

THE BLEACH-OUT ACTION OF LIGHT ON DYES.

[The following paper in the "Annalen der Physik," Vol. 24, No. 14, p. 661, although not of very recent date, has not yet been translated in full, and, therefore, in view of the growing interest in bleach-out processes of colour photography, we may very properly place the results arrived at by P. Lasareff before English workers.—Eds. "Colour Photography" Supplement.]

THE quantitative measurements of the action which light exerts on dyes possess an interest for students of physical chemistry¹ as well as in physiology² and in peripheral vision.³ In the many experiments which have been made in the photo-chemistry of dyes,⁴ either white light or light coming through a filter has been used; a closer examination of the optical properties of dyes has not been undertaken. The purpose of the following paper is, therefore, to fill in the gaps in the visible spectrum, and to ascertain the relation of the decomposed dye to its absorption constants and to the wave-length of the light falling upon it.

Preliminary Experiments.

In order to select from a great number of dyes those in which the change takes place fairly quickly, the bleaching of the dyes was first tested by the white light of a Nernst lamp. The following proved suitable:—Cyanin,⁵ lepidin-cyanin, pinacyanol, pinaverdol, chinaldin-cyanin, and pinachrome⁶, and were examined in collodion films.

The collodion films were prepared by coating a cover-glass (18 + 18 mm.) with a solution containing collodion, 1 part; ethyl alcohol, 1 part; ether, 1 part, and drying protected from dust. The films were dyed either by addition of an alcoholic solution of the dye to the collodion or by bathing the films in an alcoholic dye solution. The dried dyed films keep for a year or more without visible alteration.

On exposing a dyed film in the spectrum of a Nernst lamp for two to four days the dye bleaches out completely in the region of the absorption bands, whilst in other portions it shows

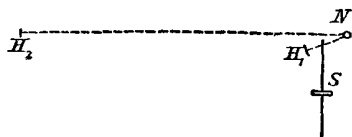


Fig. 1.

no noticeable difference. The film bleached in this way exhibits no visible change on being kept for a year in the dark.

In order to decide if the bleaching action is the result only of the energy received by the film, and is independent of the intensity of light, the following series of experiments was made:—A cover-glass, coated with the dyed film, was cut into two pieces. One, H_1 , was placed 10 cm. from a Nernst lamp, N , the other, H_2 , 100 cm. distant. In front of the film H_1 , a quickly rotating opaque screen, S , was placed, in which was cut a sector of .01 of the circular screen. The relative intensities of light were 1:100, but the energy reaching the two films was equal. The bleaching action was found equal in both cases.

From experiments with pure dye films, which were prepared according to Pfuger⁷ without a vehicle, it was ascertained that such films, when examined under the microscope, showed a grain structure, that they absorb light not as optically homogeneous bodies, and give irregularities in bleaching which appear to be independent of the granular structure of the film.

Methods of Examination.

In order to be able to take photometric measurements of the quantity of absorbed light, and, therefore, of the proportion of undecomposed dye in the dyed film, during the bleaching action by different parts of the spectrum, the arrangement shown in Fig. 2 was used. The horizontal filament of a Nernst lamp (.5 amp.) was placed at the focus of the lens A , the parallel rays therefrom allowed to pass through the direct vision prism, P , and formed as a spectrum on the cover-glass, G , attached to the prism. A König-Martens spectrophotometer⁸ K.M. is so arranged that the slit is 1 to 2 mm. behind the cover-glass G , and the rays of the Nernst lamp fall on the collimator tube of the photometer. In front of one slit is the dyed half of the

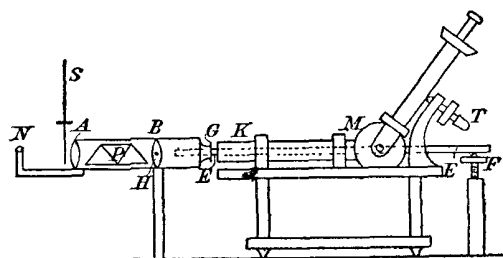


Fig. 2.

cover-glass; in front of the other, the other half of the glass with the film removed. The table E and the screw F allow of the spectrum apparatus being turned round the horizontal axis H , which passes through the horizontal diameter of the lens B . The photometric measurement can be made in different parts of the dyed film in the light falling on the latter. The wave-length of the incident light is measured with sufficient accuracy by the screw T .

For photometric measurements the light was reduced to $\frac{1}{16}$ or to $\frac{1}{32}$ by interposing (during the measurements) a quickly rotating screen, SL , with a sector opening of the proper size before the lens A .

