

A REVIEW OF THE ELECTROCHEMICAL BOUNDARIES FOR THE PHOTOCHEMISTRY OF SPECTRALLY SENSITIZED SILVER HALIDE EMULSIONS

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Abstract - By using a series of dyes chosen to vary systematically in either the lowest vacant or highest filled electronic level, it has been found possible to determine photographic thresholds for a number of photoelectronic or photohole induced processes in silver halide systems. The use of this relatively new technique is described which may have broader use in other chemical or photochemical reactions involving either electron or hole transfer acts.

INTRODUCTION

Although it is now more than 100 years since the discovery of spectral sensitization by Vogel in 1873, it is only relatively recently that a mechanistic understanding of the phenomena has progressed to the point that useful predictions may be made about the sensitizing or desensitizing properties of dyes. The fact that photography has enjoyed the progress and success it has achieved to date is a tribute to the triumph of empiricism that is a necessity of many commercial enterprises. In the rush to obtain new products and improvements in photography, many times the reason for the success is overlooked. Photographic science has matured considerably over the years and is now at a state where empirical triumphs are less easy to obtain and new technology is being based on a better understanding of the basic mechanisms which now can be better identified.

One of the tools now being used extensively in the field of photographic science which might have wide photochemical application is the use of a series of dyes which vary systematically in either the lowest vacant electronic level of the dye as determined by its polarographic reduction potential or its highest filled electronic level as determined by its oxidation potential. It is the object of this paper to review the use of this relatively new technique and describe examples illustrating how it has been applied in the field of spectral sensitization.

SUPERSENSITIZATION

One of the main goals of silver halide research is to design photographic systems that are as efficient as possible in their utilization of light to create a developable latent image that ultimately yields the photographic image. As recently reviewed, (Ref. 1) it was recognized fairly early that in the spectral sensitization of silver halide emulsions, increased photographic response could be obtained by mixing two dyes together to obtain an improvement greater than the sum of the improvements obtained with either dye alone. This phenomenon was described as supersensitization in 1937 by Mees (Ref. 2) in a series of U.S. Patents. Although supersensitization was recognized to be photographically useful even in the late 1800's and was investigated extensively in the 1930's, it was not until 1947 that any theoretical study was reported (Ref. 3) to explain the mechanism of the effect.

In 1968, it was recognized that the anodic oxidation potential of the supersensitizer must be less positive than that of the dye it supersensitizes (Ref. 4).

A useful tool in the investigation of the mechanism of supersensitization has been the use of a series of dyes that vary systematically in oxidation

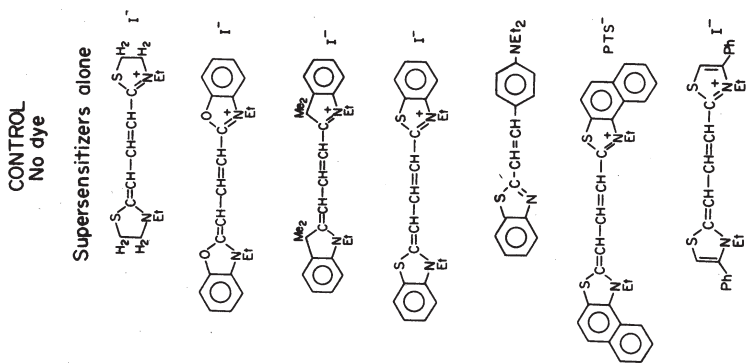
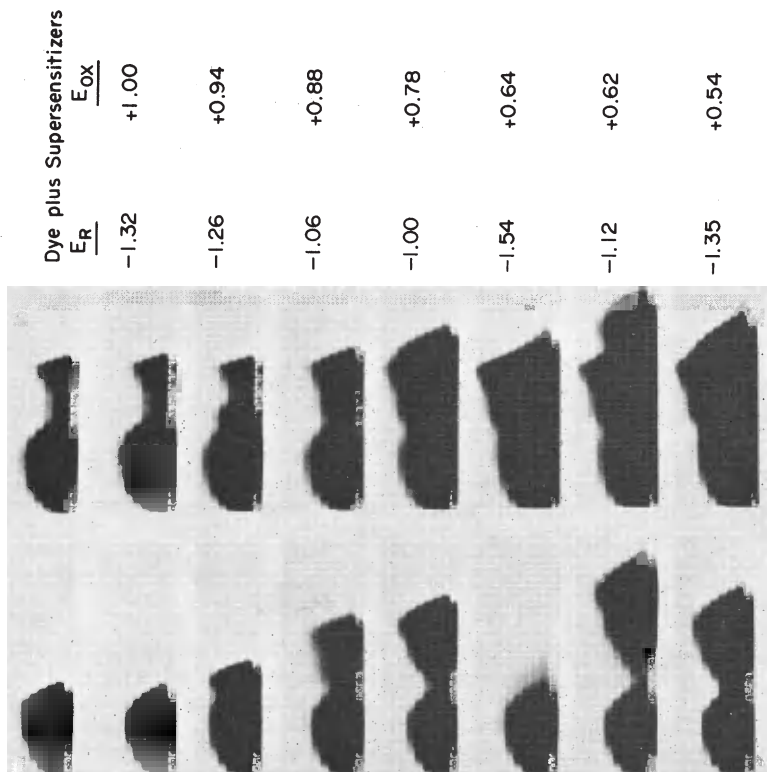
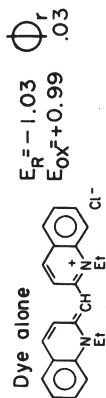


Fig. 1. Supersensitization of 1,1'-diethyl-2,2'-cyanine chloride with a series of supersensitizers having systematically decreasing oxidation potentials. This figure shows basic support for the hole trapping theory of supersensitization and the approximate location of the J-aggregate's highest filled level at +0.88 v. From P. B. Gilman, Jr., *Photogr. Sci. Eng.*, **18**, 418 (1974).

potential so that the critical potential for supersensitization may be obtained. Figure 1 shows the results from such a series used to supersensitize the J-aggregate of 1,1'-diethyl-2,2'-cyanine. The dyes with oxidation potentials more positive than +0.88 v are ineffective, whereas dyes with oxidation potentials less positive than +0.88 v are increasingly effective as supersensitizers, as the oxidation potential decreases.

The sharp improvement in spectral sensitizing efficiency obtained from supersensitizers at the threshold potential of +0.88 v suggests that this value may correspond to the effective oxidation potential of this particular J-aggregate. The technique of systematically varying the oxidation potential of a series of supersensitizers to determine the threshold for supersensitization thus provides an effective method for estimating the ground-state level of a J-aggregate, which is not yet possible to measure directly by electrochemical means.

PHOTOHOLE FORMATION

One of the most fundamental problems in the spectral sensitization of silver halide is an adequate explanation of the difference in energy between that required for latent-image formation in the intrinsic region of absorption of the silver halide and that required in the spectrally sensitized green, red, and infrared regions of the spectrum. Essentially, the question is: How can a spectral sensitizing dye absorbing in the green, red, or infrared region of the spectrum do a job that normally requires much more energy than is available from the excitation of the adsorbed dye?

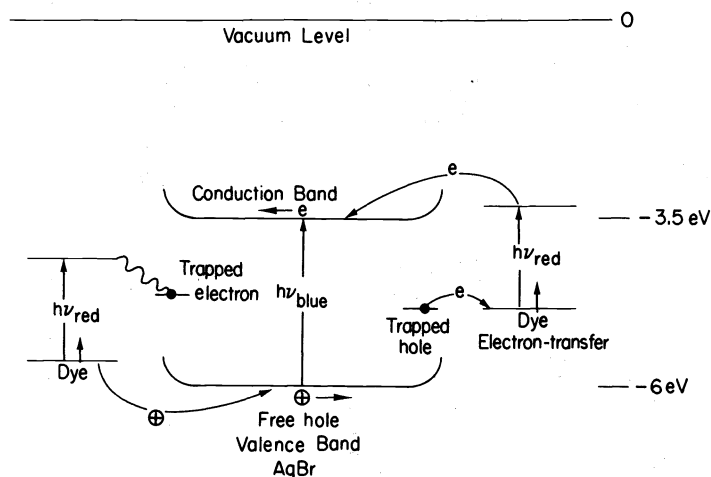


Fig. 2. A comparison of the energy levels in silver bromide with those of two red spectral sensitizing dyes, one which is capable of hole injection with a trapped electron (left) or electron injection with a trapped hole (right). From R. W. Berriman and P. B. Gilman, Jr., *Photogr. Sci. Eng.*, **17**, 235 (1973).

This energy problem is depicted in Fig. 2 for two extreme examples of possible sensitizing dyes with less energy available from excitation than necessary to match the energy requirements for band-gap excitation of silver halide. If it is possible for a dye to inject an electron directly into the conduction band of silver halide, the consequence must be a trapped hole with less energy than a valence-band hole. Conversely, if an excited dye can inject a hole directly into the valence band of the silver halide with less energy than the silver halide band gap, the consequence must be that the excited electron has less energy than required for a direct conduction band electron.

