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## Spectral Sensitivity and Light Absorption of Dye-Sensitized Photographic Emulsions\*

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Direct measurements on emulsions sensitized with certain cyanine dyes show a correspondence between the shapes of the light absorption and sensitivity curves in the region of color sensitizing. It was found that the absorption curves of silver bromide dyed with some cyanine dyes are essentially the same as the absorption curves of the dyes in saturated inorganic salt solutions. It is postulated that there are two types of adsorption of cyanine dyes to silver bromide, aggregated and molecular. An emulsion sensitized with a cyanine dye under proper conditions can show sensitivity in different spectral regions, corresponding to the light absorption characteristics of dye adsorbed in the aggregated and molecular states.

A CONSIDERABLE literature has been developed concerning optical sensitizing of photographic emulsions by dyes and the relationship between the light absorption of the emulsion and the spectral distribution of sensitivity. Reviews of the status of this question have been given by Bokinik<sup>1</sup> and Rabinovitch,<sup>2</sup> Mecke,<sup>3</sup> and Eggert<sup>4</sup> have briefly discussed the problem but were able to arrive at no definite conclusions because of the lack of experimental data.

One isolated experiment on the relation between light absorption and sensitivity has been reported. Eder<sup>5</sup> qualitatively determined the absorption of a silver bromide emulsion sensitized with eosin and found that the region of maximum light absorption coincided with the region of maximum sensitivity.

It is clear that light must be absorbed by the dyed halide of a sensitized emulsion before the latter can be photosensitive, but it is not necessarily true that sensitivity will exist at all wavelengths where absorption occurs. It is one purpose of this communication to present data which establish a direct correspondence between the shape of the light absorption curve of emulsions sensitized with certain dyes and the spectral sensitivity of the emulsions.

A second question of importance in optical sensitizing is that of the state of the dye when

adsorbed to silver halide. No definite, direct experimental evidence dealing with this question appears to have been reported. There are data in the literature<sup>6-11</sup> on the molecular states of sensitizing dyes and their light-absorption characteristics in various solvents. Sheppard<sup>6</sup> observed systematic variations in the absorption curves of some cyanine dyes with changing solvent, and found that aqueous solutions were generally different in absorption characteristics from non-aqueous solutions. As the result of another study, Sheppard<sup>7</sup> concluded that certain cyanine dyes in aqueous media exist as colloidal aggregates, and that the absorption spectra of the colloids are different from those of dyes in true solutions. Bloch and Hamer<sup>8</sup> and Jelley<sup>11</sup> observed in some cases that an aqueous salt solution of a cyanine dye exhibited markedly different absorption properties from those of a methanol solution of the same dye.

Scheibe and co-workers<sup>12</sup> and Jelley<sup>11</sup> have recently reported studies on the aggregation of a cyanine dye, *N*, *N'*-diethylpseudocyanine chloride, in aqueous solutions. Scheibe and co-workers have established that not only does this dye change its state of aggregation in aqueous media, but that it is adsorbed to certain inorganic

\* Communication No. 642 from the Kodak Research Laboratories.

<sup>1</sup> J. I. Bokinik, *Kino-Photo Industry*, **3**, 84 (1933).

<sup>2</sup> A. J. Rabinovitch, *Acta Phys.-Chim. U. S. S. R.*, **2-3**, 369 (1935).

<sup>3</sup> R. Mecke, *Trans. Faraday Soc.*, **27**, 370 (1931).

<sup>4</sup> J. Eggert, *Trans. Faraday Soc.*, **27**, 386 (1931).

<sup>5</sup> J. M. Eder, *Phot. Korr.*, **23**, 146, 574 (1886).

<sup>6</sup> S. E. Sheppard, *Phot. J.*, **32**, 300 (1908).

<sup>7</sup> S. E. Sheppard, *Proc. Roy. Soc.*, **82A**, 256 (1909).

<sup>8</sup> O. Bloch and F. M. Hamer, *Phot. J.*, **59**, 21 (1928).

<sup>9</sup> S. E. Sheppard and H. Crouch, *J. Phys. Chem.*, **32**, 751 (1928).

<sup>10</sup> G. Scheibe, *Angew. Chem.*, **49**, 563 (1936).

<sup>11</sup> E. E. Jelley, *Nature*, **138**, 1009 (1936); *ibid.*, **139**, 631 (1937).

<sup>12</sup> G. Scheibe, L. Kandler, and H. Ecker, *Naturwissenschaften*, **25**, 75 (1937). This note contains references to earlier papers.

materials in a state corresponding to that in the aqueous system. They report shifts in absorption spectra corresponding to this change.

The results of the present investigation were obtained prior to the publication of the work of Scheibe, and establish that changes in state of certain cyanine dyes occur in aqueous media. It has been found that this change can most easily be produced by adding certain inorganic salts to the aqueous system. The present investigation has led to the observation that the light-absorption characteristics of silver bromide, to which certain cyanine dyes have been adsorbed, are essentially the same as those exhibited by the dyes in an aqueous salt solution. These results are in agreement with those of Scheibe *et al.* for dyes adsorbed to glass, quartz, etc. They indicate that the dye adsorbed to silver bromide is frequently in a state of aggregation similar to, if not identical with, that exhibited in aqueous salt solutions.

In the following experiments, much of the work has been done with microcrystals of silver halide as found in photographic emulsions. These emulsion "grains" formed in gelatin solution have been used for several reasons. First, data obtained can be applied directly to the problem of the elementary photographic process. Secondly, the surface of the silver halide is more accurately reproducible in this form. Experiments made with gelatin-free silver halide have established that gelatin has little effect on the light-absorption properties of sensitizing dyes adsorbed to silver halide.

