PhotoConductivity in Photographic Systems I. DyeSensitization of Photo Conductivity

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Photo-Conductivity in Photographic Systems

I. Dye-Sensitization of Photo-Conductivity[*,†]

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Gelatino-silver halide photographic films increase in electrical conductivity on exposure to light at intensities corresponding to exposures within the normal photographic range, and above. The spectral distribution of this change in conductivity in films containing, respectively, photographic sensitizing dyes, and no dye, is found to be parallel with the spectral distribution of photographic sensitivity—the wave-lengths of maximum and minimum sensitivity in the two effects are identical and coincide with absorption maxima and minima, and there is a general parallelism in the efficiency of a dye in sensitizing the two effects to light not absorbed by the silver halide. The conclusion is drawn that the observed changes in conductivity represent a photo-conductivity originating in the photo-liberation of electrons within the silver halide, the primary act of the photographic process.

The photo-currents are proportional to the applied field up to strengths of at least 140 volts per millimeter, and at intensities of illumination within the normal photographic range and somewhat above, are proportional to the intensity. At still higher light intensities, the photo-currents verge towards a dependence on the square root of the intensity. The change in the intensity relation is interpreted as representing the passage from a situation, at low intensities, in which most of the electrons are captured by foreign traps to that, at high intensities, in which recombination with bromine atoms predominates.

It is shown that a sensitizing dye acts by causing the liberation of an electron within the conduction band of the silver halide under the stimulus of light absorbed by the dye but whether the process involves direct electron-transfer or energy-transfer is left open.

MODERN ideas of the photographic latent image spring from studies, on the one hand, of the conditions for sensitivity in photographic emulsions, and on the other, of the electrical and structural characteristics of silver halide crystals. On the photographic side, an important step was the formulation by Sheppard, Trivelli, and Loveland[1,2] of the "concentration speck theory," according to which high photographic sensitivity is associated with the presence of submicroscopic particles of silver sulfide on the surface of the grains, which act as condensation nuclei for silver produced by exposure to light. On the physical side, the silver halides were recognized to exhibit electrolytic and photoelectronic conductivity.[3] A description of the primary process of photo-excitation in silver halides in terms of quantum-mechanical views of crystal behavior was made by Webb,[4] and in 1938 Gurney and Mott[5] effected a synthesis of

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[1] S. E. Sheppard, Phot. J. 65, 380 (1925).
[2] S. E. Sheppard, A. P. H. Trivelli, and R. P. Loveland, J. Frank. Inst. 200, 51 (1925).

[3] R. Hilsch and R. W. Pohl, Trans. Faraday Soc. 54, 883 (1938); C. Wagner, *ibid*. 851.
[4] J. H. Webb, J. Opt. Soc. Am. 26, 367 (1936).
[5] R. W. Gurney and N. F. Mott, Proc. Roy. Soc. A164, 151 (1938).

all these elements into a detailed description of latent-image formation which forms the starting point of most current discussions of the subject.

Briefly, the hypothesis is that absorption of radiation by silver halides liberates electrons from the bromide ions. The electrons become free to move through the lattice until they are captured by traps; the photo-conduction of silver halide crystals is the manifestation of this process. The lattice also contains mobile interstitial silver ions, whose existence is shown by the electrolytic conductivity of the silver halides. The traps, negatively charged by capture of electrons, attract silver ions, which, after neutralization, are deposited as silver atoms. The experimental facts on the sensitivity of photographic emulsions force the assumption that the most efficient traps are particles of silver sulfide, the "concentration specks" of Sheppard, Trivelli, and Loveland, and the accretion of silver atoms on these specks by the processes just described forms the photographic latent image. The existence of a latent-image particle in a halide grain leads to the complete reduction of the grain to metallic silver on immersion in a developer. The bromine atom left in the crystal after the expulsion of the electron, is assumed to wander by electronic displacement to the surface of the grain and to be rendered harmless with respect to recombination processes by being fixed by the gelatin.

Whatever may be the fate of this hypothesis as it is subjected to the ordeal of experimental test, it seems unlikely that the first step in the mechanism, the photo-liberation of electrons within the halide, will require fundamental alteration. There is, however, much to be learned concerning the details of this primary process, and the manner in which it is influenced by photographically significant treatments in the processes of emulsion making. Hitherto, photo-conduction has been observed only in massive crystals or in fused films of the silver halides. The observations of Pohl and his co-workers are confined to relatively large single crystals of "pure" material. Similarly, the experiments of Toy and Harrison,[6] which led these authors to identify the primary step in the formation of the latent image with the photo-conductive liberation of electrons in the silver salt, were carried out on thin films of previously fused "pure" silver bromide, and more recent experiments of Kameyama[7] and collaborators have also been concerned with the photo-conductance of fused films. It is a main purpose of the program, part of whose results are contained in the present communication, to extend our knowledge of photo-conduction to normal photographic emulsions, and to show how such studies may assist in the understanding of details of the primary photographic process. Unpublished observations by J. H. Webb and C. H. Evans, of the Kodak Research Laboratories, made before the present investigation was begun, showed that photo-currents could probably be detected in normal gelatino-silver bromide emulsions, and that by the addition to the emulsion of sensitizing dyes this internal photoelectric effect could be extended to spectral regions unabsorbed by the halide, in a manner analogous to photographic sensitization by these dyes. In the course of the present investigation it has been demonstrated unequivocally that photo-currents are developed in normal photographic films, and far-reaching parallelisms have been observed between the spectral distribution of photo-conductive and photographic activity.

Sheppard, Vanselow, and co-workers[8] also furnished important clues to the mechanism of the photo-changes in silver halides by studies of the photo-voltaic effect of silver-silver bromide electrodes in conducting solutions. They concluded that the primary action of the light was the liberation of electrons from the bromide ion, which then had a period of free existence before eventual union with silver ions to form silver atoms. These authors also showed that photographic sensitizing dyes extended the sensitivity of the photo-voltaic effect in silver-silver bromide electrodes to longer wave-lengths than exhibited by the undyed salt.[9]

[6] F. C. Toy and G. B. Harrison, Proc. Roy. Soc. A127, 613 (1930).

[7] N. Kameyama and T. Fukamoto, J. Soc. Chem. Ind. Japan 42, 244B (1939); N. Kameyama and K. Mizuta, ibid. 42, 426B (1939).

[8] W. Vanselow and S. E. Sheppard, J. Phys. Chem. 33, 331 (1929); S. E. Sheppard, W. Vanselow, and V. C. Hall, ibid. 33, 1403 (1929).

[9] S. E. Sheppard, W. Vanselow, and G. Happ, J. Phys. Chem. 44, 411 (1940).