In an attempt to locate the energetic level associated with the spectral sensitization of photoholes energetic enough to enter the valence band, a series of dyes varying systematically in their oxidation potentials were coated on an internally fogged emulsion with and without an electron trap-

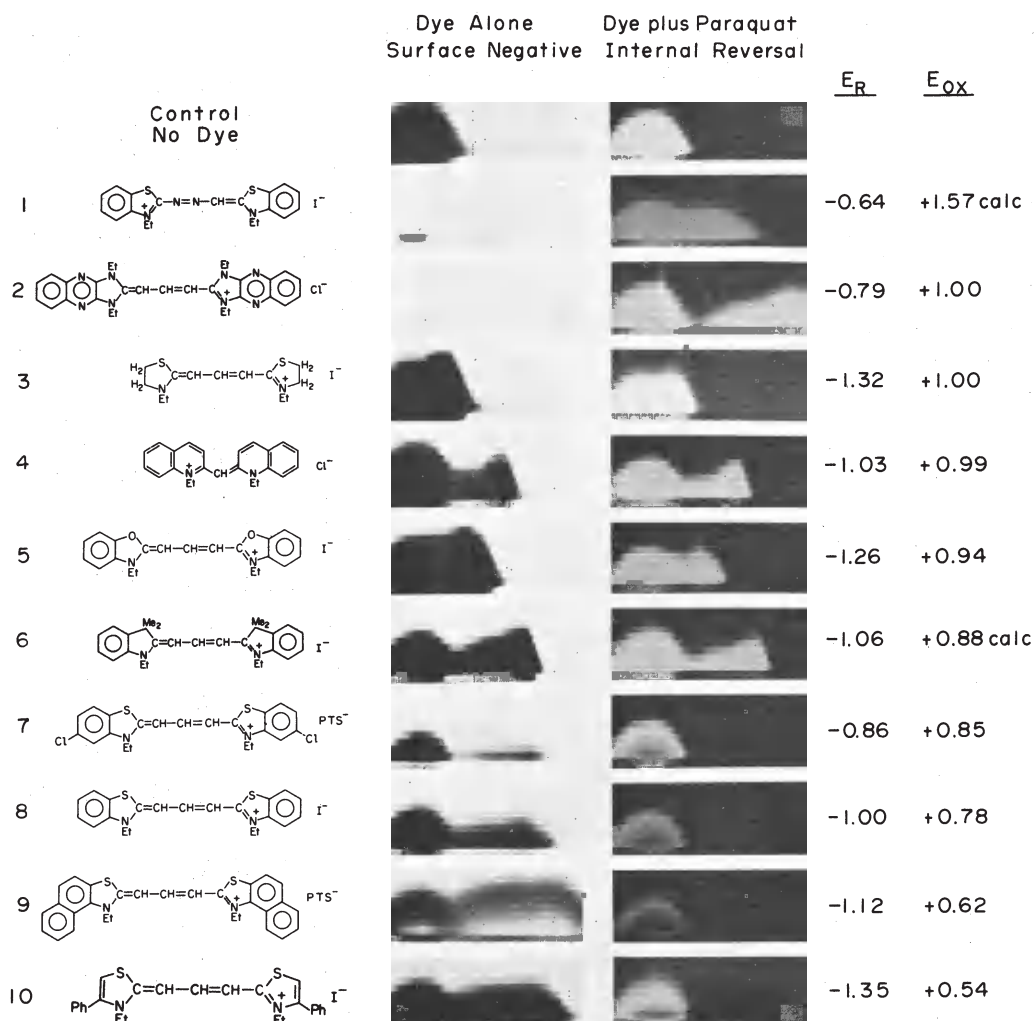


Fig. 3. Spectral sensitization of the surface negative and internal reversal for an internally fogged emulsion at $pAg = 8.0$ with a series of dyes having systematically decreasing oxidation potentials. The threshold for spectrally sensitized photobleaching of internal fog occurs between $E_{OX} = +0.88$ and $+0.85$ v. From R. W. Berriman and P. B. Gilman, Jr., *Photogr. Sci. Eng.*, **17**, 235 (1973).

ping agent 1,1'-di-n-butyl-4,4'-bipyridinium dibromide (n-butyl paraquat) (Ref. 5). The results from such a series are shown in Fig. 3.

Dyes 1 and 2 typify the type of dye suggested in Fig. 2 that would be capable of photo-producing mobile holes but not free electrons in the act of spectral sensitization. Dyes 7-10 typify the type of dye which can spectrally sensitize the production of an electron which gets into the conduction band of the silver halide but, because of a lack of excitation energy, cannot simultaneously produce a mobile hole.

The photographic threshold for photohole bleaching of internal fog has been found to be dependent on the concentration of silver ions present at the time of exposure. The influence of pAg ($pAg = -\log Ag^+$) on the spectral sensitization of surface negative image and the internal reversal of an internally fogged emulsion is shown in Figs. 4, 5 & 6.

If the thresholds for just observable spectral sensitization of the photoelectron and photohole events are selected and plotted as a function of pAg vs. the reduction and oxidation potentials of the dyes, the results shown

in Fig. 7 are obtained. This plot represents an estimate of the continuous threshold for spectral sensitizing events for both reduction and oxidation that occur over a pAg range of from 10 to 6.0.

Whether the actual energy levels of the conduction and valence bands of the silver halide change measurably with respect to vacuum is not yet known. These experiments indicate that the effect of pAg is most important on those dyes, which according to this picture, have sensitizing levels less than necessary to spectrally sensitize a conduction or valence band event. Dyes that have energy levels estimated to be well in excess of those necessary

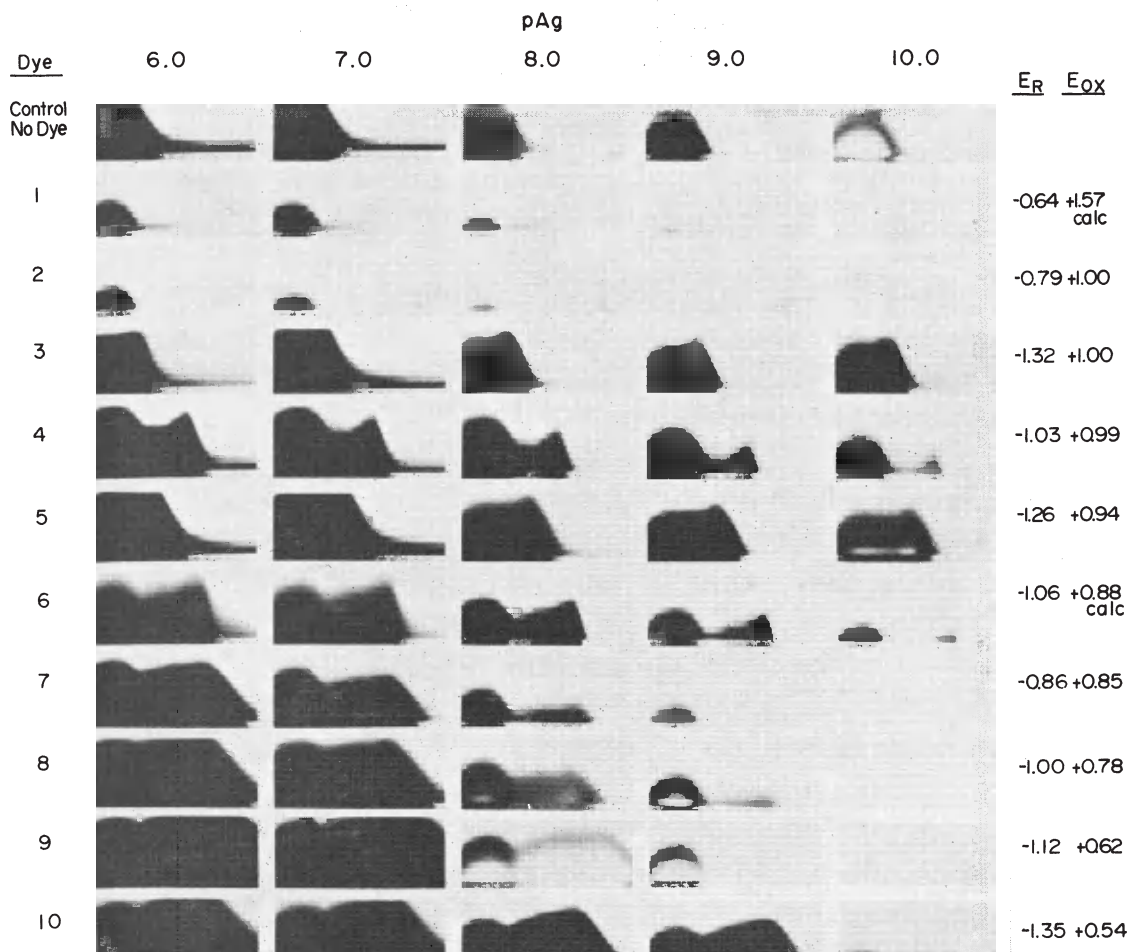


Fig. 4. The effect of pAg on the spectral sensitization of surface negative image using a series of dyes from Fig. 3 which vary systematically in oxidation potential. The recovery of desensitization with low pAg is greatest for dyes with E_{RED} less negative than -1.26 v. From R. W. Berriman and P. B. Gilman, Jr., Photogr. Sci. Eng., **17**, 17 (1973).