The sensitizers used were cyanines. Attention has been confined to these dyes because of their general superiority for photosensitization when compared with acid dyes, such as erythrosin.

#### EXPERIMENTAL

The work here reported was facilitated by the use of the automatic spectrophotometer designed and developed by Hardy.<sup>13</sup> The percentages of light reflected at any wave-length were directly measured over the region 4000Å–7000Å with this instrument; for qualitative purposes this reflection curve may be taken as the inverse of the absorption curve. The spectral distribution of

photographic sensitivity of the emulsions was qualitatively determined by exposure through a neutral optical wedge in front of a transmission grating.<sup>14</sup> The effect of energy distribution in the source has been calculated and found to produce negligible differences between the apparent and true maxima of sensitivity.

In some experiments, reflection measurements were made on sensitized emulsions coated and dried on glass plates; the emulsions contained about 4 grams of silver bromide and 6 grams of gelatin per 100 cc, and usually 2 mg of dye dissolved in 5 cc of methanol were added just before coating. In other experiments the dye was added to the emulsion, the grains were removed by centrifuging, taken up in a little water, and then pipetted onto glass plates and allowed to dry before spectral analysis.

Reflection curves were run on samples of pure silver bromide dyed from water solutions, and also on samples of pure silver bromide dyed from methanol. In both cases 4 grams of thoroughly washed silver bromide in 100 cc of water or methanol and 2 mg of dye were used; in the case of dye adsorption from alcohol, the bromide was washed several times with methanol before addition of dye. The bromide was separated either by settling or by centrifuging and was coated on glass plates for analysis. In several cases, the separated, dyed silver bromide was taken up in a small quantity of 3 percent gelatin solution, placed on glass plates and allowed to dry before the determination of its spectral reflection.

Several experiments were made with pure silver iodide and pure silver chloride. The amounts of dye and of silver halide used were approximately the same as those in the bromide experiments.

In one series of experiments the silver-ion concentration of a bromide emulsion was varied between  $10^{-3}$  and  $10^{-10}$  molar by adding silver nitrate or potassium bromide solutions before addition of the dye. The grains were separated by centrifuging and their spectral reflection determined. In another series, the pH of the emulsion was adjusted to values between 5.75 and 9.85, and the absorption characteristics of the emulsion grains were measured. In a third

<sup>13</sup> A. C. Hardy, J. Opt. Soc. Am. **18**, 96 (1929).

<sup>14</sup> L. A. Jones, *Photographic Sensitometry*, second edition (Eastman Kodak Co., 1934), p. 144.

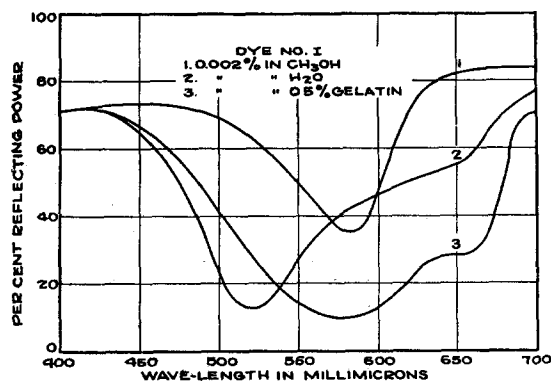


FIG. 1.

series, the amount of dye added to 100 cc of emulsion was varied between  $\frac{1}{2}$  mg and 10 mg and the reflection of the grains measured. The measurements of silver-ion and hydrogen-ion concentration were made by using a silver bromide and glass electrode, respectively, in an electrical system employing a condenser and ballistic galvanometer.

In all of the experiments, the completeness of adsorption was estimated from the color of the gelatin solution, water, or alcohol from which the silver salts had been separated. In almost all cases there was no perceptible color in the liquid medium. Mention will be made in cases where adsorption was not complete, otherwise it is understood that substantially all of the dye was taken up by the silver halide.

During the spectral analysis there was occasionally slight fading of the dye and darkening of the halide. It was therefore necessary to change the position of the sample two or three times during a single analysis. The fading and darkening effects were thus reduced but not completely obviated. For this reason the reflection curves at the regions of minimum reflection (maximum absorption) are slightly flattened. This effect does not alter the general shape of the absorption curve, and the error involved does not seem important for the purposes of the experiments.

The absorption spectra of the sensitizing dyes in methanol and in aqueous solutions were determined by the automatic spectrophotometer. It was found that during measurement with the usual spectrophotometers, bleaching of the dye was excessive. The concentration of dye in the

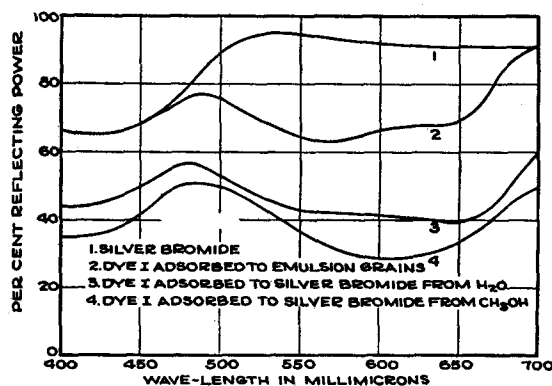


FIG. 2.