In order to ascertain the distribution of energy in the spectrum, the photometer (Fig. 2) was shifted back, and a line Rubens thermo-pile placed firmly parallel with the photometer slit. By raising and lowering the set screw F the various regions of the spectrum were brought on to the thermo-pile.

To ascertain the corresponding wave-lengths the viewing-tube

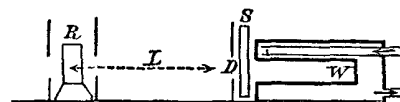


Fig. 3.

of the photometer, with a Gauss eye-piece attached, was shifted by means of the screw T until the image of the surface of the thermopile coincided with the middle of the slit of the eye-piece. The wave-length was then read off on T with sufficient accuracy. The energy was measured by means of a sensitive galvanometer.

The absolute measurement of the radiant energy was done according to R. v. Helmholtz⁹ by the use of the radiation constant measured by Kurlbaum.¹⁰ The apparatus shown in

¹ W. Nernst, "Theor. Chemie," p. 767, Stuttgart, 1906-1907. R. Luther, "Zeit. für Wiss. Phot. Z." (1905), p. 1905.

² C. Timiriazeff, "Proc. Roy. Soc." London, 72, p. 424, 1904.

³ W. Trendelenburg, "Zeit. für Psychol. de Physiol." 37, p. 61, 1904.

⁴ See "Fortschr. der Physik," from 1892-1903.

⁵ From Grabler of Leipzig.

⁶ From Meister, Lucas and Bruning, Hoescht & M.

⁷ A. Pfuger, "Wied. Ann.," 65, p. 181, 1898.

⁸ F. F. Martens, "Verhandl. de Deutsch. Physik. Gesellsch.," I, p. 280, 1899. F. F. Martens and F. Grünbaum, "Ann. der Phys.," 12, p. 984, 1903.

⁹ R. v. Helmholtz, "Die Licht und Wärme-Strahlung verbrennender Gase," Berlin, 1890, p. 12.

¹⁰ F. Kurlbaum, "Wied. Ann.," 65, p. 759, 1893.

Fig. 3 served as an absolutely black body. A blackened brass tube, W, of 2 cm. diameter, is heated in a steam jacket to 100 deg. C. In front of the tube is a circular diaphragm, D, of 1.6 cm. diameter, behind which a removable screen is let drop. At the distance, L, of 8.4 cm. from the diaphragm D the thermopile R is placed. At this spot the intensity of radiation E is:—

$$E = \frac{\sigma [T_1^4 - T_2^4] D^2}{4 L^2} \frac{\text{gm-Cal}}{\text{cm}^2 \text{ sec}}$$

As the radiation constants (according to Kurlbaum) are

$$\sigma = 1.28 \cdot 10^{-12} \vee T_1 = 373^\circ \text{ abs and } T_2 = 293.5^\circ \text{ abs.}$$

$$E = 1.39 \cdot 10^{-4} \frac{\text{gm-Cal}}{\text{cm}^2 \text{ sec}}$$

this intensity of radiation corresponds with a galvanometer (feat) of about 14 Skb. The radiation intensities in the spectrum lie between

$$E_1 = 2.08 \cdot 10^{-4} \frac{\text{gm-Cal}}{\text{cm}^2 \text{ sec}} \text{ (for } \lambda_1 = 530 \mu \mu \text{)}$$

and

$$E = 12.81 \cdot 10^{-4} \frac{\text{gm-Cal}}{\text{cm}^2 \text{ sec}} \text{ (for } \lambda = 648 \mu \mu \text{)}$$

The galvanometer feats were taken at 10 points, and the curve of the energy of the spectrum obtained graphically from these data.

Experiments.

The measurements of the decomposed dyes were made photometrically as follows:—Denoting the ratio of the intensities of the two fields for a given wave-length (by J_0) when an uncoated glass plate is placed before the photometer slit, and that by J_1 when a glass half-coated with dyed collodion is placed in front of the slit, and that by J_2 when after a certain time, Δt the bleaching action has taken place, we obtain (disregarding the slight difference in reflecting power of the coated and uncoated glass):—

$$\frac{J_1}{J_0} = e^{-KC}, \text{ i.e., } KC = \frac{\log J_0 - \log J_1}{\log e}$$

$$\frac{J_2}{J_0} = e^{-K(C-\Delta C)}, \text{ i.e., } K(C-\Delta C) = \frac{\log J_0 - \log J_2}{\log e}$$

where K is a characteristic constant for the collodion film and the respective wave-length, C the concentration of the dye solution, and ΔC the reduction in the concentration by the bleaching action of the light.