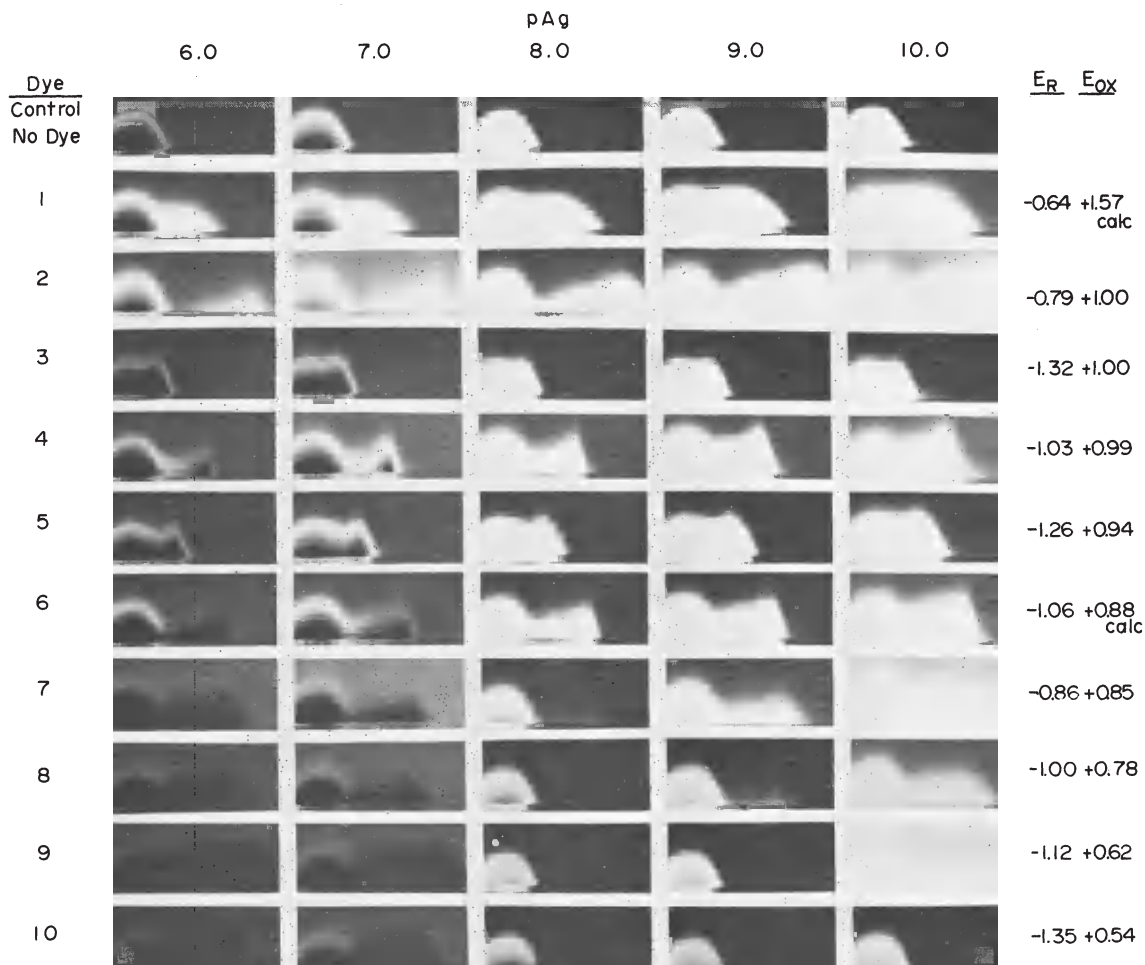


Fig. 5. The effect of pAg on the spectral sensitization of the photobleaching of internal fog using a series of dyes from Fig. 3 which vary systematically in oxidation potential and were coated with n-butyl paraquat as an electron acceptor. Decreasing pAg shifts the threshold for photobleaching to lower E_{OX} values. From R. W. Berriman, P. B. Gilman, Jr., *Photogr. Sci. Eng.*, 17, 235 (1973).

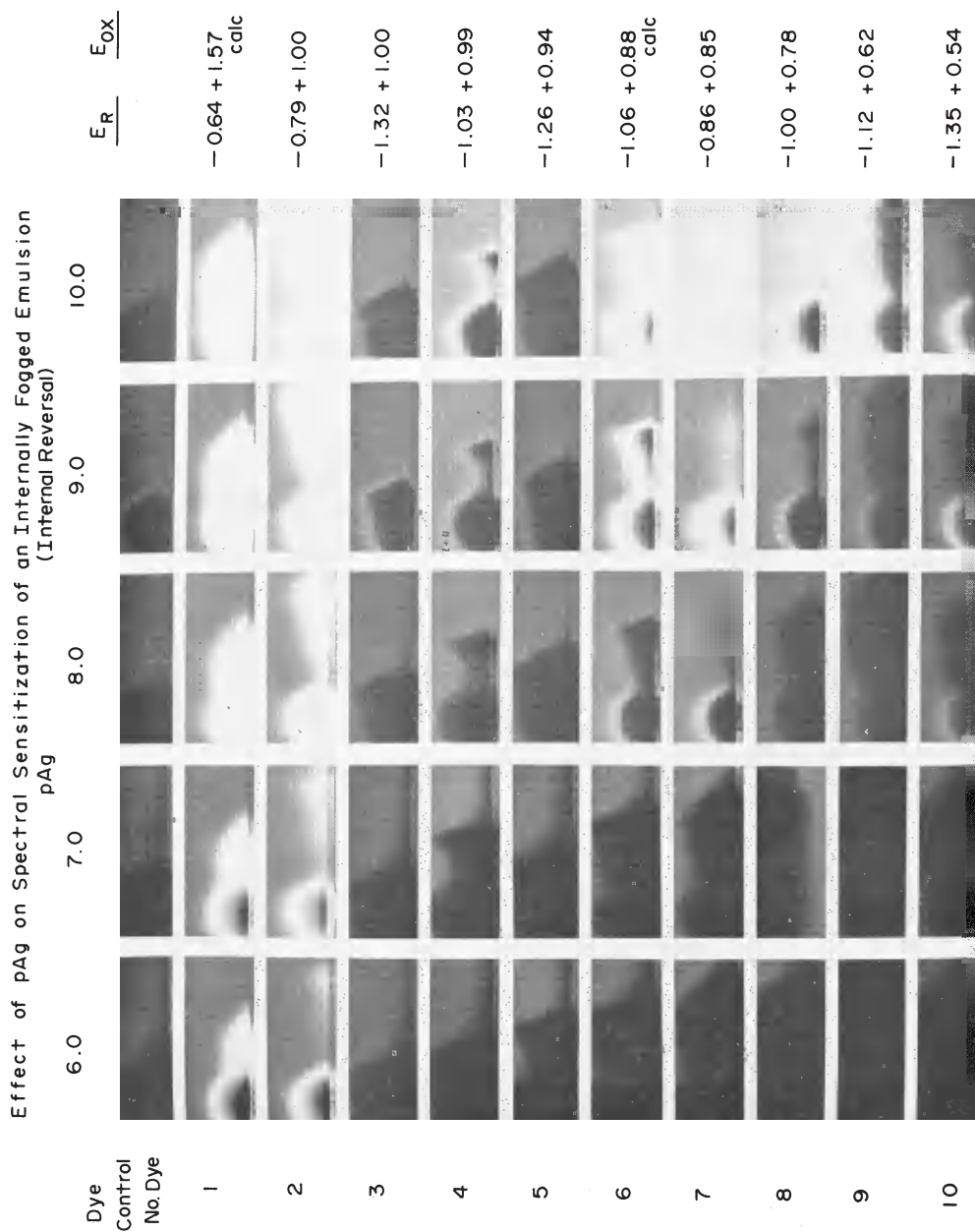


Fig. 6. The effect of pAg on the spectral sensitization of the photobleaching of internal fog using a series of dyes from Fig. 3 which vary systematically in oxidation potential and were coated with no auxiliary electron trapping agent showing that photobleaching is not dependent on the use of n-butyl paraquat for many dyes.

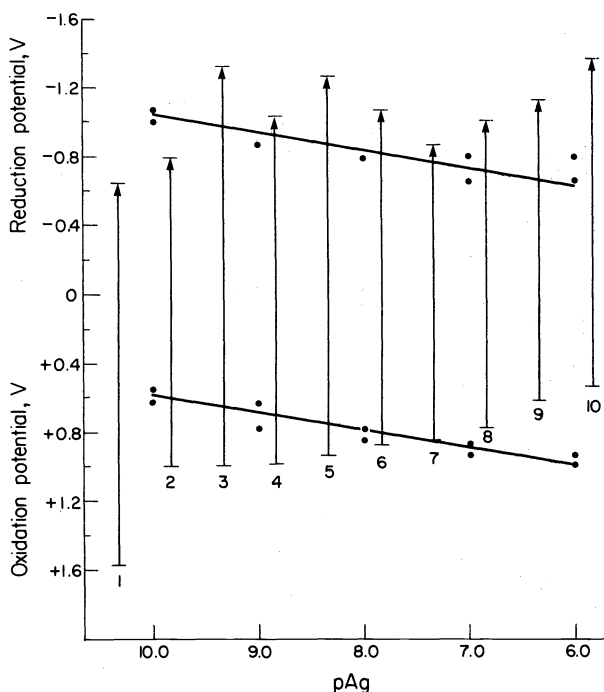


Fig. 7. A summary of the effect of pAg on the spectrally sensitized thresholds for photoelectron and photohole response as a function of the respective reduction or oxidation potential of the dye. From R. W. Berriman and P. B. Gilman, Jr., *Photogr. Sci. Eng.*, 17, 235 (1973).

to spectrally sensitize conduction or valence band events are relatively unaffected. The effect of changes in pAg thus seem primarily influential in affecting the electrochemical reduction and oxidation of silver by excitation energies that are insufficient to accomplish conduction or valence band events directly.

PHOTOELECTRON THRESHOLDS

Although the study on photohole formation (Ref. 5) did include data on photoelectron production, the dye series was not specifically designed to detail this information and results were obtained only on an AgBrI emulsion. Subsequent studies (Ref. 6) using a series of dyes systematically varying in reduction potential were coated on AgBr, AgCl and AgI emulsions. A comparison of the thresholds for spectral sensitization of AgBr and AgCl at pAg = 8.0 are shown in Fig. 8. These results agree with Vanassche (Ref. 7) who first reported such a comparison. However, a more comprehensive study of the effect of pAg showed that the threshold for spectral sensitization of AgBr and AgCl occurred at the same point at sufficiently low pAg's. This is shown in Figs. 9 and 10, using the same dye series as shown in Fig. 8. These results show that dyes with reduction potentials more positive than -0.80 v do not recover their spectral sensitizing properties at pAg's as low as 4.0, even though blue desensitization may be considerably decreased.