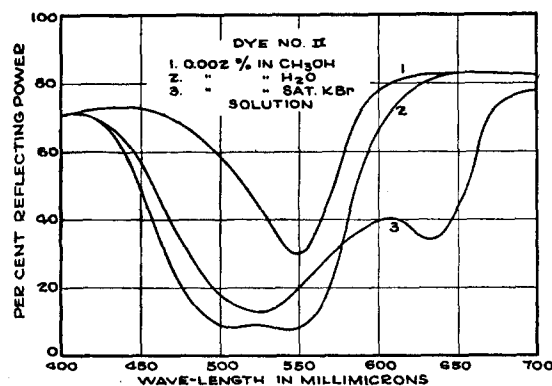


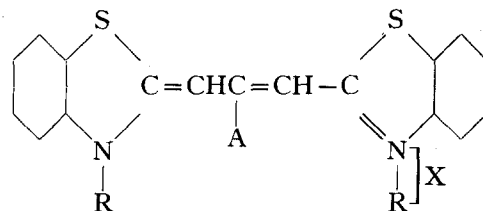
FIG. 3.

solutions was 0.002 percent. The amount of inorganic salt, usually potassium bromide, when added to the aqueous solutions of dye, was determined by the individual dye. In general, solid halide was added until a point of incipient dye precipitation was reached. In some cases the solutions became slightly turbid. Absorption measurements were made on these aqueous systems without further treatment.

More complete information about individual experiments is given below.

#### EXPERIMENTAL RESULTS

The dyes used in this investigation are thiacyanines of the general formula:



in the cases of dyes I, II, IV, and VI, in which  $R$  is an alkyl group,  $A$  a hydrogen or an alkyl group, and  $X$  a halide ion. Several of these dyes are substituted in the nucleus. Dye III is a thia-pseudo- (or 2'-) cyanine, and V a pseudo- (or 2,2'-) cyanine.

The properties and preparation of the various sensitizers used have been described in the literature.<sup>15-19</sup>

Typical dyes of known photographic properties were chosen for investigation, and from their study it is felt that a broader viewpoint may be obtained concerning the mechanism of sensitizing by cyanine dyes. The dyes used in this investigation were kindly supplied by Dr. L. G. S. Brooker and Mr. F. L. White of these Laboratories.

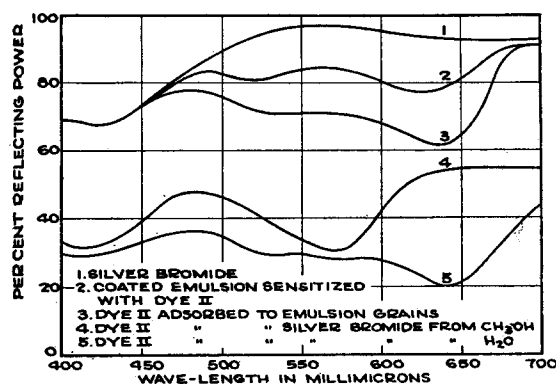


FIG. 4.

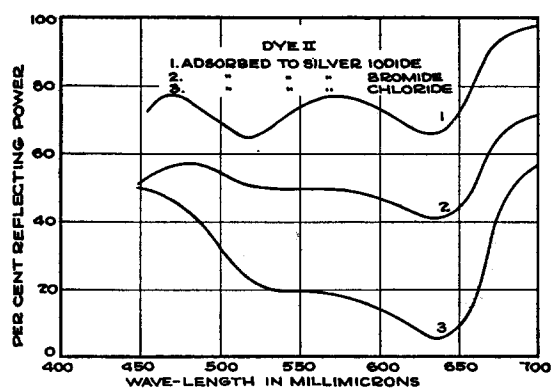


FIG. 5.

<sup>15</sup> L. G. S. Brooker and F. L. White, *J. Am. Chem. Soc.* **57**, 547 (1935).

<sup>16</sup> L. G. S. Brooker and F. L. White, *J. Am. Chem. Soc.* **57**, 2480 (1935).

<sup>17</sup> F. M. Hamer, *J. Chem. Soc.* 206 (1928).

<sup>18</sup> L. G. S. Brooker and G. H. Keyes, *J. Am. Chem. Soc.* **57**, 2488 (1935).

<sup>19</sup> F. M. Hamer, *J. Chem. Soc.* 3160 (1928).

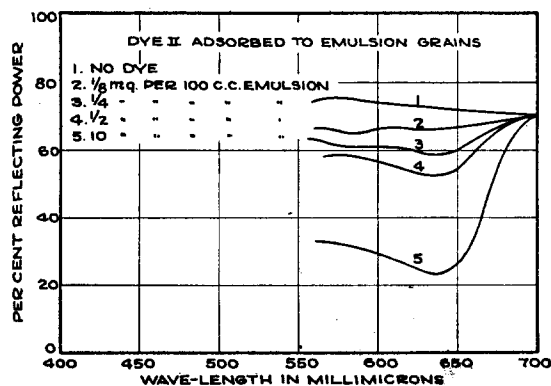


FIG. 6.

The results of a number of experiments on the absorption characteristics of several dyes under a variety of experimental conditions are presented in Figs. 1, 2, 3, 4, 5, 6, and 7. The ordinates in these figures represent either the reflecting power of the solid samples or the transmission of the dye in various solutions. As stated earlier, the absolute value of the reflection at any wave-length is not significant, but the relative reflection values in any curve are sufficiently accurate to give a very fair qualitative determination of its shape. The curves in some of the figures are deliberately spaced to avoid intersection, but their respective shapes are maintained.