MEASUREMENT OF PHOTO-CONDUCTIVITY IN PHOTOGRAPHIC FILMS

(a) General Principles

The principle of the measurements in this report is the same as that employed by Toy and Harrison.[6] A piece of film is suitably mounted between electrodes, between which a potential difference is imposed by means of a battery. Part of the film-battery circuit consists of a high resistance of 10^8 to 10^{10} ohms which acts as the input resistance of a direct-current amplifier. The effect of the electrolytic dark current is eliminated by applying a counter potential to the grid, in which condition the amplifier is balanced and the corresponding reading of a galvanometer in the output circuit forms the zero for the measurements. Exposure of the film to light is accompanied by a diminution of resistance and an increase in current in the film-battery circuit, translated in the usual way by the amplifier to a proportional change in the output current. The corresponding deflections of the galvanometer from zero are measured as "photo-currents." Calibration in terms of the current in the input circuit is effected by noting the effect of a small known potential drop applied across the known input resistance.

The electrical system represented by the photographic film, consisting as it does of a suspension of minute photo-conducting crystals, usually 1μ or less in diameter, imbedded in a gelatin matrix of low, presumably electrolytic conductivity, is admittedly more complicated than that represented by the fused film of silver halide, and still more so than the single crystal. Difficulties of interpretation, absent in the simpler systems, might well be anticipated to arise. Moreover, the background of "dark current" against which the photo-currents are observed, exceeds them by some 50-fold at the highest intensities of illumination used and by several thousandfold at lower intensities. In the latter experiments, the photo-currents were of the order of 10^{-12} and 10^{-13} amperes. Although the method of measurement depends only on the change of current produced by exposure to light, it is very necessary to guard against confusion of photo-currents with changes in the dark current produced by spurious incidental effects of the radiation, such
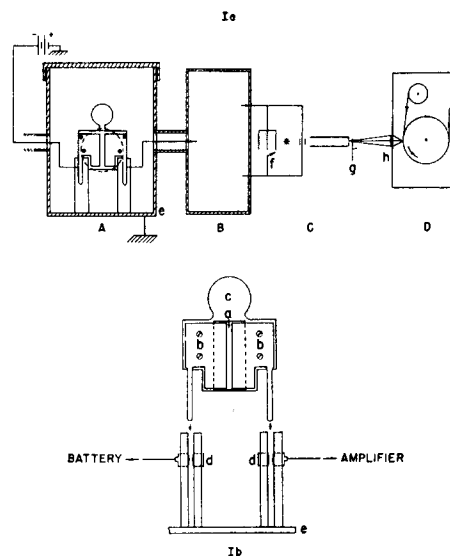

FIG. 1. Apparatus for measuring photo-conductivity of photographic film.

as heating. Low luminous intensities, quick-acting recorders and short exposures facilitate in this discrimination.

The photographic film, however, in spite of some unfavorable electrical characteristics, offers certain important advantages in the search for clear-cut correlations between photographic and photo-electric properties. In the first place, many features of photographic sensitivity depend on the presence of adsorbed layers on the halide grains; one of these is optical sensitization, which has been our principal interest in this study. Without the high ratio of surface to volume characteristic of the emulsion, enough dye for adequate absorption of radiation cannot be adsorbed. Moreover, in apparently simpler systems like single crystals and fused films of the pure salt, it is difficult to evaluate photographic sensitivity as distinct from direct photolysis to visible silver, and conclusions concerning the photographic process from observations on photolytic systems involve extrapolations that are always uncertain and often unreliable. In attempting to correlate photographic sensitivity with other physical properties of the silver halides it is, in general, a wise principle to make the measurements, as far as possible, on the emulsion for which the sensitivity data have been obtained.

(b) Apparatus and Method

Figure 1a is a diagrammatic sketch of the electrical part of the apparatus, consisting of the four parts: A, the box containing the sample, B, a d.c. amplifier, C, a string galvanometer, and D, its recorder. The film sample, a (Fig. 1b), was mounted, emulsion side outwards, between silver-plated electrodes, b, 48 mm long and 1 mm apart, carried by a polystyrene support, c. The diagram, A, depicts the arrangement of film, holder, and electrodes as it faced the incident light which is supposed to be directed on the film perpendicularly to the plane of the paper. Ready withdrawal and reproducible replacement of the sample were secured by mounting the film holder in the sockets, d, by plugs soldered to the electrodes. The metal sockets were carried in stout polystyrene pillars mounted on the floor of the metal box, e, serving as shield. One electrode was connected to the input of the d.c. amplifier, B, the other to the negative terminal of a dry-cell battery variable up to 135 volts. The output of the amplifier was connected to the string galvanometer, C, Type P of the Cambridge Scientific Instrument Company. The string was a gilded quartz fiber of some 2000-ohms resistance. A set of shunts, f, permitted variation of the sensitivity from very low values used in preliminary adjustment to the full sensitivity. The deflections of the string were recorded photographically, time and deflection scales being registered by means of a rotating spoked disk, g, driven by a Telechron motor, and an engraved scale on the cylindrical lens, h, of the camera, D. Calibration was effected by applying to the input of the amplifier, by means of the potentiometer used to compensate for the dark current, an accurately known potential of 1.5 millivolts.

A single-stage amplifier containing a General Electric FP-54 electrometer tube in the circuit of DuBridge and Brown[10] was first used; more recently a linear three-stage amplifier with feed back, of considerably higher sensitivity, has been employed. We are indebted to Dr. R. W. Tyler, of these Laboratories, for the design and for supervising the construction of this amplifier. A voltage sensitivity of 5×10^4 divisions of the gal-

vanometer scale per volt change of the input potential was normally used, corresponding to a current of 5×10^{-15} amperes per division at an input resistance of 10^{10} ohms.

Exposure times of 0.3 second were usually given, determined by a vane shutter of 2-inch aperture placed in front of the glass window of the measuring box, although currents were measurable at exposures of 0.02 second. An auxiliary beam was arranged to pass through this shutter without entering the measuring box, A, and by appropriate optical contrivances was focused at one side of the strip of photographic paper in the recording camera so as to form a mark on the developed record indicating the beginning and end of the exposure. In this way it has been ascertained that the photo-current begins immediately the shutter is opened and starts to fall immediately it is closed.

The dark resistance of the film was found to depend on the humidity of the circumambient atmosphere, and the ease of measurement of the photo-currents depended on this resistance. Very low humidity was associated with high film resistance and low values of the photo-currents, while high humidity was associated with experimental difficulties originating in large background currents. Films of the size required for the holder depicted in Fig. 1b were conveniently measured at relative humidities of 30 to 40 percent. Measurements were most easily carried out when the general room humidity was in this range; otherwise, the films were preconditioned in a desiccator over a saturated salt solution of appropriate humidity, e.g., saturated $CaCl_2 \cdot 6H_2O$ (relative humidity, 31 percent at 24.5°C) or saturated $K_2CO_3 \cdot 2H_2O$ (r.h. $= 43$ percent at 24.5°), and the measuring box was also provided with the same solutions. At humidities from about 30 to 50 percent, the magnitude of the photo-current was not highly sensitive to the value of the dark resistance, and no other control than those mentioned was necessary to secure reproducible readings on different samples of the same film.