The photographically limiting threshold for photoelectron production under room-air conditions has been found to occur at the same potential for all of the silver halides with the major dividing line occurring for dyes with reduction potentials less negative than -0.86 v.

PHOTOCONDUCTIVITY THRESHOLD

Because the photographic results record the integrated consequence of photoelectron, photohole and silver ion interactions, experiments were also performed to examine the photoconductive response of dyed emulsion samples

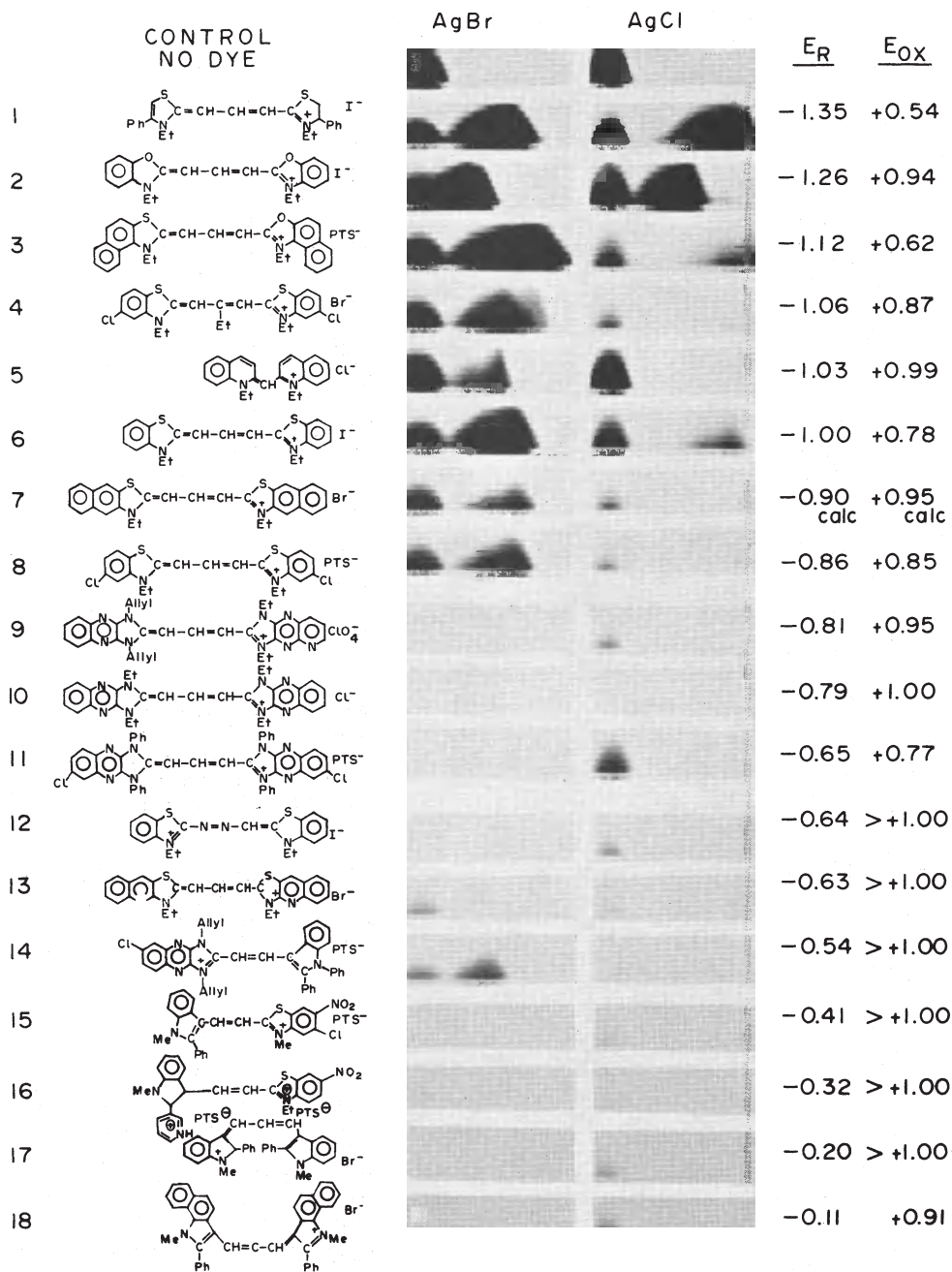


Fig. 8. A comparison of the spectral sensitization of pure AgBr and AgCl at pAg = 8.0 for a series of dyes varying systematically in reduction potential. From P. B. Gilman, Jr., *Photogr. Sci. Eng.*, 18, 475 (1974).

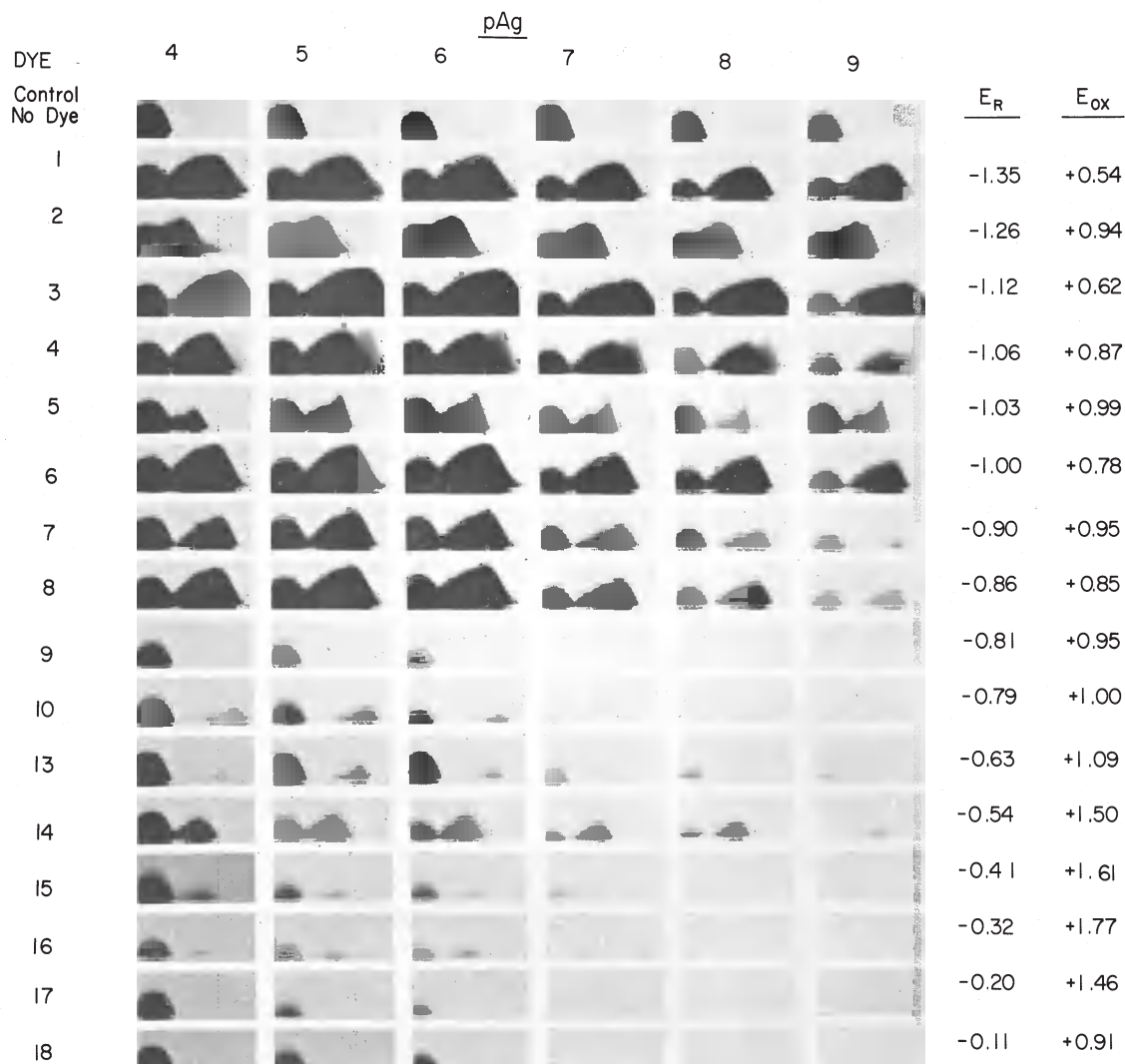


Fig. 9. The effect of coating pAg on the spectral sensitization of AgBr using the dye series from Fig. 8. From P. B. Gilman, Jr., Photogr. Sci. Eng., 18, 475 (1974).