It can be seen in Fig. 1 that the absorption curves of dye I in water, in methanol, and in aqueous gelatin, are strikingly different. The absorption behavior of dye II under similar conditions is shown in Fig. 3. The addition of gelatin solutions to an aqueous solution of dye II does not produce a change in absorption spectrum, as is the case with dye I, but the introduc-

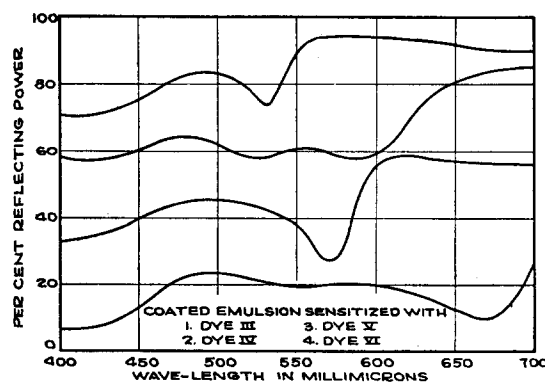


FIG. 7.

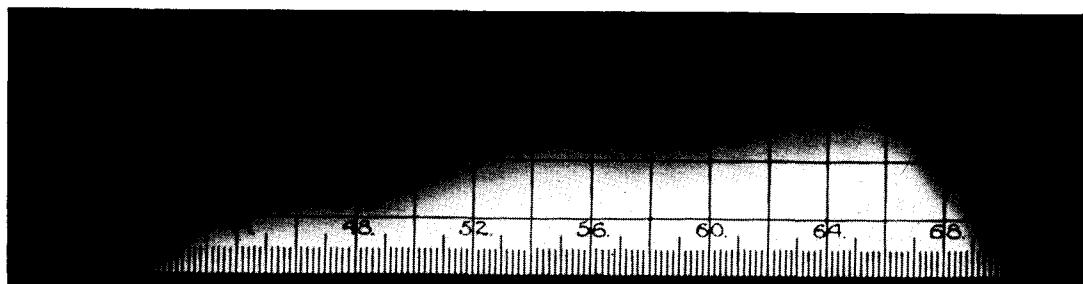


FIG. 8.

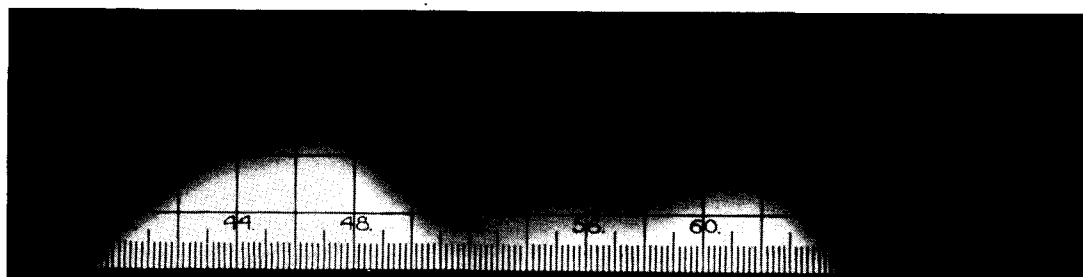


FIG. 9.

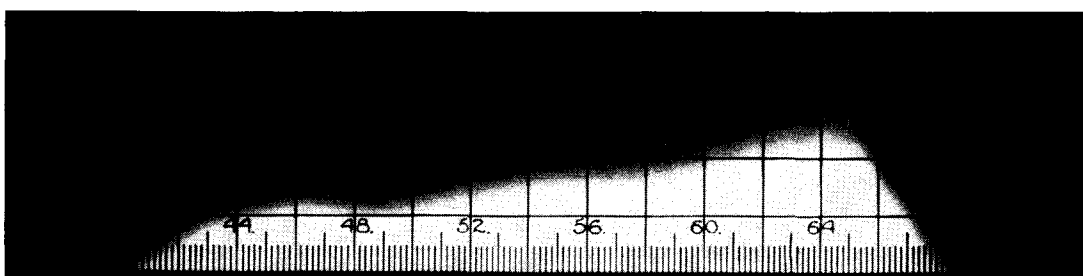


FIG. 10.

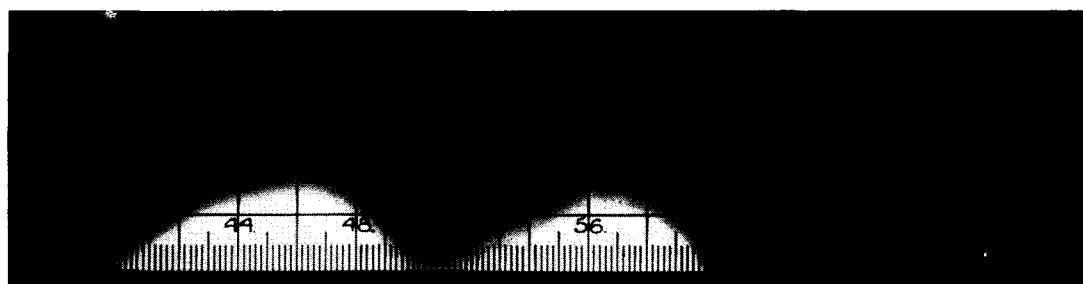


FIG. 11.

tion of solid potassium bromide caused the shift, as shown in Fig. 3. With some dyes, due to salting out, the aggregated state could not be obtained. The saturation of aqueous solutions of dye II with the following salts resulted in an absorption curve like that observed in saturated potassium bromide: sodium carbonate, potassium carbonate, potassium nitrate, sodium chloride,

and sodium thiocyanate. The following salts were without effect: calcium acetate, sodium acetate, sodium sulfate, sodium oxalate, and sodium sulfite.

In Fig. 2 are shown the reflection curves for dye I adsorbed to emulsion grains, to pure silver bromide and to pure silver bromide when dyed from methanol solution. The reflection curve of

FIG. 12.