Re-exposure of a sample once exposed usually yielded a smaller photo-current than the initial current, and for this reason a new sample was used for every determination, for instance, in a set of measurements of a given film at different

[10] See J. Strong *et al.*, *Procedures in Experimental Physics* (Prentice-Hall, Inc., New York, 1939), p. 418.

wave-lengths. Pieces were cut from adjacent places in the roll of film, the operations of mounting the sample in the holder and of placing the holder in the measuring box being carried out, of course, in non-actinic light.

The optical arrangement consisted of a 500-watt tungsten-filament projection lamp, focused on the entrance slit of a lens-grating monochromator of aperture $f:2$, from the exit slit of which beams of desired wave-length, covering a band of about 11 mμ, were projected on the sample so as to cover all of the film between the electrodes. Variation of intensity was effected by introducing "neutral filters" into the exit beam from the monochromator. The grating was a replica furnished by Professor R. W. Wood, with a ruled surface 3 inches by 4 inches, and threw a large percentage of the incident light into one order. In some earlier experiments, isolation of the radiation was effected by filters.

Energy measurements of the light incident on the film were made by means of a Moll micro-thermopile placed in the position of the film. The thermopile was used with a Cambridge D'Arsonval galvanometer of 40-ohm resistance, and the arrangement was calibrated against a standard lamp furnished by the Bureau of Standards. Transmissions of filters were measured by a photronic cell and the same galvanometer. The linearity of response of these energy-measuring instruments with intensity was established experimentally in the intensity ranges of interest.

The range of exposures (intensity$\times$time) in the photo-conductive experiments extended from values within the normal photographic range to values a thousand or more times greater. Fast negative emulsions were used, as normal film coatings. The lowest intensities used were such that, on developing the film after the photo-conductive exposure, the density of developed silver corresponded to a point on the shoulder of the Hurter and Driffield characteristic curve, definitely below the maximum density for the emulsion and not in the region of solarization. The very high exposures were made by increasing both the intensity and the time of illumination and produced visible print-out silver. Certain quantitative differences are to be found in the behavior of the photo-conductance at low

and at high intensities, but no fundamental difference exists in the spectral distribution or in the general correlation with the spectral distribution of photographic sensitivity. In particular, wave-lengths at which maxima and minima in photo-conductivity occur are independent of the intensity level.

The absorption spectra of the films used were determined by means of a General Electric automatic recording spectrophotometer. We are indebted to Mr. E. E. Richardson, of these Laboratories, for these measurements. The percentage transmission and reflection were measured directly, and the percentage absorption was computed as 100 (percent transmission+percent reflection).

(c) Some Characteristics of the Photo-Currents in Photographic Films

When a film mounted in this apparatus was exposed to light of appropriate wave-length, the galvanometer index began to deflect simultaneously with the start of the exposure period, but reached a steady value only in a period greater than that of the galvanometer-amplifier system. The period of growth depended on the type of film and on the intensity and wave-length of the exciting light. In fast photographic emulsions, times of the order of 0.2 to 1.0 second were required for the deflection to assume a steady value in the intensity range in which current was proportional to intensity. At high intensity (for example, at 1000 ergs/sq. cm/sec.), a steady terminal current might not be observed within some seconds, constant illumination producing a rapid initial deflection followed by a prolonged slower rate of increase. At the end of the exposure, the deflection began immediately to fall, approximately exponentially with time, to a value representing a dark resistance lower than the initial resistance, from which there was a slow recovery of the initial resistance.

The absence of a nearly instantaneous component in the photo-currents measured at room temperature is in contrast to the situation in single crystals at low temperature in which the presence of an inertialess component is taken as a criterion of the production of primary photo-electric emission. The immeasurably rapid rise
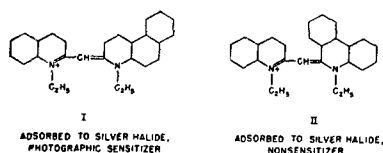
FIG. 2. Dye I, adsorbed to silver halide, photographic sensitizer; dye II, adsorbed to silver halide, non-sensitizer.

and fall of the photo-current at low temperature is probably associated with the permanent trapping of the photoelectrons, the value of the steady current being equivalent to the motion of the electronic charge through a certain distance, the "mean displacement," towards the anode before trapping.[3] At room temperature, however, some of the trapped electrons may be ejected again into the conduction band, making additional contributions to the current, equivalent to an increase in the mean displacement, and the exponential fall of current after the stoppage of the exposure probably represents the decay of thermally ejectable trapped electrons according to a unimolecular law.

The fact, moreover, that the system consists of minute isolated photo-elements, will tend to prolong the time over which photo-current is gaining. In the first instants of exposure, few grains have acquired enough quanta to produce substantial currents, and during exposure the contributions of more and more grains are added to the observed current, which therefore increases at a measurable rate. We have, in fact, found experimentally that the rate of increase of the photo-currents with time becomes greater the larger the grain size. In gelatinless systems composed of grains of silver chloride about 0.1 mm in diameter, 90 percent of the rise to the final steady value is accomplished in a few hundredths of a second.

RESULTS

Variation of Photo-Currents with Voltage

Numerous tests have shown proportionality of the photo-currents in photographic films to the applied field strength, up to the maximum used, 140 volts per mm, at all wave-lengths. No evidence of saturation of these currents has been observed.

TABLE I. Photo-conductivity in dye-sensitized and unsensitized photographic films.

Dye	Relative photo-currents for light of wave-length, in mμ (Hg arc)				Inertia speeds for light of wave-length, in mμ (tungsten)		
	>620	580	546	(436, 410)	>590	>500	400–500
—	0	<5*	11	171	0	3	575
I	10	180	85	330	73	1640	406
II	0	8	15	300	0	0	406
III	0	<8*	4	153	0	0	406

Dye-Sensitization of Photo-Conductivity

The first experiments were designed to show whether the currents produced by illumination of photographic films as described in the last section were in fact related to photographic sensitivity or whether they were influenced by heating effects of the radiation on the electrolytic conductivity of the grain or of the gelatin. Measurements were made on films prepared from the same basic bromoiodide emulsion containing, respectively, (a) no dye, (b) the efficient sensitizing cyanine dye, I (Fig. 2), with an absorption maximum and a sensitized photographic maximum at 585 mμ,[11] (c) the non-sensitizing cyanine
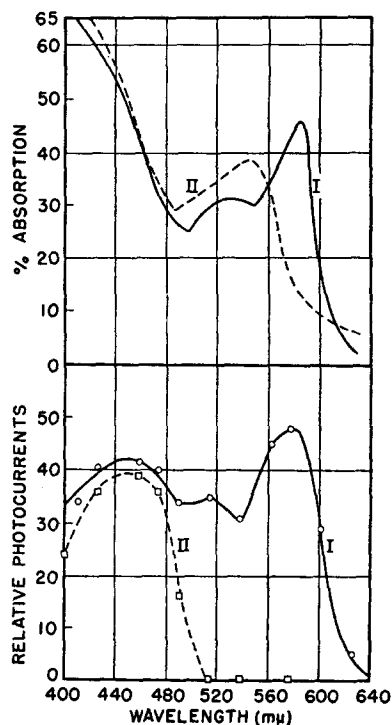

FIG. 3. Percent absorption and photo-conductivity of films containing dyes I and II.