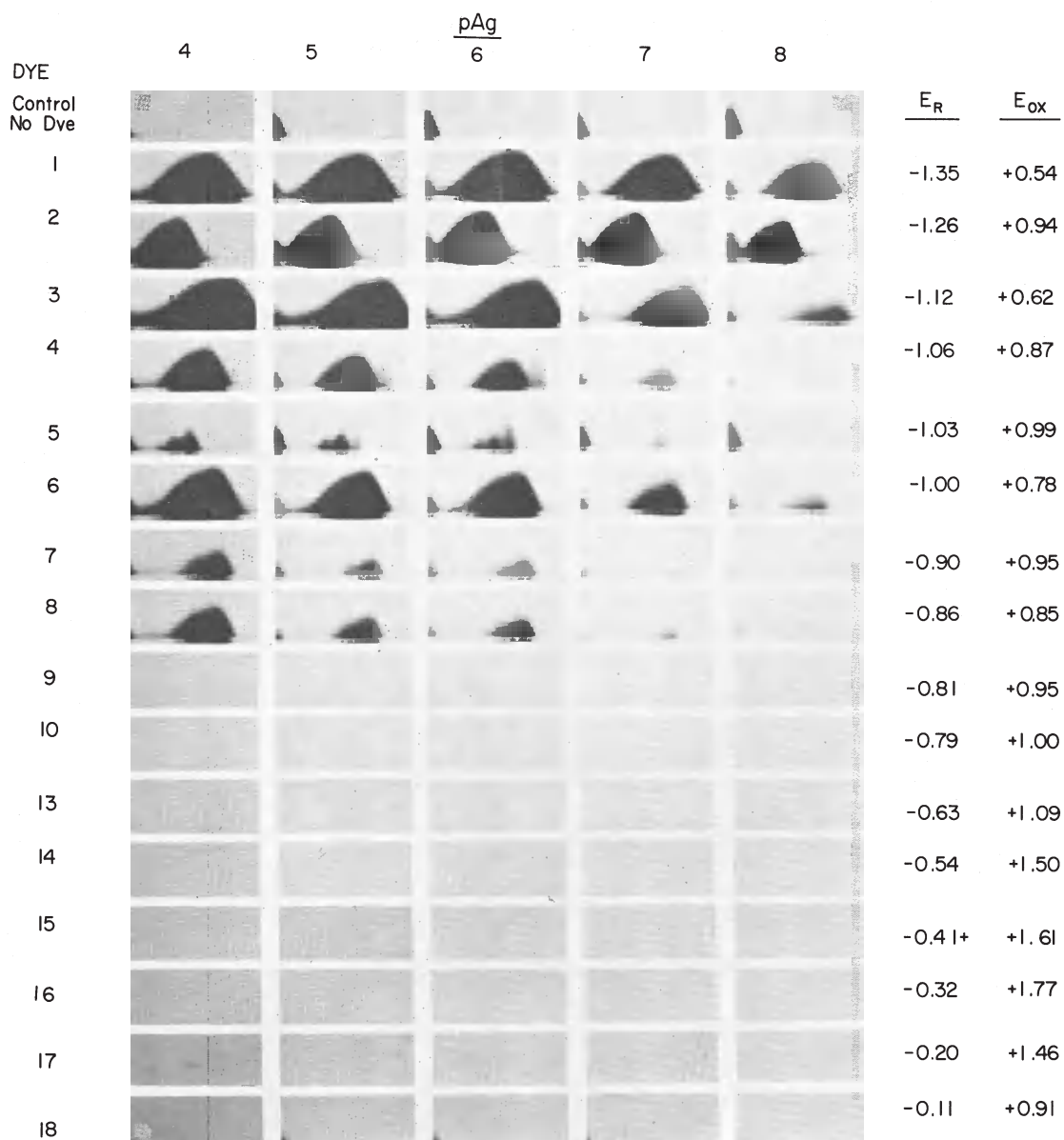


Fig. 10. The effect of coating pAg on the spectral sensitization of AgCl using the dye series from Fig. 8. From P. B. Gilman, Jr., *Photogr. Sci. Eng.*, **18**, 475 (1974).

as a function of dye reduction potential (Ref. 6). These results are shown in Fig. 11 and are to be compared with the photographic response of the same coatings shown in Fig. 12.

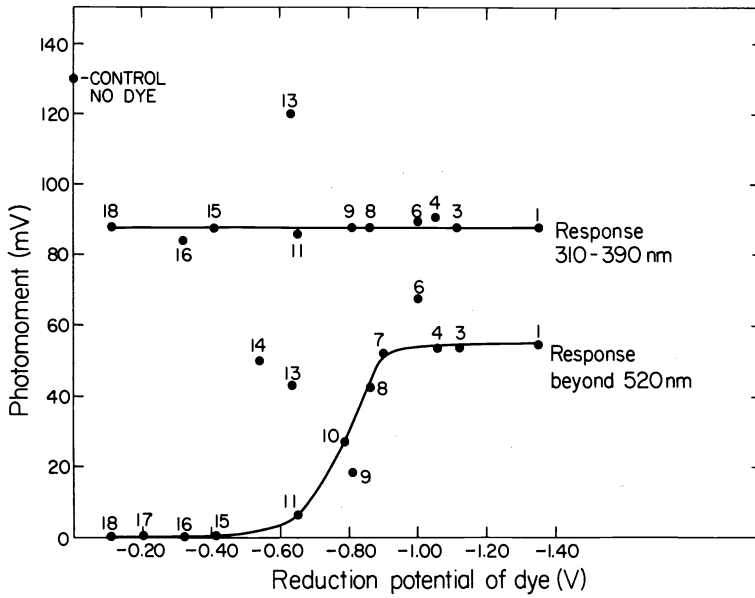


Fig. 11. The effect of dye reduction potential on the intrinsic and spectrally sensitized photoconductive response of AgCl at $pAg = 4.0$ for a room air exposure, $0.2\text{-}\mu\text{sec}$ flash, field = 100 v using dye series from Fig. 8. From P. B. Gilman, Jr., Photogr. Sci. Eng., 18, 475 (1974).

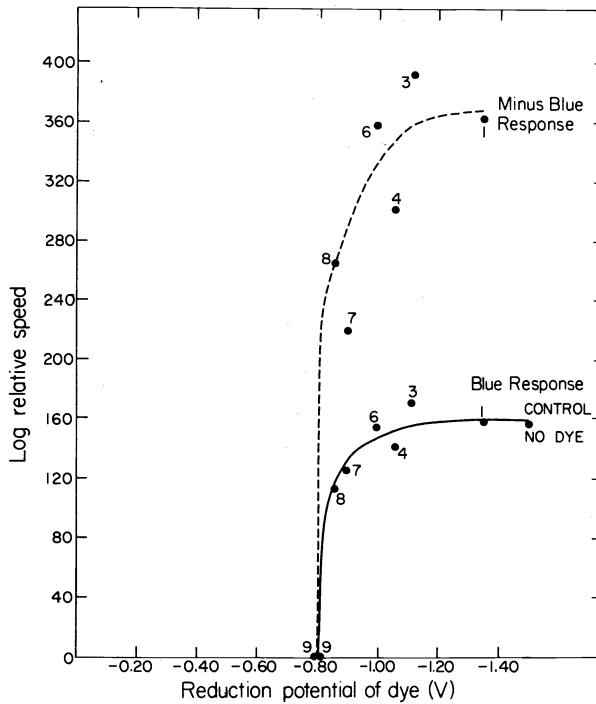


Fig. 12. The effect of dye reduction potential on the intrinsic and spectrally sensitized photographic response of AgCl at $pAg = 4.0$ for a room air exposure using dye series from Fig. 8. From P. B. Gilman, Jr., Photogr. Sci. Eng., 18, 475 (1974).

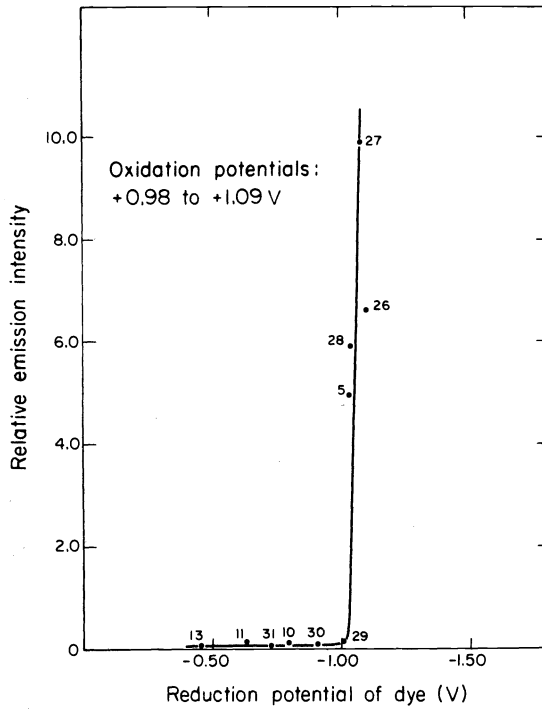


Fig. 13. Spectrally sensitized AgBrI luminescence intensity as a function of dye reduction potential. Dye series as shown in Fig. 15. From T. L. Penner and P. B. Gilman, Jr., *Photogr. Sci. Eng.*, **19**, 102 (1975).

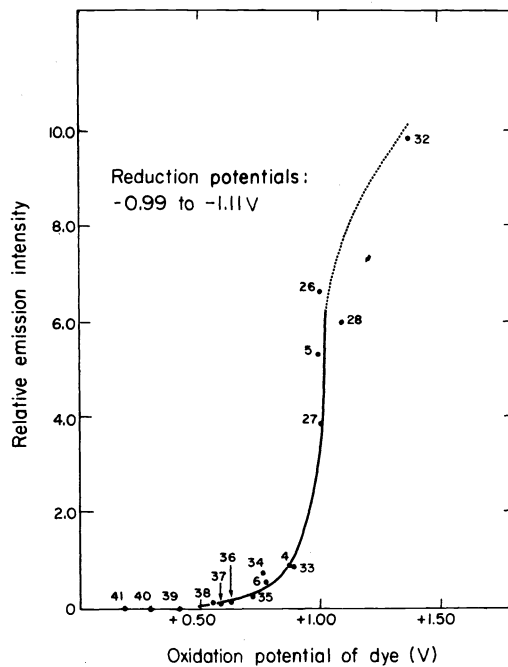


Fig. 14. Spectrally sensitized AgBrI luminescence intensity as a function of dye oxidation potential using dye series from Fig. 16. From T. L. Penner and P. B. Gilman, Jr., *Photogr. Sci. Eng.*, **19**, 102 (1975).

