, the orientation would be changed, and the magnetic dichroism-time curves would alter their forms. During the last decade G. N. Lewis, M. Calvin, M. Kasha and their colabolators[3] have shown that organic molecules, having conjugated double bonds, turn into a phosphorescent state in rigid media by the illumination of visible and near ultraviolet rays, and its effect is due to a triplet state of $\pi$-electrons. Molecules in triplet state are paramagnetic, and these investigators confirmed the fact by determining the paramagnetic susceptibility of acid fluorescein dissolved in rigid boric acid glass by means of an excellent method using Theorell's micro balance.[4] This phenomenon is the so-called "Photomagnetism," named by them. Dye molecules have remarkable conjugated double bonds. Dye-gelatin films are also good phosphors[5]; in them, gelatin is to a certain extent a suitable rigid glassy solvent. Dye-gelatin phosphors may be due to a triplet state of $\pi$-electrons of double bonds.

From this view-point the author has examined the magnetic dichroism of dye-gelatin films excited by light, and obtained the following results.

## Experimental

**Materials.**—The materials used were the same as mentioned in the previous paper. Dyes were dissolved in a gelatin-water solution at 50°, and smeared on glass plates and then dried. They were good phosphors. Nonphosphoric dyes like azo-dyes were also examined.

**Apparatus.**—All equipment is shown in Fig. 1. The magnet and measuring polarimeter were the same as mentioned in the previous paper, but the distance of the poles was taken as 7 mm. and all experiments were carried out under 9800 gauss (measured by fluxmetre). The sample was a strip of 6 mm. × 20 mm. and it was set in a magnetic field, whose direction was parallel to the surface of the film. The exciting light source was a 6~8 amp. carbon arc or a mercury lamp. Between the light source and the sample along the optical path were set filters of water, $CuSO_4$-water solution, $CuCl_2$-alcohol solution or colored glass filters for each purposes. The excitation of materials by light was carried out by a uniform image of diaphragm projected on the film. The opening of the diaphragm was 10 mm.×10 mm., and the size of the image was 6 mm.×6 mm.

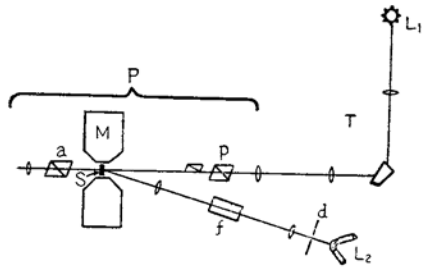


Fig. 1.—Schematic diagram of the equipment for studying the magnetic dichroism: S, sample; P, polarimeter; M, magnet; T, monochrometer; $L_1$, measuring light source; $L_2$, exciting light source; p, polariser; a, analyser; f, filter; d, diaphragm.

Dichroism was measured by means of the polarimeter which F. Weigert[6] used for his studies on the photodichroism. In this method dichroism $D$ is given according to the following relation,

$$D = 2 \log \tan (45° \pm \alpha) = 0.015 \times 2\alpha$$

where $\alpha$ is the angle of rotation of the analyser.

**Difficulties in the Experiments.**—There are many difficulties in this experiment. They are as follows:

(1) D. Yamamoto, *J. Chem. Soc. Japan.* **72**, 693 (1951).
(2) D. Yamamoto, *ibid.*, **72**, 782 (1951)
(3) Their works have been summarized by M. Kasha, *Chem. Rev.*, **41**, 401 (1947).
(4) G. N. Lewis, M. Calvin and M. kasha, *J. Chem. Phys.*, **17**, 804 (1949).
(5) *e. g.*, P. Fröhlich and Z. Gyulai, *Z. Phys.*, **104**, 549 (1937). Now in the author's laboratory dye-gelatin phosphors are being studied by the author with Mr. R. Iwaki.
(6) F. Weigert, *Z. Physik. Chem.*, (B) **3**, 377, (1929).

(1) Dyes are decomposed by light (bleaching or discoloring), especially by near ultraviolet rays.

(2) Phosphorescence and fluorescence of films lead to errors in measured values of dichroism.

(3) Absorption bands of dyes are not necessarily in a suitable position for excitation.

The Difficulty of (1) is removed by using proper filters, and the author's studies on the photodichroism of such materials make clear the effect of bleaching or discoloring in dyes, so we are able to know the most suitable condition for experiments.[7] (2) is very troublesome because of the interruption of the measuring light, so that monochromatic rays for observation diminish. But if we use such materials as phosphorecent bands in long wave length region *e. g.* orange or red, and if their intensities are weak, we can read the correct value of dichroism. (3) is not so troublesome, for we can choose proper materials which have absorption band in the vicinity of 430 or 546 m$\mu$ for mercury lamp. But in practice the intensity of a mercury lamp is not very satisfactory, so that an arc light and proper filters are used for examination after testing by the monochromatic rays of a mercury lamp.