[11] Dye I was brought to a state of maximum photographic efficiency in the emulsion by the addition of a

dye, II, isomeric with I, adsorbed to the halide in the emulsion, with an absorption band in the green comparable in intensity to that of I, and (d) a non-sensitizing dye, III, of the oxonol class, with an intense absorption band in the green, but present in the gelatin and not on the grains. All three dyes absorb light in the same general region of the spectrum; effects caused by any heating of the grains or gelatin by the absorbed energy would, therefore, be expected to be similar, but only dye I is a photographic sensitizer.

A particularly crucial experiment is summarized in Table I. The source was a mercury arc from which different spectral regions were isolated by filters and exposures of two seconds were made. Under these conditions of high intensity and relatively long exposure, any spurious thermal effects of the radiation would be comparatively large. The photographic characteristics of the films are denoted in the right-hand side of the table as inertia speeds[12] with respect to filtered light from a tungsten source; no quantitative comparison can be made between the relative photographic and photo-conductive sensitivities owing to the difference in the nature
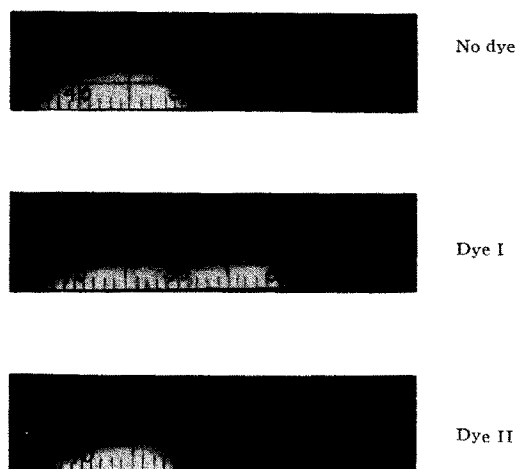

No dye

Dye I

Dye II

FIG. 4. Spectrograms of emulsion: unsensitized, containing dye I, and containing dye II.

small quantity of a "supersensitizer" 1-(p-diethylaminostyryl) benzothiazole, itself non-absorbent and photographically inactive when exposed to light in the sensitization band of the dye. (B. H. Carroll and J. A. Leermakers, U. S. Patent 2,313,922 (1943).) See Part II of this series.

[12] C. E. K. Mees, *The Theory of the Photographic Process*, (The Macmillan Company, New York, 1942), p. 204.
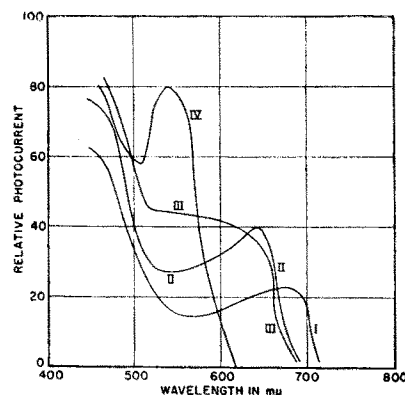

FIG. 5. Photo-conductance in various dye-sensitized photographic films. Dyes: I, a dibenzothiacarbocyanine bromide; II, a thiacarbocyanine iodide; III, a selenacarbocyanine bromide; IV, a merocyanine.

of the sources. The essential fact emerges, however, that only the film showing sensitized photographic activity in the green and yellow exhibited currents on exposure to the green and yellow mercury lines comparable in magnitude and other characteristics to those produced by blue light. The small deflections denoted by the asterisks in the unsensitized films were noticeably more sluggish than correspondingly small deflections produced by blue light, and since later experiments with lower exposures showed no photo-conductivity in unsensitized films exposed to green and yellow light, they probably represent spurious effects. There seems no doubt that the relatively large currents produced by blue light in all four films, and by green and yellow light in the film containing the sensitizing dye are to be ascribed to true photo-conductivity.

The photo-conductivities of the films containing dyes I and II were later determined with the apparatus using the three-stage amplifier at intensities of 14 to 50 ergs per cm^2 per second and exposure times of 0.3 second to light from a continuous source isolated by the monochromator. Figure 3 shows the spectral absorption and photo-conductivity so determined, while Fig. 4 reproduces the neutral-wedge spectrograms of a tungsten source as recorded by the films containing the dyes and by the undyed film. The photo-conductivity data in Fig. 3 and the sensitometric data in Fig. 4 are both uncorrected to equal incident intensities at the various wave-lengths. Comparison of the figures
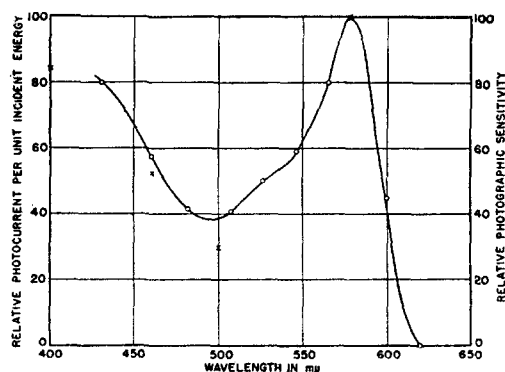
FIG. 6. Spectral distribution of photo-conductance and photographic sensitivity. Dye; 1,1'-diethyl-2,2'-cyanine iodide+supersensitizer. o, photo-currents; x, photographic sensitivity.

shows a very considerable degree of parallelism in the spectral distribution of photo-conductive and photographic sensitivity. From these and many similar experiments, there seems no doubt that the currents discussed in this paper are due to a true photo-conductivity originating in the primary photographic process of the photo-liberation of electrons within the halide grains and that sensitized photo-conduction can be induced by the same dyes as cause sensitized photographic activity, at the same wave-lengths and of relative magnitudes comparable to those shown in photographic sensitization.

The existence of dye-sensitized photo-conductivity in fused films of silver bromide bathed in certain sensitizing dyes was reported by Kameyama and co-workers.[7] No details are given in the notes published by these authors.

We have compared the spectral distribution of photo-conductivity and of photographic sensitivity for emulsions containing a considerable number of dyes of the cyanine, carbocyanine, dicarbocyanine, and merocyanine classes. Figure 5 records some of the results on photo-conductivity. The photographic maxima of the dyes represented by curves I, II, III, and IV are at 680, 640 (550 and 615), and 550 mμ, respectively. Invariably a parallelism in the spectral sensitivity of the two phenomena in dyed photographic films has been found; maxima and minima in the magnitudes of the effects occur at the same wave-length, determined by maxima and minima in the amount of energy absorbed.