The photographic results for the blue and minus-blue parallel each other closely with a striking onset of complete desensitization for both blue and minus-blue response in room air for dyes with reduction potentials less negative than -0.80 v. The spectrally sensitized, photoconductive response also decreases for dyes with reduction potentials less negative than -0.80 v, whereas the photoconductive blue response does not. This very distinct divergence between the spectrally sensitized and intrinsic photoconductive response at a dye reduction potential of -0.90 v for a $pAg = 8.0$ and at -0.86 v for a $pAg = 4.0$ strongly suggests a basic limitation in the ability of dyes with reduction potentials less negative than -0.80 v to spectrally sensitize silver chloride by the direct injection of an electron into the conduction band in the primary exposure act. The photoconductivity results also suggest that for dyes with reduction potentials more negative than -0.90 v, excitation of the dye results in an electron in the conduction band which is photographically indistinguishable from an electron resulting from band-gap excitation.

LUMINESCENT THRESHOLD

In addition to the spectral sensitization of photoconduction (Ref. 6) and photographic phenomena dependent on photoelectrons (Ref. 6) or photoholes

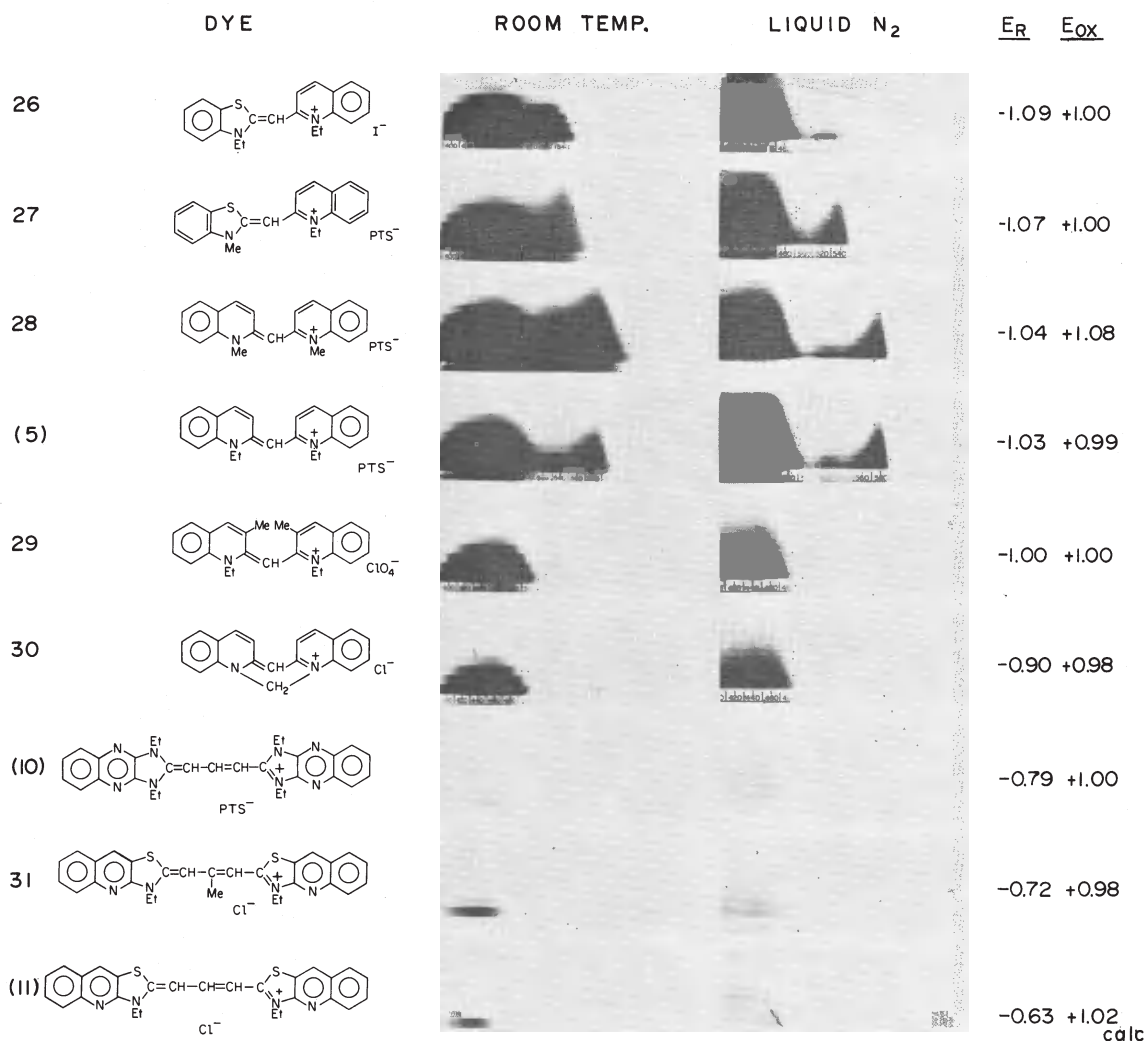


Fig. 15. Spectral sensitization of negative image formation in an AgBrI emulsion as a function of dye reduction potential at room temperature and at 77 K. From T. L. Penner and P. B. Gilman, Jr., *Photogr. Sci. Eng.*, **19**, 102 (1975).

SPECTRAL SENSITIZING PROPERTIES OF DYE SERIES WITH VARYING OXIDATION POTENTIALS ($E_R = -0.99$ to 1.11V)

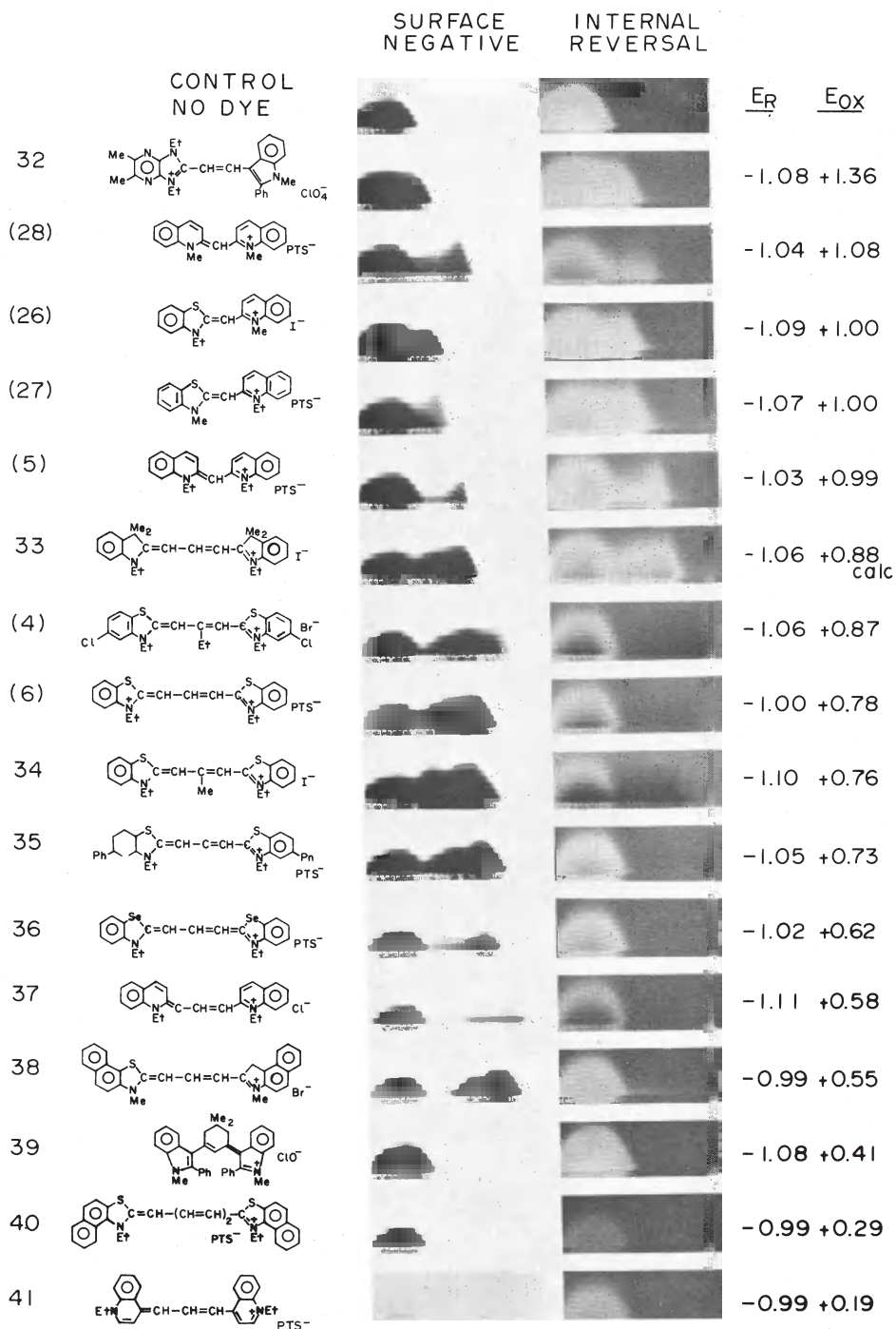


Fig. 16. Spectral sensitization of surface negative and internal reversal photographic response of an internally fogged AgBrI emulsion as a function of dye oxidation potential. From T. L. Penner and P. B. Gilman, Jr., *Photogr. Sci. Eng.*, 19, 102 (1975).

(Ref. 5), dyes adsorbed to silver halide may also spectrally sensitize the intrinsic luminescence of AgBrI emulsion grains. In a study (Ref. 8) of the behavior of several series of sensitizing dyes, varying systematically in reduction or oxidation potential adsorbed to a 0.8- μm silver bromiodide emulsion, it was found that the energy levels that limit the spectral sensitization of the photographic processes also tend to limit the spectrally sensitized luminescence. Examples of the dependence of the spectrally sensitized AgBrI luminescence as a function of dye reduction and oxidation potential are shown in Fig. 13 & 14. The corresponding photographic results obtained from exposures made at room- and liquid-nitrogen temperatures are shown in Fig. 15 & 16.