## Results Obtained

Results obtained on the malachite green, rhodamine-B, fuchsine, fluorescein, pinachrome, pinacyanol, azo-dyes *e. g.* chrysoidine, congo red-gelatin films were as follows:

(1) **1.25% Malachite Green-Gelatin Film.**—Malachite green-gelatin film has an absorption band near 620 m$\mu$[8] which is due to shift of $\pi$-electron. By intense illumination of red rays (600~650 m$\mu$, filter: red glass+water) dark deep red phosphorescence[9] (probably about 700~800 m$\mu$) is found. There was no discoloring by excitation for 10 minutes, and it is confirmed by means of a study on photodichroism. Magnetic dichroism—time curves are shown in Fig. 2. A curve in no excitation was the same as mentioned in the previous papers. But by excitation of red rays, curves had altered their shapes as seen in the figure. As soon as the exciting light was shut off the value of dichroism came back rapidly to that of mere magnetic dichroism.

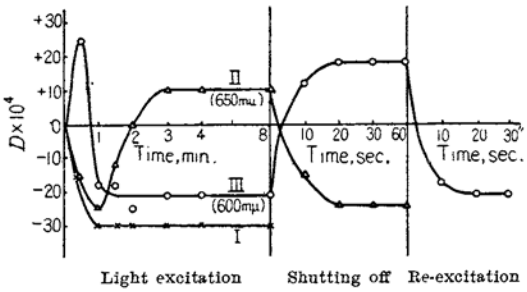


Fig. 2.

In Fig. 2, curve I is due to mere magnetic dichroism, and its dichroism is measured by 650 m$\mu$, curve II is due to the excitation by red rays and measured by 650 m$\mu$, and curve III is due to the same exciting light, but measured by 600 m$\mu$. The opposite sign is due to dispersion. The dispersion of magnetic dichroism in both non-exciting and exciting states was examined. Results obtained are shown in Fig. 3. Both curves are in relation to mirror images.

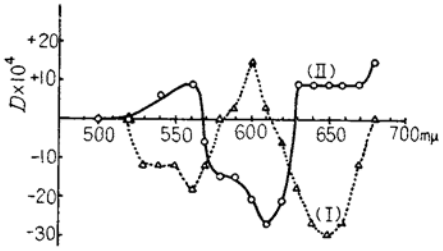


Fig. 3.—Dispersion of dichroism: (I), non-excitation; (II), excitation.

(2) **1.25% Rhodamine B-Gelatin Film.**—Rhodamine B-gelatin film has a green absorption band, and its phosphorescence is orange-red. As exciting light, the following filters were used. (1) $CuSO_4$-water for 546 m$\mu$ Hg, (2) blue glass+water, (3) $CuCl_2$-alcoholic solution and (4) blue glass+$K_2Cr_2O_7$-water for arc light. In each case phosphorescence was visual, and so measuring was hard. (Bleaching was not found.) The effect is evident in the case of filter (2), (3) and (4). Results obtained are shown in Fig. 4. Dispersion of both states is shown in Fig. 5.

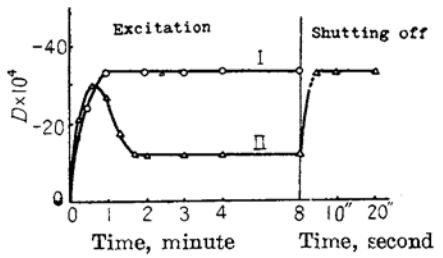


Fig. 4.—(I), non-excitation; (II), excited by blue light (filter No. 2), measured by 560 m$\mu$.

(7) D. Yamamoto and R. Iwaki, *J. Chem. Soc., Japan*, **72**, 852, 854 (1951).

(8) Absorption bands of following dye-gelatin films were given by unpublished works of Mr. R. Iwaki.

(9) Phosphorescence of dye-gelatin films was examined by 1800 r. p. m. phosphorscope.

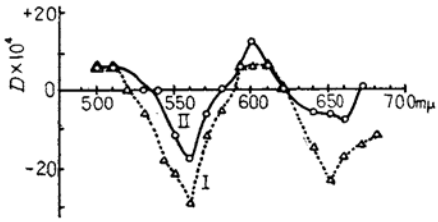


Fig. 5.—Dispersion of dichroism; (I), non-excitation; (II), excited by green light (filter No. 4).

**(3) 1% Fuchsine-Gelatin Film.**—Fuchsine-gelatin film has an absorption band near 546 mμ Hg. Phosphorescence is yellowish orange. The effect of excitation by green light was evident. One of the results is shown in Fig. 6.