A good photographic sensitizer gives relatively large sensitized photo-currents and *vice versa*.

While parallelisms in the spectral distribution of photographic and photo-conductive sensitivity have always been found, over the whole intensity range studied, quantitative correspondence between the two effects is closest when they are measured at comparable intensities. The photographic sensitivity is measured by the reciprocal of the incident energy in ergs per cm^2 required to produce a developed density of 0.5. In Fig. 6, the relative photographic sensitivity so defined and the relative values of the photo-currents for unit incident energy are plotted as functions of the wave-length for a film containing the sensitizer, 1,1'-diethyl-2,2'-cyanine iodide, with a small quantity of a supersensitizer.[11] The photo-currents were measured at exposures corresponding to the shoulder of the characteristic sensitometric curve. There is good quantitative agreement between the spectral distribution of sensitivity in the photographic and photo-conductive effects. On the other hand, when the photo-conductivity is measured at intensities which produce visible silver, the ratio of sensitized photo-conductivity to that produced by absorption by the silver halide tends to be lower than the corresponding ratio of the photographic speeds, which are measured at much lower intensities. Partial destruction of the dye at high intensities may be the explanation.

Variation of the Photo-Currents with Intensity

Within the limits of experimental error, the photo-currents vary with intensity according to the relation $C=kI^\alpha$, where C is the photo-current, I the intensity of illumination, k a constant of proportionality, and the exponent α varies from 1 to 0.5 according to the intensity level. Up to intensities of about 150 ergs per cm^2 per second, the relation of the current to the intensity was usually linear. At higher intensities, the value of α fell, reaching a lower limiting value of 0.5 (Fig. 7). The value of the exponent was the same for unsensitized and dye-sensitized photo-conductivity. The square-root law at high intensities recalls the behavior of systems such as selenium cells, molybdenum crystals, and zinc

sulfide phosphors which show a similar current-intensity relation.[13]

Let us assume that the observed photo-currents in photographic emulsions are determined by the primary liberation of electrons from bromide ions into the conduction band. These electrons move towards the anode, but are brought to rest after traversing a certain mean range by being captured by some kind of trap.[14] Two cases can arise: the electrons, after a period of freedom, may be trapped (a) by "foreign centers," for example, crystal imperfections, traces of impurities, photographic sensitivity specks, self-trapping sites,[15] etc., or (b) by the "positive holes" (essentially bromine atoms) left in the lattice after their expulsion. Schematically, the situations are:

$$\text{(a)} \quad Br^- + h\nu \rightarrow Br + \epsilon$$
$$\epsilon + M \rightarrow M^-. \quad\quad (1)$$
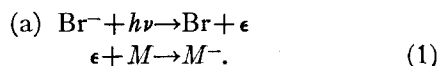
If n is the momentary concentraton of free electrons, m the concentration of foreign traps, M and I the intensity, then

$$dn/dt = k_1 I - k_2 nm.$$

In the steady state, the rate of production equals the rate of trapping of electrons, so that

$$k_1 I = k_2 nm$$
$$n = (k_1/k_2 m)I.$$

Since the steady photo-current is proportional to n, it is, by this mechanism, directly proportional to the intensity, provided m is independent of intensity.

$$\text{(b)} \quad Br^- + h\nu \rightarrow Br + \epsilon \quad\quad (1')$$
$$Br + \epsilon \rightarrow Br^-. \quad\quad (2')$$
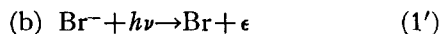
In this case, in the steady state,

$$k_1' I = k_2' n[Br] = k_2' n^2$$
$$n = [(k_1'/k_2') \cdot I]^{\frac{1}{2}}.$$

Here the current is proportional to the square root of the intensity; if both mechanisms are at work, the current is proportional to I^α; $0.5 < \alpha < 1$.

At sufficiently high intensities, the electronic concentration could be so great as to cause saturation of foreign traps, and recombination with bromine atoms would become the main process terminating the mean range. At low intensities, however, recapture by bromine atoms seems, in the light of the linear intensity photo-current relation, improbable compared with trapping by foreign centers. If this interpretation is correct, loss of primary photoelectrons by bromine-capture is a relatively minor factor in a normal photographic exposure at moderate intensities.

DISCUSSION, AND THE MECHANISM OF PHOTOGRAPHIC SENSITIZATION BY DYES

The results of the present investigation complete the chain of evidence on the photographic function of sensitizing dyes started by the observations of Leermakers, Carroll, and Staud concerning the relation between the absorption of the dye and the photographic sensitivity of dyed emulsions.[16] These workers established the correspondence between the photographic sensitivity and the absorption of the dye as adsorbed on the silver salt; here, we interpret the parallelism between photo-conduction, absorption, and photographic sensitivity to indicate that the function of the light absorbed by the dye is to cause free electrons to appear in the halide, which then participate in the formation of the latent image in the same way as those generated directly by the self-absorption of the silver salt.
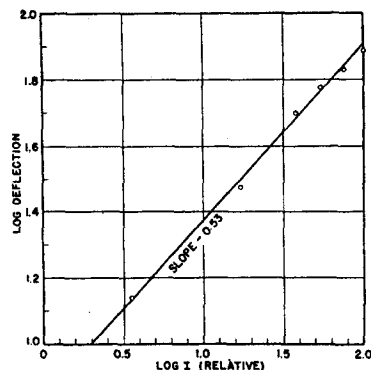
FIG. 7. Intensity photo-current relation at high intensity. $I = 100$ is equivalent to an incident intensity of 2483 ergs/sq. cm/sec. Exposure time $= 0.3$ sec.

[13] See, for example, D. S. Elliott, Phys. Rev. **5**, 53 (1915); W. W. Coblentz and H. Kahler, Sci. Pap. Bur. Stand. **15**, 121 (1919); H. Gudden and R. Pohl, Zeits. f. Physik **35**, 243 (1925).

[14] R. W. Pohl, "Report of conference on the conduction of electricity in solids," Proc. Phys. Soc. **49**, 16 (1937).

[15] L. Landau, Physik. Zeits. Sowjetunion **3**, 664 (1933).

[16] J. A. Leermakers, B. H. Carroll, and C. J. Staud, J. Chem. Phys. **5**, 878 (1937); J. A. Leermakers, *ibid*. **5**, 889 (1937).

The question may be asked: Does the photo-conduction observed in dyed photographic films really originate in the flow of electrons throughout the silver halide grain, or is it confined to the adsorbed layer of dye, a photo-conductivity of the dye? In the first place, the close correlation that exists between the photo-conductivity of dyed films and the photographic sensitivity, particularly the "supersensitizing" effect to be discussed in Part II of this series, is strong presumptive evidence in favor of the essential similarity of the photo-currents produced by the self-absorption of the silver halide and by the absorption of the dye. Moreover, direct experimental evidence indicates that no appreciable photo-conductivity of adsorbed dye layers can be detected under conditions similar to those prevailing in the photographic film, unless in the presence of a light-sensitive substrate. Dyed suspensions of lead chloride crystallites in gelatin were formed into films similar to photographic films. Lead chloride is photographically insensitive to visible light, and no photo-conductivity was observed either in dyed or undyed dry gelatin films of this material. Silver bromide films containing the same dye showed high sensitized photographic and photo-conductive sensitivity. Gelatin films containing sensitizing dye were likewise found photoelectrically insensitive to visible light. We conclude, therefore, that the observed photo-conduction of photographic films exposed to light absorbed by sensitizing dyes is caused by a flow of electrons within the silver halide grain.