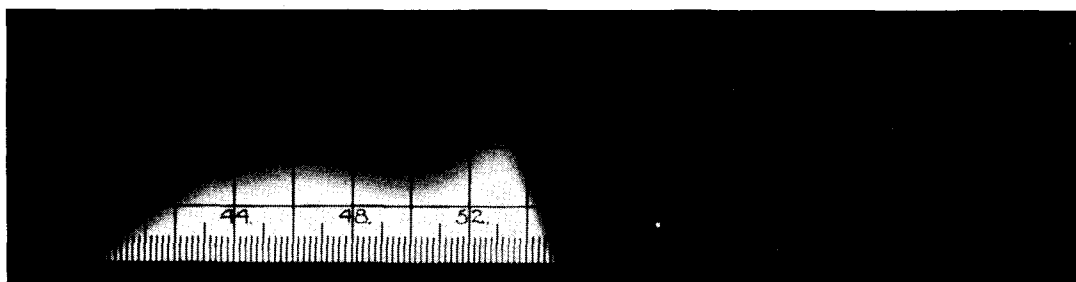


FIG. 13.

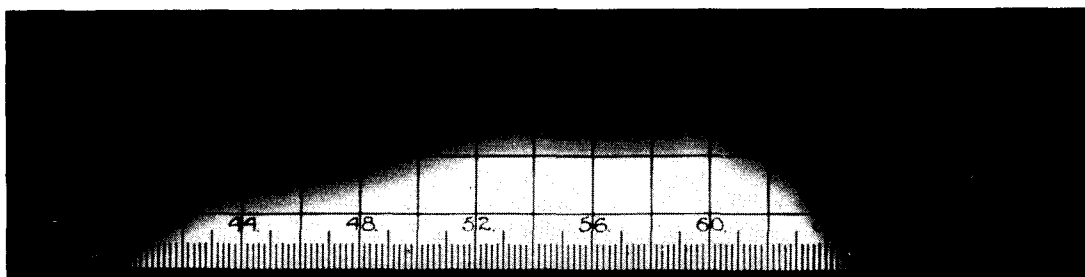


FIG. 14.

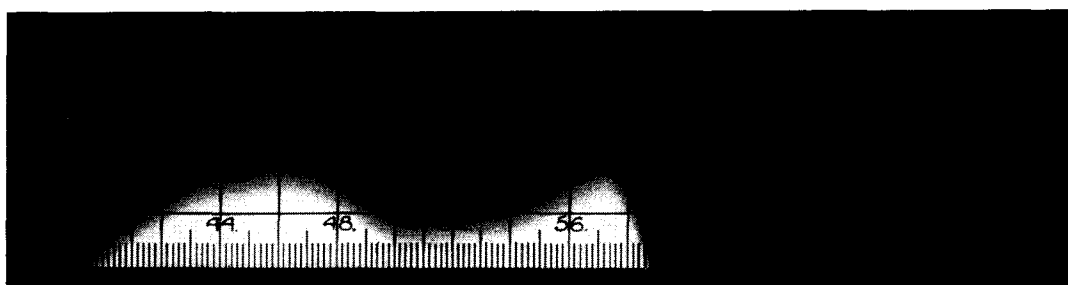
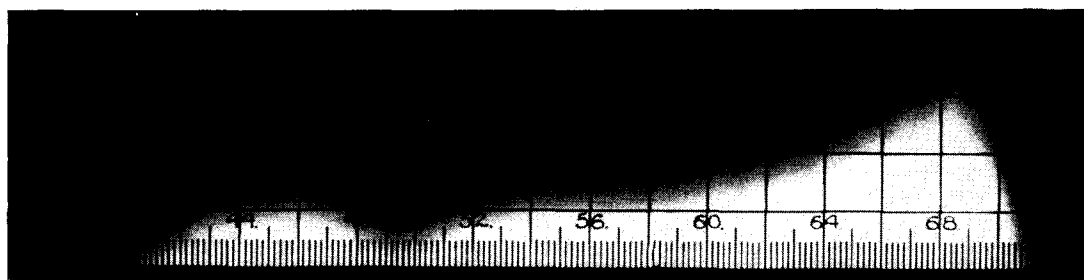


FIG. 15.



silver bromide dyed from water is independent of gelatin and is different from the curve of silver bromide dyed from methanol. Fig. 4 presents similar curves for dye II and also a curve of a normally coated photographic emulsion sensitized with this dye. It is seen from Fig. 4 that dye II adsorbed to silver bromide from water exhibits a reflection curve which is independent

of the presence of gelatin. The absorption curve of dye II adsorbed to silver bromide from methanol solution is markedly different from the curve of the dye adsorbed to the bromide from water.

Figure 5 shows reflection curves of dye II adsorbed from water to silver iodide, silver bromide, and silver chloride. The curve of silver

iodide dyed with dye II from methyl alcohol is identical with that of silver bromide dyed from the same solvent.

In Fig. 6 are found the reflection curves of an emulsion sensitized with various quantities of dye II. The quantities used were  $\frac{1}{8}$ ,  $\frac{1}{4}$ ,  $\frac{1}{2}$ , and 10 mg of dye per 100 cc of emulsion, respectively. It is significant that not only does the amount of light absorption decrease with decreasing dye concentration, but that the shape of the curve also changes. At the lowest dye concentration, the absorption maximum at 6350Å has vanished, and a new maximum at 5750Å has appeared. This maximum is in the same position as the maximum of the curve shown by silver bromide dyed with dye II from methanol. This effect is frequently observed, but there are many cases where the position of the maximum changes but little with concentration.

In Fig. 7 are given the reflection curves of normally coated, dried emulsions, sensitized with dyes III, IV, V, and VI, respectively. In each case 1 mg of dye was added to 100 cc of emulsion before coating.