The alteration in the proportion of dye due to the decomposition is

$$\frac{\Delta C}{C} = \frac{\log J_2 - \log J_1}{\log J_0 - \log J_1}$$

Given the proportion of incident radiant energy E for the respective wave-length, the dyed film at the commencement of the experiment absorbs the energy e_1

$$e_1 = E \left(1 - \frac{J_1}{J_0}\right)$$

and at the end of the experiment the energy e_2 ,

$$e_2 = E \left(1 - \frac{J_2}{J_0}\right)$$

As the quantities J_1 and J_2 differ but little from one another, the total value of Q of the energy absorbed in bleaching during the time Δt can be placed as a first approximation of sufficient accuracy at

$$Q = \left(1 - \frac{J_1 + J_2}{2 J_0}\right) \Delta t.$$

and E can be taken from the energy curve of the spectrum.

The experiments were made as follows:—The rotating sector screen S (Fig. 2) was set up and the intensities J_0 ascertained by

1 to 4 readings for a series of wave-lengths read off at T. Next the cover-glass with dyed collodion film was put in and the measurements of intensities J_1 taken in the same way for the same wave-lengths. The screen S was then removed and the film exposed to the unscreened light for 3 to 17 minutes, the screen again inserted, and the intensities J_2 measured for the same wave-lengths.

The intensities J_0 were practically identical. The intensities J_1 in the absorption maximum of the collodion film amounted to about .2 to .9, and the bleach-out action was adjusted so that ratio $J_1 : J_2$ was about .9 to .7. Remembering that as the measurements can be made in a mean of within $\pm .3$ to .5 per cent., the measurement of $\Delta C/C$ is accurate in the absorption maximum to about 15 per cent.

The series of measurements of J_1 and J_2 took about three minutes, the bleaching action from three to seventeen minutes. As the photometric measurements were done with light of $\frac{1}{15}$ to $\frac{1}{30}$ the strength, further alteration of the film was not possible, the more so that the series of measurements in the two series were very similar.

The results of the measurements for different wave-lengths λ are given in the tables for the different dyes, in which the ratios J_1/J_0 and J_2/J_0 are given, as well as the calculated fraction $\Delta C/C$ of the bleached dye. Also, the measured radiant intensities E for the different wave-lengths and the proportions of energy Q (in gm-cals) absorbed during the experiments are also given.

The results can be epitomised as follows:—Within errors of observation the decomposed dye in an absorption band is directly proportional to the absorbed energy, and independent of the wave-length of the incident light.

In order to ascertain how great is the radiant energy necessary for the decomposition of 1 gm dye, collodion solutions of definite strength of dye were coated on large glass surfaces in uniform films. The area was ascertained and the dye per sq. cm. calculated. The dried film was then exposed to the spectrum, as already described, and the dye decomposed in a certain time ascertained, in addition to the energy absorbed in this time. The energy spent in the decomposition of 1 gm. of dye would thus be calculated. The results were as follows:—

Chinaldin-cyanin	16,000	} gm-cals.
Pinachrome	30,000	
Cyanin	48,000	
Lepidin-Cyanin	58,000	
Pinaverdol	117,000	} gm-dye.

Comparing the above data with the heat of combustion of organic bodies, it would seem that only a small fraction of the absorbed radiant energy is used in the photo-chemical decomposition of the dye. The larger part is spent in warming the absorbent film.

TABLE I.
Cyanin (Time of Bleaching, 3 min.).

λ in $\mu \mu$	554	573	593	604	617	642
J_1/J_0	0.759	0.569	0.495	0.542	0.640	0.893
J_2/J_0	0.769	0.610	0.566	0.624	0.701	0.906
E.g.—Cal./cm ² sec ..	$3.47 \cdot 10^{-4}$	$4.51 \cdot 10^{-4}$	$6.25 \cdot 10^{-4}$	$7.29 \cdot 10^{-4}$	$9.02 \cdot 10^{-4}$	$13.53 \cdot 10^{-4}$
$\Delta C/C$	0.05	0.12	0.19	0.23	0.21	0.12
Q.g.—Cal./cm ²	0.0147	0.0334	0.0529	0.0547	0.0536	0.0246
K. $\Delta C/K_m \Delta C_m$	0.10	0.49	0.95	1.00	0.66	0.10
KQ/K _m Q _m	0.11	0.51	1.00	0.90	0.65	0.07

TABLE II.
Pinachrom (Time of Bleaching, 4 min.).