Although the characteristics of photo-currents produced in the spectral region of dye-absorption are quite similar to those of the currents produced by silver-salt absorption, there is a difference in detail—the sensitized currents exhibit a rather more rapid rise to their stationary value than the non-sensitized currents. But there are also photographic differences in the behavior of films to light of the two regions; the contrast of the film is usually greater in the dye-sensitized spectral region than in the region of self-absorption. This difference is often attributed to the adsorption of a higher proportion of the dye to the smaller, normally less sensitive grains in the film. The sensitivity of these grains to light absorbed by the dye is therefore increased relative to their sensitivity to light absorbed by the silver salt. If the inertia observed in these photo-currents is partly caused by the relatively gradual "bringing-in" of the contributions of the individual grains, as previously suggested, it seems quite likely that the dye can influence the rate at which the contributions become effective in a manner somewhat analogous to its effect on the photographic contrast.

We are now in a position to discuss the bearing of our observations on the mechanism of photographic sensitization by dyes. Their function is to cause, through their absorption of light, a flow of electrons through the grain. The subsequent fate of these electrons is the same as that of electrons directly produced in the halide.

As to the manner in which the energy primarily absorbed by the dye causes electrons to appear in the silver salt, these measurements do not furnish a definitive answer. The alternative mechanisms are[17] a direct electron transfer from an optically excited adsorbed dye molecule to the conduction band of the halide, or a transfer of excitation energy from the dye in some way which causes a bromide ion of the lattice to expel an electron into the conduction band. There is a certain definiteness about the concept of direct electronic transfer that is lacking in the other mechanism, nor, in view of current notions of the high mobility of the π-electrons in conjugated chains,[18] does such a transfer appear improbable.

As Sheppard, Lambert, and Walker have emphasized, regeneration of the dye molecule may be an important stage in the process of sensitization. In the dye-sensitized production of visible silver in illuminated silver bromide, several silver atoms may be produced for each dye molecule present. Under these conditions, a given dye molecule can evidently participate more than once in the sensitizing act. It therefore seems probable that in the production of the latent image, the dye likewise is not destroyed in the sensitization act, although in that case the amount of dye on the grain is relatively so great compared with the silver produced that it is improbable that any given dye molecule partici-

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[17] J. A. Leermakers, J. Chem. Phys. **5**, 889 (1937); S. E. Sheppard, R. H. Lambert, and R. D. Walker, J. Chem. Phys. **7**, 426 (1939).
[18] E. Hückel, Zeits. f. Elektrochemie **43**, 752 (1937).

pates more than once, and sensitization could be realized even if the sensitization act involved the destruction of the dye. If sensitization consists in an energy transfer from the excited dye to an electron in a bromide ion in the lattice, regeneration of the normal dye molecule occurs automatically at the instant of transfer. On the concept of electron transfer, the dye will have, after donating an electron to the halide, a vacant level corresponding to its original ground state, and if an electron can pass from a bromide ion in the lattice to this vacant level, the dye will be regenerated and a bromine atom produced— the whole process of transfer and regeneration leading to material changes in the silver salt exactly the same as those called forth by its self-absorption. At first sight, this regeneration would seem to require considerable energy of activation, particularly in the case of a sensitizer whose absorption band was far displaced from the region of silver halide absorption. Mott and Gurney,[19] however, have argued that, as a result of the excess positive charge on the adsorbed dye left after electronic transfer to the grain, mobile silver ions in the lattice will be repelled, and the electrons in the bromide ions at the grain surface will therefore be in a weaker posi-

tive field than before. The energy level of the electrons in these bromide ions is therefore raised nearer the value of the unoccupied dye level, with the result that the activation energy for transfer is lowered or may vanish. In support of this concept may be adduced the observations of Fajans[20] and his co-workers on the effect of adsorbed ions on the light absorption of silver halides. Adsorbed silver ions were found to displace the long wave-length limit of the absorption band of the silver halides to longer wave-lengths, and adsorbed halide ions in the opposite direction, effects consistent with the suggestion of Mott and Gurney of an upward displacement of the electronic levels associated with negative ions by positively charged adsorbed layers. The transition from the displaced level to the conduction band requires less energy, and the absorption limit is shifted towards longer wave-lengths.

It must be emphasized, however, that our present observations on dye-sensitized photo-conductivity do not decide between the mechanisms of electron and energy transfer, but are limited to showing the production of electrons within the halide as a result of energy absorbed by the dye.

[19] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1940), p. 242.

[20] K. Fajans and G. Karagunis, Zeits. f. physik. Chemie 5B, 385 (1929).

II. Some Applications to the Phenomena of Supersensitization, Desensitization, and the Becquerel Effect*,†

Studies of the photo-conduction of photographic films afford a means of discriminating between photographic effects originating in effects on the primary liberation of electrons and those due to actions effective at later stages in image formation. For example, the photographic action of certain supersensitizers in increasing the sensitizing effect of dyes of the 2,2'-cyanine class has its counterpart in a supersensitized photo-conductivity, showing that the supersensitizer influences the efficiency of the primary

Part I described photo-conductivity in photographic emulsions characterized by a marked

transfer of energy (or of an electron) from the sensitizing dye to the halide. On the other hand, photographically desensitizing dyes have only secondary effects on photo-conductivity, showing that their action is not essentially to inhibit the photo-liberation of electrons.

The photographic Becquerel effect—the conferring of sensitivity to light of wave-lengths longer than those absorbed by the silver halide by the presence in the film of photolytic silver—has an analog in photo-conductivity.

parallelism in spectral distribution with photographic sensitivity. The photo-currents were concluded to be intimately connected with the primary liberation of photoelectrons in the first step of generation of the latent image. In this communication, observations will be recorded which afford further evidence of the truth of this
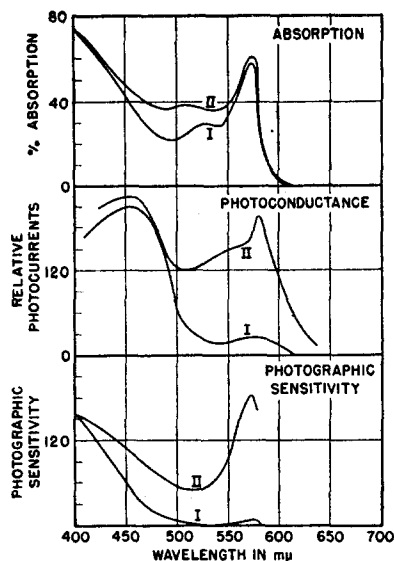
FIG. 1. Supersensitization of photo-conductance and photographic sensitivity. I. 1,1'-diethyl-2,2'-cyanine iodide alone. II. dye+supersensitizer.

conclusion, and also show how the results of studies in photo-conductivity can throw light on certain problems of photographic theory.