The shape of the reflection (or absorption) curve of bromide emulsion grains dyed with dye II was found to be independent of the silver-ion concentration over the range of  $10^{-3}$  to  $10^{-10}$  molar. The dye was completely adsorbed at a silver-ion concentration lower than  $10^{-7}$ , but incompletely at concentrations greater than  $10^{-6}$ . This breaking point occurs at a silver-ion concentration equal to that of the solubility of silver

TABLE II. Wave-lengths of absorption maxima given in Å.U.

STATE OF DYE	DYE IV	DYE III
CH <sub>3</sub> OH soln.	5500	4800
H <sub>2</sub> O soln.	5500	4800
Saturated KBr soln.	5150; 2nd max. 6150	4800; 2nd max. 5300
Adsorbed to AgBr:		
from H <sub>2</sub> O	5900; 2nd max. 5200	5350
from CH <sub>3</sub> OH	5700	5150
from 1% gelatin	5900; 2nd max. 5200	5350

bromide. At a silver-ion concentration of  $5 \times 10^{-3}$  molar, no dye was adsorbed. In general, the higher the silver-ion concentration, the smaller was the amount of dye adsorbed to the grains.

It was found that the shape of the reflection curve of emulsion sensitized with dye II was independent of pH in the range studied, 5.75 to 9.85.

Some qualitative observations were made. If dye II is adsorbed to silver bromide from water in the absence of gelatin, the absorption curve of the wet, dyed bromide is that given in Fig. 4, curve 5. If the sample is allowed to dry, the shape of the absorption curve changes to that of silver bromide dyed from methyl alcohol solution. The original color is restored if the bromide is moistened with water. If silver bromide is dyed from water, the grains separated and then moistened with a 3 percent gelatin solution, the curve is that of Fig. 4, curve 5. Upon air drying, the shape of the absorption curve of the grains does not change. The small amount of gelatin present prevents the change in state upon drying.

Silver bromide was dyed from water, the grains separated by settling and methyl alcohol added. The color of the grains changed to that characteristic of halide dyed from methanol. During the change of color, no dye appeared to leave the grains and go into the alcohol; the change apparently occurred at the surface of the bromide. By decanting the alcohol and adding water to the settled grains, the original color was restored. The system is therefore reversible.

The behavior just described for dye II adsorbed to silver bromide is not specific. Dye I also may be made to change its absorption properties by drying, wetting with water, wetting with alcohol, etc.

Figures 8 to 15 are the spectrograms of normally coated emulsions sensitized as described in Table I. In Table I, the fourth column

TABLE I.

FIGURE	DYE	CONCENTRATION (mg/100 cc emul.)	COMPARE WITH FIGURE
8	I	5.0	2, curve 3 1, curve 3
9	I	0.02	2, curve 4
10	II	4.0	4, curve 3 3, curve 3
11	II	0.1	4, curve 4
12	III	1.0	7, curve 1
13	IV	1.0	7, curve 2
14	V	1.0	7, curve 3
15	VI	1.0	8, curve 4



TABLE III. *Wave-lengths of sensitivity maxima given in A.U.*

DYE	HIGH CONCENTRATION	LOW CONCENTRATION
IV	5900	5700
III	5300	5200

lists the absorption curves of the sensitized emulsions with which the spectrograms should be compared. For dyes I and II, two spectrograms corresponding to two different concentrations of dye are given. This will be discussed later.

The qualitative agreement between the absorption (by reflectance measurement) curves of the dye adsorbed on silver bromide and the spectral distribution of sensitivities of the various sensitized emulsions is very good. Any differences are easily within the experimental error.

Absorption (by reflectance) and sensitivity measurements have been made on about one hundred sensitized emulsions, and in no case has any disagreement been found between the shape of the absorption curve of the emulsion and the spectral distribution of sensitivity.

The absorption curves of dyes III and IV, dissolved in alcohol, water, and saturated potassium bromide, were determined, as well as their reflection curves when adsorbed to silver bromide from water and methanol. The results may be seen in Table II.

In Table III are given the maxima of spectral sensitivity.

#### DISCUSSION

The experimental results establish for the dyes investigated the qualitative correspondence between the light absorption of a sensitized emulsion and the spectral sensitivity distribution. This correspondence appears to hold not only for the positions of the maxima and minima of the absorption and sensitivity curves, but also for the relative strengths of absorption and sensitivity in the spectral region where light is absorbed by the dye. No correlations have been found which allow the prediction of the sensitivity of an emulsion sensitized with a dye when compared with the unsensitized emulsion.

The discussion of the fact that some cyanine dyes sensitize silver halide emulsions to wave-lengths several hundred angström units longer

than those at which light is absorbed in non-aqueous solvents resolves itself, in view of the present results, into the consideration of the causes for the unpredictable shift in the light absorption of the dye in methanol to that observed when the dye is adsorbed to silver halide. The experiments on the light absorption of some of these dyes in nonalcoholic media provide an insight to this phenomenon.

The observations of other workers<sup>6-12, 20</sup> have established that some cyanine dyes are aggregated in aqueous media. Scheibe and co-workers<sup>12</sup> consider this phenomenon to be due to a polymerization of dye molecules. Jelley,<sup>11</sup> however, has shown for the dye used by Scheibe in his investigation that the state is very probably not a polymeric one, but that the dye takes the form of a one-dimensional (nematic) crystal. His crystallographic evidence for this conclusion is supplemented by observations on the fluorescence behavior of the dye in saturated aqueous salt solutions. The question as to the exact states of cyanine dyes in aqueous media must await further detailed studies by these investigators.