The most significant thresholds for the onset of the most intense spectrally sensitized luminescence thus appear to be at $E_{OX} = +1.0$ v and $E_{RED} = -1.05$ v. Although these thresholds are most important for the onset of intense luminescence, detectable sensitized luminescence was obtained with dyes with less positive E_{OX} values and less negative E_{RED} values. Since the sensitized luminescence requires the injection of both an electron and a hole comparable in energy to those produced by excitation in the intrinsic region of absorption by the silver halide, severe energy restrictions are imposed on the type of dye that can spectrally sensitize this process. A model, which has been proposed (Ref. 8) to explain the apparent energy discrepancy between excitation and emission, is based on the concept that dyes adsorbed to silver halide may exhibit a distribution of ground and excited levels. Such an energy distribution model has been proposed by Sturmer et al. (Ref. 9 & 10) and by Nelson (Ref. 11) and is shown schematically in Fig. 17. Since the excitation energy for the molecules would remain the same, the distribution of states would not be observed in the absorption spectrum. Independent excitation of two dye molecules, one having a high enough excited level (E_{LV}) to inject electrons into the silver halide and the other having a highest occupied level E_{HO} at an energy sufficient to transfer a hole to I^- would overcome the energy deficiency. The shape of the probability distribution of dye levels is only meant to be conceptual rather than a proposal of a quantitative distribution. In terms of this model, dye levels that previously have been depicted as single-valued would, in fact, represent average values.

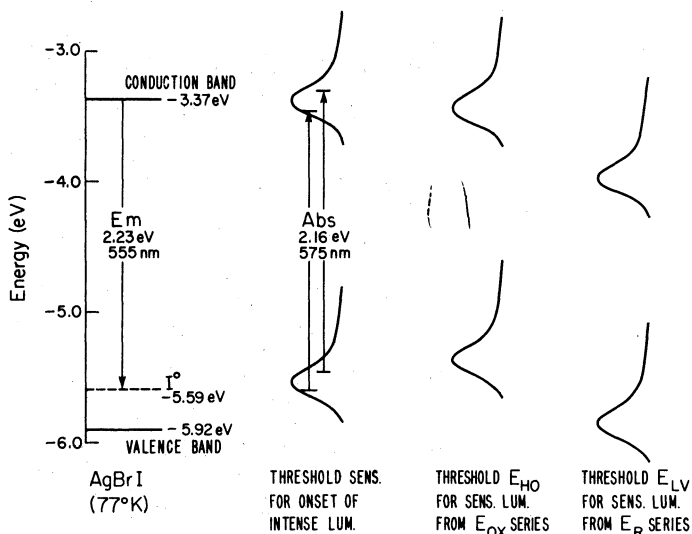


Fig. 17. Energy levels of AgBrI and a model for the dye energy-level distribution for the threshold luminescent events. From T. L. Penner and P. B. Gilman, Jr., *Photogr. Sci. Eng.*, 19, 102 (1975).

EFFECT OF ENVIRONMENT ON PHOTOGRAPHIC THRESHOLDS

All of the data discussed thus far have been derived from photographic exposures made in room-air conditions. It has been shown by Lewis and James (Ref. 12) that evacuation of silver halide coatings containing desensitizing dyes markedly improves the photographic spectral sensitizing properties of the dyes. Later experiments by Babcock and James (Ref. 13) have shown that evacuation followed by a treatment in hydrogen gas almost completely removes desensitization resulting from electron trapping dyes adsorbed to $0.2 \mu\text{m}$ silver bromide emulsions. This phenomenon is illustrated in Fig. 18 and shows that while the threshold for spectral sensitization was between -0.86 and -0.81 v in room air, there appears to be no such threshold for dyed coatings exposed after evacuation and treatment with hydrogen. At first, these "no-threshold" results obtained in vacuum placed some interesting stresses on the theory which previously assigned the energy level of the dye and the conduction band of the silver halide to match at a reduction potential of the dye around the -1.0 v to -0.8 v level. This apparent contradiction between theory and experiment has now been resolved at least to the satisfaction of the author. An important question in the interpretation of the experimental results obtained in vacuum is whether the latent image that is formed in the primary step results from the direct injection of an electron into the conduction band of the silver halide. Previously reported experiments on the spectrally sensitized photoconductivity indicated dyes with reduction potentials more negative than -1.0 v produced a strong

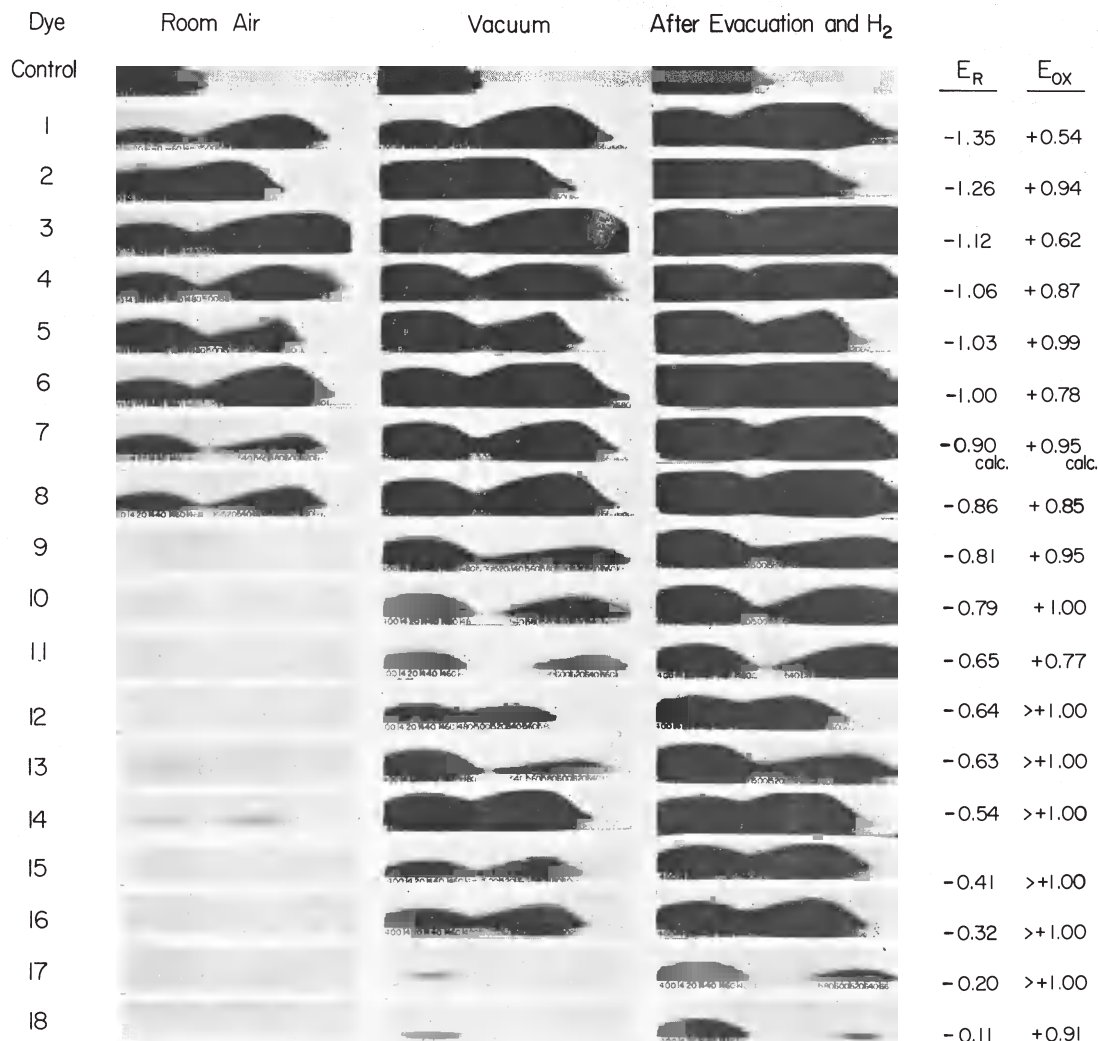


Fig. 18. A comparison of the spectral sensitization of AgBr in room air, vacuum and vacuum plus hydrogen treatments using the dye series from Fig. 8.