It will be recalled that the measurements made in these investigations refer to unsaturated photo-currents produced in the gelatino-silver halide system represented by the normal photographic film. Assuming that the currents are essentially conditioned by the primary liberation of electrons within the grains, it follows that their magnitude will be directly proportional to the rate of liberation of electrons and to the mean range traversed by the free electrons before capture by traps. Other things being equal, an increase in the primary rate of liberation of electrons will increase the photo-currents produced by a given applied field; and other things being equal, an increase in the number of trapping centers or of the efficiency of trapping will decrease the observed currents. In general, therefore, increased photographic sensitivity can be associated with either an increase or a decrease in photo-conductivity, as measured in these experiments. In dye-sensitization, an increase is observed because of the increased rate of liberation of electrons on excitation in spectral regions absorbed by the dye, but increased photographic sensitivity might also be effected by increasing the efficiency of

trapping, which would be expected to produce a fall in the magnitude of the photo-currents.

The sensitivity of photographic layers can be greatly influenced by a wide variety of substances added during the preparation of the emulsion or by bathing before exposure. The effect of the addendum may be exerted at any one or more stages in the series of processes elapsing between the primary act of light absorption and the final production of developed silver, and it is not always easy to determine, from observations on the developed image, at what link in the chain the addendum has intervened. If, however, it increases the photo-conductivity, its function is very probably to increase the primary electronic emission. Dye-sensitization is a simple example of such an effect, and certain cases of the phenomenon of supersensitization seem to depend on a similar increase in electron flow within the halide.

SUPERSENSITIZATION[1]

Certain substances, when added to a photographic dye-sensitizer, cause an enhancement of the sensitizing effect, without themselves absorbing light in the sensitized spectral region, or necessarily being themselves sensitizers. A case of this phenomenon was first recorded by Bloch and Renwick.[2] In the course of comprehensive studies, Mees[3] found that the effect, which he termed supersensitization, occurred in most classes of sensitizing dyes, although the cases are by no means common. Other examples are contained in the later patent literature. The effect is somewhat analogous to promotor action in catalysis, and, like that phenomenon, probably has different origins in different cases. The experiments described here are restricted to one type of example, the supersensitization of the dye, 1,1'-diethyl-2,2'-cyanine iodide, and other 2'-cyanines by small quantities of another dye not absorbing in the same spectral region, for example, 1-(p-diethylaminostyryl)benzothiazole.[4]

Figure 1 shows the absorption spectrum and

[1] C. E. K. Mees, *The Theory of the Photographic Process* (The Macmillan Company, New York, 1942), pp. 975 and 1070.
[2] O. Bloch and F. F. Renwick, Phot. J. **60**, 145 (1920).
[3] C. E. K. Mees, U. S. Patents 2,075,046-8 (1937).
[4] B. H. Carroll and J. A. Leermakers, U. S. Patent 2,313,922 (1943).

the spectral distribution of photo-conductivity and of photographic sensitivity of photographic films containing the sensitizing dye without and with a supersensitizer. The photo-conductivity curve represents the photo-currents excited by light at various wave-lengths as actually incident on the film from the exit slit of the mono-chromator, while the photographic sensitivity is expressed in terms of the reciprocal of the inci-dent energy in ergs per square centimeter re-quired to produce a density of 0.5 in the developed image. The maximum in the photo-conductive sensitivity at about 460 mμ is therefore only apparent; when the currents are computed for equal incident energy at different wave-lengths, the curve rises steadily with diminishing wave-length from 500 mμ in a manner parallel with the photographic sensitivity. (See Part I of this series, Fig. 6.) In the experiments summarized in Fig. 1, the photo-conductivity was measured at high intensity (about 2000 ergs per square centi-meter per second at 460 mμ and 5000 ergs per square centimeter per second at 575 mμ); later experiments, in which the intensities used in the photoconductivity and photographic determina-tions were more nearly equal, disclosed more exact quantitative parallelism between the two effects.

It is quite clear that the effects of the super-sensitizer on photographic and photo-conductive sensitivity are parallel; and also that the super-sensitizer does not function by influencing the absorption spectrum of the sensitizer. It is true that the intensity of absorption of the adsorbed sensitizer at the maximum at 575 mμ is somewhat increased by addition of the supersensitizer, but the increase in absorbed energy is small compared with the increase in photographic and photo-conductive sensitivity. It is not lack of absorbed energy which makes the sensitizer alone ineffi-cient; the inefficiency must lie in the transfer of the absorbed energy (either directly or as a moving electron) to the halide. The increase in photo-conductivity with relatively little increase in absorption demonstrates that the function of the supersensitizer is, in some way, to produce a greater yield of free electrons in the silver halide for every unit of energy absorbed by the dye; these additional electrons then act in the usual way in initiating the growth of the latent image,

and the net result is an increase in photographic sensitivity.

It is not our purpose to discuss here in any detail the interesting question of the mechanism of supersensitization in general, but some con-sideration of the special case just illustrated may be appropriate. It might be suggested that the action of the supersensitizer is to influence the manner of adsorption of the sensitizing dye to the silver halide so as to facilitate transfer. The minor changes produced in the spectral absorption seem, however, to be inconsistent with such an action.

It is possible that the action of the super-sensitizer is connected with its disturbing a flow of energy within the adsorbed layer of dye, which otherwise would be retained in the dye and ultimately be dissipated as fluorescence and thermal energy of the dye molecules. When a molecule in a closely packed monolayer of dye absorbs a photon, there will be, with suitable mutual orientation of the dye molecules, a high probability of the propagation of the excited state throughout the layer by resonance inter-action between molecule and molecule.[5] Such a layer might well interact inefficiently with the silver halide substrate; only when the excited state happened to reach a dye molecule adjacent to some foreign molecule would the propagation be disturbed, and a transfer to the halide occur. The function of the supersensitizer, which is assumed to be dilutely dispersed as individual molecules throughout the layer of sensitizer, may be to increase the numbers of these loci of dis-turbance and thus facilitate transfer. The super-sensitizing molecule may participate actively in the final transfer, for instance, by first absorbing the energy of excitation in the dye layer and communicating it to the halide layer as a moving electron or as a quantum of energy, as the case

TABLE I. Desensitizer action on photo-conductivity and photographic sensitivity.

Dye	Relative photo-current for illumi-nation at wave-lengths in mμ				Photographic threshold speed for illumination at wave-lengths in mμ		
	>620	>550	500–570	400–500	>590	>500	400–500
—	0	5	11	171	0	3	580
Desensitizer	3	18	9	147	0	0	0

[5] Cf. J. Franck and E. Teller, J. Chem. Phys. 6, 861 (1938).