Bloch and Hamer<sup>8</sup> have presented absorption curves of a number of different cyanine dyes in methanol and water. For almost all of these dyes the curves are very similar in the two solvents, and the dyes are therefore probably in the same state. On the other hand, the curves of Figs. 1 and 3 show that dyes I and II are not in the same state in water and methanol. Table I presents evidence that dye IV is in different states in alcohol and water, whereas dye III is in the same state.

The addition of certain salts, typified by potassium bromide, to aqueous solutions of dye II causes a definite change in the state of aggregation of the dye. The fact that nonhalide salts are capable of modifying the state of a halide containing dye is an indication that this change is not primarily due to some electrolytic dissociation effect, since there is no common ion. It is of even greater significance that the addition of a dilute gelatin solution alone can modify the state of dye I. In view of the contradictory evidence as to the exact state of cyanine dyes in aqueous systems, the arbitrary term "aggre-

<sup>20</sup> B. H. Carroll and D. Hubbard, *Nat. Bur. Stand. J. Research* 9, 529 (1932).

gated" will be used hereafter to designate the state of a dye in an aqueous medium characterized by an absorption spectrum essentially different from that of the dye in alcohol. As indicated by the absorption measurements, there are several degrees of aggregation possible for a given dye. Dyes I and II are different in water and in alcohol. For each of these dyes there is a third state which is definitely identified by sharp absorption maxima. Any system of dye, water, and salt may include a variety of states, dissociated and undissociated. The absorption curve of such a system is probably made up of several individual curves, each characteristic of a single species. The absorption coefficients of the several absorption maxima will be determined by the relative amounts of the various absorbing species, and consequently may vary within wide limits. It is not felt that with the present information further speculation is warranted.

A comparison of curve 3 of Fig. 1 with curve 2 of Fig. 2, and of curve 3 of Fig. 3 with curve 2 of Fig. 4, shows the striking similarity between the light-absorption curves of dyes I and II in an aggregated state, and of the same dyes when adsorbed to silver bromide from water or gelatin. There is a similar correspondence for dye III, as shown in Table II, but for dye IV the absorption curves of associated dye and of dyed silver bromide are not identical.

The agreement shown between the absorption maxima of dye in the aggregated state and adsorbed to silver bromide leads to the conclusion that the state of the dye is the same in the two cases. It is therefore consistent to term as "aggregated adsorption" the taking up of dye by silver bromide under conditions which give light-absorption curves similar to those of aggregated dye. In connection with this arbitrary definition, reference is made to the work of Sheppard and Crouch<sup>9</sup> who considered the possibility of adsorption of a colloidal type for the cyanine dye, Orthochrom T. These authors concluded that this dye was more probably adsorbed in a molecular-ionic condition.

With dye IV there is not exact agreement between the absorption curves of aggregated dye and dye adsorbed to silver bromide. The conditions under which association to form a definite aggregate occurs are probably the balance of a

number of factors. It is not surprising that conditions have not been found which reproduce accurately the state of the adsorbed dye. The significant fact is that in several cases excellent agreement between the absorption curves of the dye in the aggregated and in the adsorbed state has been observed.

In Fig. 6 are shown the absorption curves of dye II adsorbed to silver bromide emulsion grains, the ratio of dye to silver varying by a factor of 80. At the lowest concentration of dye, the absorption maximum is at 5800Å. In the higher concentration, the dye exhibits maxima at 6400Å and 5800Å. In the highest concentration, there is a single maximum at 6400Å. It is evident that the state of the adsorbed dye has changed with concentration. At high concentration, adsorption is probably aggregated. At the lowest concentration, the dye is adsorbed in some other form. It may be postulated that this latter is characteristic of dye adsorbed in the molecular (unassociated) state.

In Figs. 2 and 4 are given reflection curves of dye adsorbed to silver bromide from methanol solution. These curves are strikingly different from those of the dyes adsorbed from water. Sheppard<sup>6</sup> has shown that in methanol, cyanine dyes are probably in true solution. Any dye adsorbed to silver halide from this solvent is therefore in equilibrium with a molecular rather than with an associated species. It is therefore reasonable to conclude that dye adsorbed to silver halide from methanol solution is in a non-aggregated or molecular form.

From Fig. 4, curve 4, and Fig. 6, curve 2, it is seen that the absorption curve of dye II adsorbed from gelatin solution at very low concentration is, within the precision of measurement, the same as that of dye adsorbed from methanol at high dye concentration. This is consistent with the concept of molecular adsorption, since it might be expected that dye in very low concentration would be adsorbed from gelatin in the molecular or nonaggregated state. It has been found that dye II which has been brought into the aggregated form by addition of potassium bromide to an aqueous solution can be transformed into the state existing in methanol solution by diluting with water.

The change in distribution of spectral sensi-

tivity of emulsions when using large and small quantities of dye is entirely consistent with the change in absorption. This is shown when Fig. 6, curve 2, is compared with Fig. 10, and Fig. 6, curve 5, with Fig. 11. That emulsion sensitized with a very low concentration of dye is similar in light-absorption characteristics to silver bromide dyed from methanol is shown by comparing Fig. 4, curve 4, with Fig. 6, curve 2.

For all of the cyanine dyes which have been studied, the sensitivity curve of emulsion sensitized with a low dye concentration is similar to the light-absorption curve of silver bromide dyed from a methanol solution of the sensitizer.

The change of the color of silver bromide dyed from water upon drying corresponds to a change of dye from aggregated to molecular form. As has been pointed out, this change is reversible. There are two plausible explanations for this behavior. The first of these is that the absorbing species are an electrolytically dissociated aggregated electrolyte and its nondissociated form. Upon drying, the dissociated form ceases to exist. Moistening will cause dissociation with consequent change in color. The fact that very small amounts of gelatin prevent the change from the dissociated to nondissociated form may be due to prevention of complete desiccation by the gelatin.