λ in $\mu \mu$	536	554	574	584	596	620
J_1/J_0	0.811	0.805	0.711	0.703	0.813	0.939
J_2/J_0	0.822	0.815	0.753	0.746	0.834	0.989
E.g.—Cal./cm ² sec.	$1.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$
$\Delta C/C$	0.07	0.05	0.17	0.17	0.12	0.00
Q.g.—Cal./cm ²	0.0044	0.0059	0.0122	0.0146	0.0115	0.001
K. $\Delta C/K_m \Delta C_m$	0.23	0.19	0.96	1.00	0.42	0.00
KQ/K _m Q _m	0.18	0.25	0.81	1.00	0.46	0.00

TABLE III.
Lejdincyanin (Time of Bleaching 6 min.).

λ in μ μ	536	554	574	596	620	648
J_1/J_0	0,843	0,750	0,613	0,514	0,762	1,00
J_2/J_0	0,843	0,764	0,632	0,583	0,802	1,00
E_g —Cal./cm ² sec. ...	$1,04 \cdot 10^{-4}$	$1,46 \cdot 10^{-4}$	$1,87 \cdot 10^{-4}$	$2,50 \cdot 10^{-4}$	$3,33 \cdot 10^{-4}$	$5,41 \cdot 10^{-4}$
$\Delta C/C$	0,00	0,06	0,10	0,19	0,23	0,00
Q_g —Cal./cm ²	0,0059	0,0128	0,0257	0,0406	0,0267	0,0000
$K\Delta C/K_m\Delta C_m$	0,00	0,15	0,38	1,00	0,51	0,00
KQ/K_mQ_m	0,04	0,14	0,48	1,00	0,28	0,00

TABLE IV.
Chinaldincyanin (Time of Bleaching, 16 min. 40 sec.).

λ in μ μ	536	554	574	596	620
J_1/J_0	0,190	0,113	0,111	0,634	0,957
J_2/J_0	0,221	0,146	0,160	0,695	0,957
E_g —Cal./cm ² sec. ...	$1,04 \cdot 10^{-4}$	$1,46 \cdot 10^{-4}$	$1,87 \cdot 10^{-4}$	$2,50 \cdot 10^{-4}$	$3,33 \cdot 10^{-4}$
$\Delta C/C$	0,09	0,12	0,17	0,20	0,00
Q_g —Cal./cm ²	0,083	0,127	0,162	0,084	0,014
$K\Delta C/K_m\Delta C_m$	0,41	0,71	1,00	0,25	0,00
KQ/K_mQ_m	0,39	0,78	1,00	0,11	0,00

TABLE V.
Pinaverdol (Time of Bleaching 15 min.).

λ in μ μ	536	554	574	596	620
J_1/J_0	0,376	0,210	0,241	0,794	0,964
J_2/J_0	0,392	0,242	0,291	0,805	0,966
E_g —Cal./cm ² sec. ...	$1,04 \cdot 10^{-4}$	$1,46 \cdot 10^{-4}$	$1,87 \cdot 10^{-4}$	$2,50 \cdot 10^{-4}$	$3,33 \cdot 10^{-4}$
$\Delta C/C$	0,04	0,09	0,13	0,06	0,06
Q_g —Cal./cm ²	0,058	0,102	0,124	0,045	0,010
$K\Delta C/K_m\Delta C_m$	0,32	0,74	1,00	0,07	0,01
KQ/K_mQ_m	0,32	0,90	1,00	0,06	0,00

TABLE VI.
Mixture of Pinaverdol + Pinacyanol (Time of Bleaching 10 min.).

λ in μ μ	554	566	568	573	582	593	604	630
J_1/J_0	0,372	0,288	0,277	0,310	0,512	0,372	0,279	0,671
J_2/J_0	0,461	0,432	0,447	0,447	0,569	0,559	0,648	0,719
E_g —Cal./cm ² sec. ...	$3,47 \cdot 10^{-4}$	$3,82 \cdot 10^{-4}$	$4,16 \cdot 10^{-4}$	$4,51 \cdot 10^{-4}$	$5,21 \cdot 10^{-4}$	$6,25 \cdot 10^{-4}$	$7,29 \cdot 10^{-4}$	$11,10 \cdot 10^{-4}$
$\Delta C/C$	0,22	0,32	0,37	0,31	0,16	0,46	0,53	0,17
Q_g —Cal./m ²	0,122	0,147	0,159	0,168	0,144	0,195	0,257	0,203
$K\Delta C/K_m\Delta C_m$	0,32	0,60	0,70	0,54	0,16	0,68	1,00	0,16
KQ/K_mQ_m	0,37	0,56	0,62	0,60	0,29	0,59	1,00	0,25

P. LASAREFF.

THE GRADATION OF PLATES IN DIFFERENT COLOURED LIGHTS.