TABLE II. Photo-conductive Becquerel effect.

Galvanometer response to 578 mμ before exposure to blue	0
Galvanometer response to blue	500
Galvanometer response to 578 mμ after blue exposure	30
Galvanometer response to 578 mμ after a blue exposure 5 times as intense as first	70

may be. To this concept of the action of the supersensitizer, support is furnished by certain observations on fluorescence made in these laboratories. The 2,2'-cyanine dye under discussion, adsorbed to the silver salt in a photographic layer, fluoresces (although the intensity is not sufficient in itself to account for the inefficiency of photographic sensitization), and this fluorescence is readily quenched by dyes such as 1-(p-diethylaminostyryl) benzothiazole, that act as supersensitizers, and not by dyes such as 3,3'-diethyloxacarbocyanine iodide which do not supersensitize. The bright fluorescence of the aqueous gel of the chloride of the dye is also very readily quenched by supersensitizers sufficiently soluble in water. These substances are in fact the most efficient and complete quenchers found for this particular fluorescence. Here seems to be evidence of a capacity of the supersensitizer to interrupt the propagation of the excitation energy through the "aggregate" of sensitizer and to use it for its own purpose.

We can also see how, according to this proposed mechanism, the requirements that supersensitizers must fulfill cause examples of the phenomenon to be fairly rare. The supersensitizer must be dilutely dispersed in a state resembling "solid solution" in the two-dimensional crystal represented by the adsorbed sensitizer; it must not segregate on the halide grain apart from the sensitizer. It is therefore likely to be a dye, which must fulfill rather restricted "solubility conditions" in the adsorbed sensitizer and moreover, when in contact with the silver halide grain, it must make no permanent claim on the energy acquired by the sensitizer.

DESENSITIZATION[6]

As is well known, certain dyes, for example, phenosafranin, when incorporated into a photo-

graphic emulsion, greatly diminish photographic sensitivity. Desensitizing dyes afford an example of a class of addenda which have profound photographic effects and relatively minor effects on photo-conductivity.

Table I contains data obtained at high intensity of illumination on the action of the desensitizing azacyanine, 3,3'-diethyl-8,9-diazathiacarbocyanine iodide,[7] on photographic and photo-conductive sensitivity. The photographic sensitivity is expressed as inversely proportional to the inertia.[8]

While the addition of the desensitizer practically eliminated photographic sensitivity, photo-conductivity as measured by the steady terminal current was little impaired. Particularly interesting is the small increase in photo-conductivity over that of the undyed film for illumination by orange light, the region of absorption of the adsorbed dye. A slight sensitization for photo-conduction is indicated, and, although in this emulsion no trace of photographic effect was observed in the sensitometric exposure, in other emulsions, a slight optical sensitizing effect of this dye has actually been observed.

The desensitizer does have some effect in slowing the rate of increase of photo-current with time at the start of the exposure and may decrease the final value by some 10 to 15 percent; further studies will be necessary for a complete description of the effect of desensitizers on the photo-conductivity of photographic films. It is clear, however, that the effect of a desensitizer incorporated in a photographic layer is not to inhibit the primary emission of photoelectrons, but must be exerted at a later stage in the sequence of processes concerned in the production of a latent-image speck, for instance, possibly, by acting as a source of alternative electron traps to the sensitivity centers, or by attacking the sensitivity specks or the nascent latent image.

AN ANALOGY TO THE BECQUEREL EFFECT IN PHOTO-CONDUCTIVITY

In 1843 E. Becquerel[9] showed that the photolytic sensitivity of silver chloride papers could be extended into the green, yellow, and red regions

[6] C. E. K. Mees, *The Theory of the Photographic Process* (The Macmillan Company, New York, 1942), pp. 1040 *et. seq.*

[7] Fuchs and Grauaug, *Ber.* **61**, 57 (1928).
[8] See reference 6, p. 712.
[9] E. Becquerel, *Ann. chim. phys.* (3) **9**, 257 (1843).

if a pre-exposure to blue light sufficient to produce some visible photolytic silver was first made. Later studies include those by Eggert and Noddack[10] and by Sheppard.[11]

It is therefore interesting that what appears to be the photo-conductive analog of this photographic effect has been observed. A bromide film, originally inert photo-conductively to light longer than 500 mμ, becomes active to long-wave illumination (in this case 578 mμ) after an exposure to blue light sufficiently strong to produce a slight visible amount of photolytic silver. Table II includes illustrative data. The light source was a mercury arc, General Electric Type H4, the wave-lengths from which were isolated by filters. Further increase in the exposure to blue light caused little increase in sensitivity to yellow. The "sensitized" photo-conduction, like the sensitized photographic effect in the Becquerel phenomenon, is small compared with the effects induced in the region of self-absorption.

A plausible mechanism for the extension of photo-conductivity toward longer wave-lengths by a pre-exposure of the film to blue light is afforded by the discussion of Mott and Gurney[12] on the photoelectric behavior of metals in contact with photo-conducting salts. The "print-out" deposit produced by the blue pre-exposure almost certainly consists of colloidal particles of metallic silver in intimate contact with silver bromide. Although photoelectric emission from metallic silver into a vacuum requires excitation by ultraviolet light, Mott and Gurney point out that silver immersed in silver bromide will be able to emit electrons into the conduction band of the salt under the stimulus of a considerably smaller quantum. Having entered the conduction band, the electron primarily yielded by the silver particle participates in photo-conduction like any other electron raised to that state.

It will be seen that photoelectric emission from "print-out" silver particles followed by the normal fate of electrons ejected into the conduction band of the bromide would lead merely to a redistribution of silver throughout the grain, whereas Eggert and Noddack's observations on the photolytic Becquerel effect point to an increase in silver during the exposure to long wave-lengths, though with low quantum efficiency. It would seem, therefore, that the photolytic Becquerel effect involves something more than the photo-liberations of electrons from silver particles into the conduction band of the salt; this may be the passage of electrons from disturbed sites in the halide lattice adjacent to the silver particle into the metal. On the other hand, there is evidence that the Herschel effect,[13] the regression effected by red and near infra-red light of the photographic image produced by pre-exposure to blue light, is accompanied merely by a redistribution of silver, and it may be that the sensitized photo-conduction produced by print-out silver represents the primary act in this effect. Having lost an electron by absorption of long wave-length light, the colloidal silver particle is likely to lose a silver ion by thermal agitation, which however may be reunited to the electron when the latter is trapped. No change in the total amount of silver is produced by this process, although the original particles may be reduced in size.

[10] J. Eggert and W. Noddack, *Zeits. f. Physik* **31**, 922 (1925).

[11] S. E. Sheppard, J. Frank. Inst. **210**, 587 (1930).

[12] N. E. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England 1940), p. 245.

[13] See reference 6, pp. 277 *et. seq.*