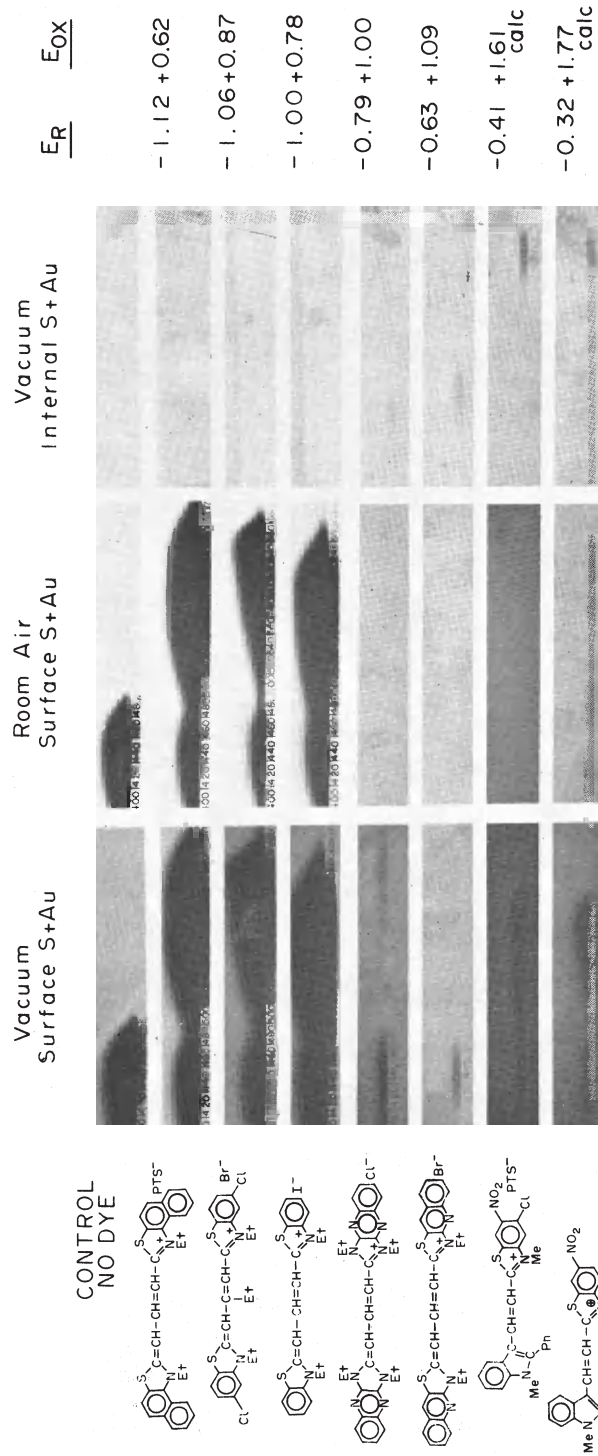


Fig. 19. Effect of environment on the spectral sensitization of surface image for two emulsions, one surface-sensitized, the other internally sensitized. Both emulsions contain 1.2 μ m octahedral AgBr grains (1/25 second exposure).

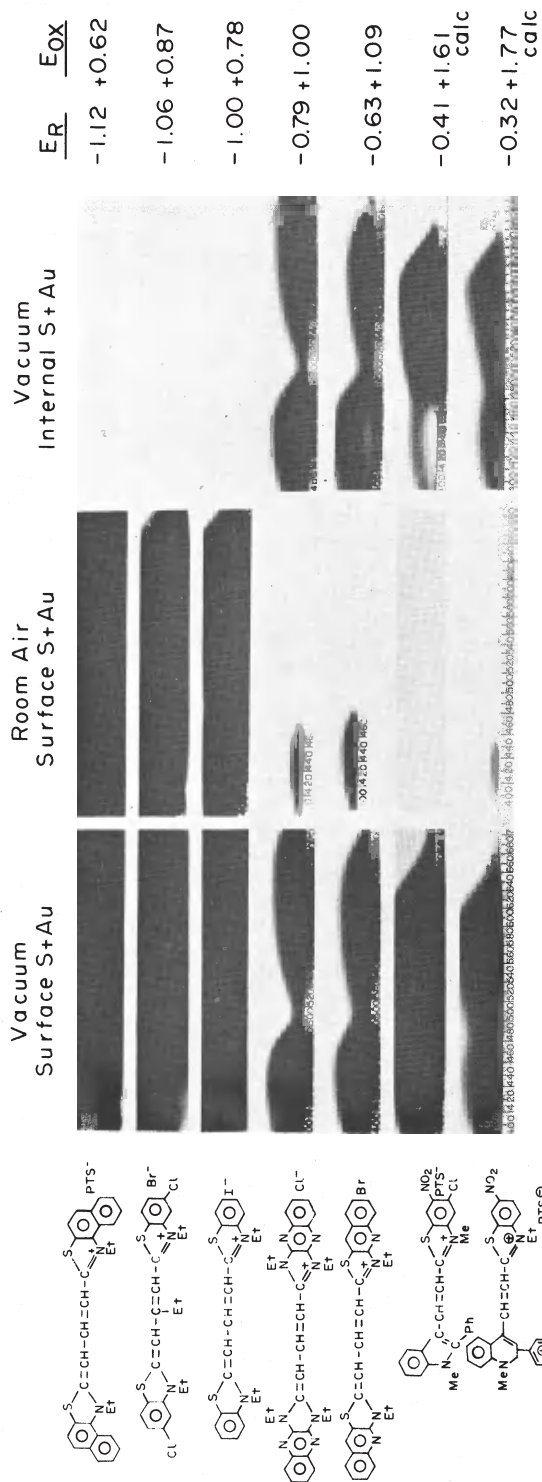


Fig. 20. Effect of environment on the spectral sensitization of surface image for two emulsions, one surface sensitized, the other internally sensitized. Both emulsions contain 1.2 μm octahedral AgBr grains (10 second exposure).

photoconductive response (Ref. 6) while dyes with less negative values produced weaker signals which progressively decreased with decreasing reduction potentials, yet in vacuum all the dyes are capable of spectral sensitization.

In an attempt to obtain an answer to this basic question of whether a conduction band event is involved in the spectral sensitization by dyes with reduction potentials less negative than -1.0 v, a series of dyes varying systematically in reduction potential were coated on two separately prepared silver halide emulsions (Ref. 14). The first emulsion was prepared by conventional means and surface sensitized with sulfur and gold according to standard techniques. The second emulsion was first precipitated, chemically sensitized with sulfur and gold then covered by the core/shell technique described by Moisar (Ref. 15 & 16) and Junkers, Klein and Moisar (Ref. 17).

The most significant results from this study are summarized in Fig. 19 & 20 in which the photographic effect of exposure in room air and vacuum for the surface sensitized emulsion is compared with the internally sensitized emulsion exposed in vacuum. Figures 19 & 20 differ only in exposure time (1/25 sec. for Fig. 19; 10 sec. for Fig. 20). Figure 18 shows that the vacuum treatment did not result in the removal of desensitization which is easily obtained with finer grain emulsion systems (Ref. 18). However, as shown in Fig. 20, considerable difference exists between the room-air and vacuum-exposed coatings at higher exposure levels. When the surface sensitized emulsion is exposed in room air there is a definite threshold for spectral sensitization and desensitization which is independent of exposure time. This threshold occurs between the dyes with the reduction potentials -1.00 and -0.79 v. When the same coatings are exposed in vacuum at 10 sec. exposure times (Fig. 20), a very dramatic recovery is obtained. A serious point in question is whether this recovery observed in vacuum for strong desensitizing dyes is the result of a conduction or sub-conduction band event. Some insight into this basic question comes from observing the results of this same series of dyes on an internally sensitized emulsion. When the coatings of the internally sensitized emulsion were exposed in room-air and surface-developed, no image was observed for any of the coatings, even for 10 sec. exposures.

A possible explanation why the spectral sensitizers with reduction potentials more negative than -0.80 v did not sensitize any surface response of the internally sensitized emulsion is because the dye, upon excitation, injected an electron directly into the conduction band of the silver bromide; the electrons were thus able to sample the internal chemical sensitization and were trapped inside the silver bromide grains. Internal development of the coatings with the dyes having reduction potentials more negative than -0.80 v shows spectral sensitization equivalent to the surface response of the surface sensitized emulsion (Ref. 14). The desensitizing dyes with reduction potentials less negative than -0.80 v produced no image on the surface for room-air exposures and very little internally because of their recognized very strong oxygen dependence, even for the silver bromide grains with strong surface chemical sensitization.

When the internally sensitized emulsion was exposed in vacuum for 10 sec. (Fig. 20) a new photographic threshold was observed, which was symmetrical to the ones previously observed. All of the dyes with reduction potentials more negative than -0.80 v still showed no surface latent image from a vacuum exposure since 100% of the latent image was internal, but the dyes with reduction potentials less negative than -0.80 v showed a very strong surface image, which represented more than 90% of the total latent image for most of these dyes.

This threshold for the onset of surface image in vacuum appears to be identical to the threshold for the desensitization observed for exposures in room air. These thresholds, established by two different photographic experiments, are believed related to the energy level for the conduction band of silver bromide. Energy levels of dyes which are below the conduction band of the silver halide thus would be expected to compete with latent-image formation in room air since the dye is only a transient electron trap prior to a reaction with oxygen to form O_2^- (Ref. 16). However, in the absence of oxygen, an electron trapped at a dye molecule may be neutralized by a surface silver ion and lead to latent-image formation without ever entering the conduction band of the silver halide. Although this effect is similar to the Capri blue effect (Ref. 19 & 20) in which low levels of desensitizing dyes may chemically sensitize the intrinsic response of the silver halide, it is believed different because of the strong spectral sensitization

response. The effect of vacuum on spectral sensitizers that desensitize in room air is thus proposed to be one of preventing the electron loss process in oxygen and allowing the silver ion neutralization of an electron trapped at a dye molecule from either a conduction band event from exposure in the intrinsic silver halide region of absorption or from exposure of dye molecules which are energetically deficient at putting electrons directly into the conduction band of the silver halide. Although this process is efficient for fine-grain emulsions, it seems considerably less efficient for the large-grain emulsions studied here. The reason for this loss in efficiency may be related to the relative surface area of the grains and the decreased availability of silver ions to neutralize electrons trapped at the surface of the large emulsion grains.

SUMMARY

It now seems that the ability to predict the spectral sensitizing behavior of a wide variety of photographic phenomena rests firmly on an understanding of where the energy levels of the dyes lie with respect to the energy levels of the substrate being sensitized.

By running systematic series of dyes varying in either the lowest vacant or highest filled energy level, it now seems possible to locate effective photographic thresholds for any phenomena of interest.

As shown by the above examples, this new experimental tool has proven quite effective at elucidating the mechanism of the photochemistry involved in the spectral sensitization of silver halide. Perhaps the future will show that this tool may also be helpful at determining chemical or photochemical thresholds in other systems in which an electron transfer act is involved in the reaction of interest.

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