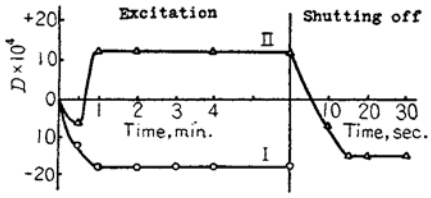


Fig. 6.—(I), non-excitation; (II), excited by green light.

**(4) 0.75% Fluorescein-Gelatin Film.**—Fluorescein- and uranin (Na-fluorescein)-gelatin films are not so good as phosphors. They show, however, the effect by the excitation of blue light. They have absorption bands in 480~490 mμ. Excitation by 490 mμ Hg is suitable, but it is so weak that it can not be used for excitation. Then, excitation by blue light (blue glass+water, arc light) showed the effect. Results obtained are shown in Fig. 7.

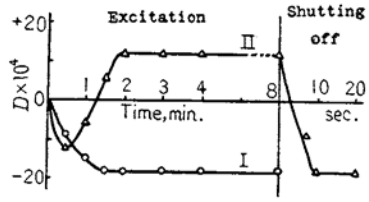


Fig. 7.—(I), non-excitation; (II), excited by blue light, measured by 570 mμ.

**(5) Cyanine Dyes-Gelatin Films.**—1.25% Pinachrome- and 1.25% pinacyanol-gelatin films were examined. They showed weak phosphorescence. Pinachrome-gelatin films showed effect by excitation of blue light, and pinacyanol-gelatin films by red light. But in them slight bleaching was observed. Results are shown in Figs. 8 and 9.

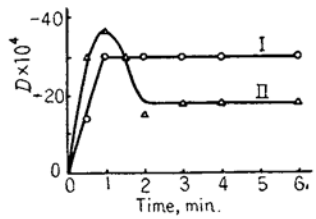


Fig. 8.—1.25% Pinachrome-gelatin film: (I), non-excitation; (II), excited by blue light, measured by 610 mμ.

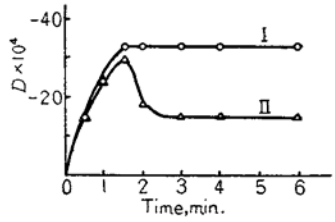


Fig. 9.—1.25% Pinacyanol-gelatin film: (I), non-excitation; (II), excited by red rays, measured by 580 mμ.

**(6) Azo-dyes-Gelatin Films.**—For azo-dyes chrysoidine and congo red were used. Azo-dyes-gelatin films are non-phosphors and they show strong bleaching by illumination of light. Chrysoidine is a very simple monoazo-dye, on the other hand, congo red is a very complicated disazo-dye. On 1% chrysoidine-gelatin film

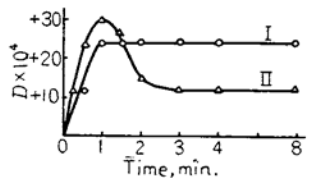


Fig. 10.—1% Chrysoidine-gelatin film: (I), non-excitation; (II), excited by blue light (without water filter), measured by 550 mμ.

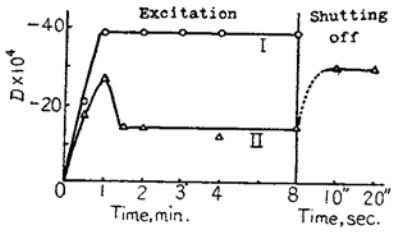


Fig. 11.—1.5% Congo red-gelatin film: (I), non-excitation; (II), excited by blue light, measured by 580 mμ.

the effect was not distinct. 1.5% congo red-gelatin film showed the effect by excitation of blue light, but after shutting off the light the value of dichroism did not come back to that of mere magnetic dichroism. These results are shown in Figs. 10 and 11.

## Summary

There were found considerable changes in magnetic dichroism of some dyes-gelatin films by excitation of light. In malachite green and rhodamine B-gelatin films this effect was very evident, and cyanine dyes-and azo-dyes-gelatin films also showed the same effect. This effect may have something to do with the phosphorescent state of dye molecules, having conjugated double bonds, but nothing to do with bleaching by light. Azo-dyes-gelatin films are non-phosphors, but G. N. Lewis and M. Kasha[10] thought that these materials would have a phosphorescent band in near infra red regions. It is difficult to decide between phosphor and non-phosphor by limited observation in the visible region. This will be discussed in another paper if those experimental results are due to photomagnetism or to other causes.

The author wishes to express his sincere thanks to Prof. Jitaro Shidei for his kind guidance and to Mr. Ryojiro Iwaki for his valuable discussions of these problems, and also to the Ministry of Education for grants in aid out of the Scientific Research Expenditure.

*Department of Chemistry, Faculty of Science,*
*Tokyo University of Education,*
*Otsuka, Tokyo*

(10) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).