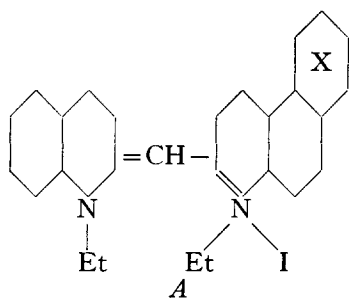
The second explanation of the reversible color of dyed silver bromide is that of aggregated and molecular adsorption. Upon drying silver bromide dyed from water, the forces (possibly those due to water dipoles) which tend to maintain the aggregated state are weakened or destroyed, and the individual dye molecules wander over the surface of the bromide until they form a uniformly distributed molecularly adsorbed layer. Moistening restores the forces which cause aggregation, and the molecules rearrange themselves to give the stable, associated form. The effect of gelatin in preventing change of color may be due to its adsorption at the unoccupied spaces on the bromide surface. Since the surface is then saturated with adsorbed material, there is no place to which the dye can wander, and hence forces much weaker than usual are capable of retaining the dye in its aggregated form. Furthermore, the thin coating of dry gelatin might offer considerable resistance to wandering of dye molecules over the surface.

The idea of dissociated and nondissociated forms of colloidal dye is not favored for several reasons. First, the amount of gelatin which is necessary to prevent change of color upon drying is extremely small, and the amount of water retained upon air drying is also very low. Secondly, an attempt was made to cover the surface of a fresh silver bromide precipitate as completely as possible by dyeing it from water with as much of dye II as would be adsorbed. This quantity was ten times that normally used in the other experiments. Upon air drying for five days, there was a slight regression of the maximum at 6400A, but there was by no means a complete change of color indicative of transformation to the molecular form. Presumably, the bromide surface was so completely covered with aggregated dye that even when dry the molecules could not wander to form a uniform molecular layer. This second observation cannot be explained on the basis of dissociated and nondissociated forms.

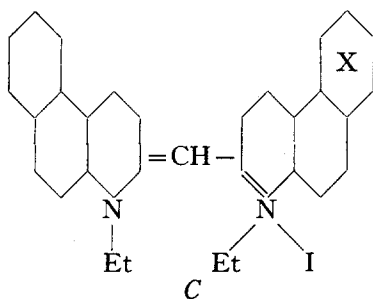
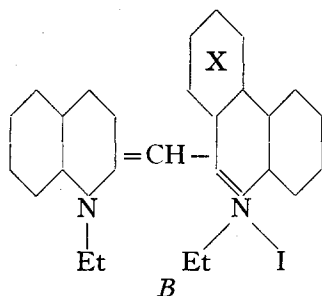
There is insufficient evidence at this time to afford a detailed picture of the state of the adsorbed dye. There is, however, a further observation of interest. It is that the halide ion is responsible for the adsorption of the cyanine dyes to silver halides. Many experiments have been made on the adsorption to insoluble compounds of some of the dyes here described. The dyes have been found to be adsorbed to the insoluble halides of lead, mercury<sup>1</sup> and copper<sup>1</sup>. They are not adsorbed to the insoluble carbonate, oxalate, or phosphate of silver, nor to lead sulfate or oxalate. When adsorption from water occurs, the light absorption of the dyed material is like that of dyed silver halide. The light absorption of salts dyed from methanol solution is similar to the absorption of the dye adsorbed to silver halide from methanol. The above facts indicate strongly that the light absorption of dyed silver halide is characteristic of the dye and halide ion, and is independent of the silver ion.

Another observation should be presented. The following isomers were supplied by Dr. L. G. S. Brooker and Mr. G. H. Keyes<sup>21</sup> of these Laboratories:

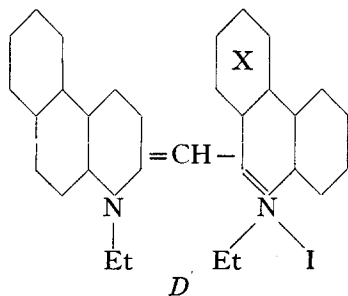
<sup>21</sup> L. G. S. Brooker and G. H. Keyes, *J. Am. Chem. Soc.* **58**, 659 (1936).



and



and



Dyes *A* and *C* sensitize photographic emulsions, while dyes *B* and *D* do not. Emulsion grains were dyed with each of the compounds: *A*, *B*, *C*, and *D*, and it was found that the dye was strongly adsorbed in each case. The gelatin was removed by centrifuging, and the reflection curves of the grains determined. The curves of all four dyes showed pronounced absorption maxima.

A probable explanation of the difference in sensitizing characteristics of the isomers is that the phenyl groups, *X*, in dyes *B* and *D* interfere with the proper exchange of energy between dye and silver halide, because of some steric effect in the molecule. Whether this inhibition of energy exchange is due to improper orientation of adsorbed dye at the bromide surface or to interference with collisions suitable for such exchange cannot be decided. The facts indicate that for photosensitization, not only is adsorption of dye to silver halide necessary, but also accessibility of the light-absorbing group to the silver bromide crystal.

The question of the mechanism by which energy is transferred from the light-absorbing dye-silver halide complex to the silver bromide crystal has been discussed. Bokinik<sup>1</sup> in particular has presented the views of various investigators. No discussion will be given at this point of the abundant speculation on this question. Recent developments in the theory of crystals, as applied to the photographic elementary act, have been presented by Webb.<sup>22</sup> It is felt that a theory of optical photosensitization should be compatible with this or a similar interpretation.

<sup>22</sup> J. H. Webb, J. Opt. Soc. Am. **26**, 368 (1936).