DR. R. LOHMEYER has published, in the "Zeitschrift für Reproduktions-technik," a lengthy paper on the above subject, using both bathed and emulsion-dyed plates. The article is illustrated by numerous curves and tables, which do not permit of useful abstraction, but the following are the author's conclusions drawn from his results:—

1. All curves begin with a convex part curved to the abscissæ, and then pass through the point of flexion to a part which is concave. The transition is in many cases so gradual that there is a straight line portion between the two curves. It is possible therefore to divide the curve into three parts. These three parts correspond to the three stages which are photographically known as under-, normal-, and over-exposure, and these three stages are found with every wave-length, whether these are those of the characteristic maximum of the plate, of the colour-sensitiveness, or a minimum. (a) The more rapidly the curve passes from the first to the second phase and the greater the whole curve, the higher the sensitiveness of the plate; the longer the straight part the better the gradation, even with great differences of exposure. (b) The more gradual the transition from the second to the third stage the greater the latitude of the plate and its value for practical work.

2. There is an exposure of maximum action for every wave-length, and when this is passed the activity of this kind of light is exhausted, even with increase of exposure. There must be, therefore, particles of different sensitiveness in the film.

3. With sensitised plates the characteristic silver bromide maximum and that of the dye can always be seen. (a) Independently of any slight fogging action a dye may shift the blue maximum towards the green. (b) The dye also influences the original gradation of the plate, so that the gradation of the blue maximum runs more or less parallel to that of the dye. (c) This action decreases with increase of spectral separation of the absorption band of the sensitiser from the silver bromide maximum. It is most striking with an erythrosine bathed plate, whilst with a dimethyl-chinoline blue plate, where the distance of the maxima is very great, the maxima curves, even in the phase of normal exposure, cut one another. This difference of gradation can be even seen in an eosine plate, though not very markedly. (d) The addition of a second dye with an absorption between the characteristic maximum of the plate and the first sensitiser makes the curves again parallel. Efforts to utilise as many parts of the spectrum as possible, and to lessen the minima has thus the further advantage of giving a better total gradation.

4. The maxima of the eosines give a comparatively hard gradation in the normal region, and almost no gradation in the region of over-exposure. The cyanines not only work much softer, but their gradation can be used further in the over and under-exposed parts, as the transition is more gradual.

5. No marked difference was found between the emulsion-dyed and bathed plates as regards gradation, but merely a shift of the maxima of the sensitiveness curves.

Correspondence.

** Correspondents should never write on both sides of the paper. No notice is taken of communications unless the names and addresses of the writers are given.

** We do not undertake responsibility for the opinions expressed by our correspondents.

AUTOCHROME PHOTOGRAPHY FOR THE TOURIST.

To the Editors.

Gentlemen,—Now that we are hoping for warmer days and thinking about summer outings it would help many who are interested in the new Autochrome plate if you would give us some hints for its use by tourists. It would be a great advantage to develop the plates on the spot, but it is obviously impossible to take on one's travels the large number of solutions recommended by Messrs. Lumière. One of your correspondents recently told us that the Autochrome plate can be successfully treated with two solutions only—a rodinal developer and the C reversing solution. I have not had the opportunity of testing this for myself, but if your correspondent's conclusions are confirmed by the experience of others the traveller's outfit will be very much lightened, and the development of Autochromes on tour comes at once "within the range of practical politics." Rodinal is the easiest possible reagent to use on a journey, and the "Almanac" for 1908 contains suggestions which will make it a specially handy developer for the tourist.

Is it possible, I should like to ask, to put up the reversing solution C into a handy form for travel? Does it keep well, and can it be used over and over again with impunity?

Then will a few inches of magnesium wire do as well as daylight for the traveller who finds impossibilities for development at his hotel, except in his bedroom at night? Or do any of the new daylight developing machines meet his often hard case?

An answer to these questions, and such as these, would, I am sure, help many besides myself, who look forward with constant pleasure to the monthly appearance of your "Colour Photography" Supplement.—I am, Sirs, yours, etc.,

J. M. J.

[We have had very little experience of the two-solution method of treating Autochromes, but others have used it, and we see no reason why it should not be successful. If intensification proves to be necessary it can easily be done at a later time. The C solution could no doubt be applied in the form of tablets, and we believe that one firm already supply it in this form. Magnesium ribbon can certainly be used for exposure, and we often find it convenient at night. Messrs. Beck have introduced a tank for developing Autochromes that could be used in daylight with the help of a changing bag.—Eds. "Colour Photography" Supplement.]