

Chemistry of Spectral Sensitization Processes—A Review*

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In this review the evolution of the concepts of AgHal spectral sensitization by the organic dyes is presented. The author comes to the unexpected conclusion that the very first chemical theories of spectral sensitization are, in essence, correct. One hundred years of detailed investigations of spectral sensitization have, in fact, proved the correctness of the early chemical concepts of spectral sensitization processes.

Journal of Imaging Science and Technology 46: 89–100 (2002)

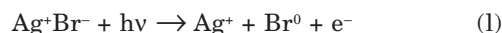
Introduction

Spectral sensitization of silver halide photographic materials is one of only a few examples of practical importance that has been created by man. More than 120 years have passed since Hermann Vogel's the invention of the spectral sensitization phenomenon.¹ During this period, development of spectral sensitization has become highly successful. As for understanding the essence of that phenomenon, up to now, and despite the large number of serious and talented investigations, it would be stretching the truth to say that the mechanism of spectral sensitization is completely established. This indicates, firstly, the complexity of the processes collected under the common "spectral sensitization" name, and, secondly, that this field of knowledge continues to develop.

Physical and Chemical Concepts of the Spectral Sensitization

Let us consider the evolution of ideas on the spectral sensitization mechanism. The very first theories of the spectral sensitization could be arbitrarily divided into physical and chemical.² It should be noted that there were numerous such theories or hypotheses.^{3–5} The well known physicist J. Frank, who, together with Cario, discovered that mercury vapors sensitized the dissociation of hydrogen to atoms. They explained the spectral sensitization as a transfer of excitation energy from the photoexcited dye (Dye*) to the silver halide (AgHal) through a secondary collision, i.e., from the impact of the Dye* against AgHal surface. S. Sheppard's work,

which formed an entire epoch in scientific photography, and later, R. Mecke's investigations, explained sensitization by a photoelectric effect involving the adsorbed dye molecule, i.e., by light induced extraction of an electron from the molecule and its transfer to the silver ion, which is converted to the atom. This hypothesis corresponded essentially to the evolution of ideas on the elementary photochemical process in the silver bromide. These concepts were being developed nearly simultaneously by Fajans in Germany and Sheppard and Trivelli in the United States. The process is described by the following equations:



An electron (e^-) induced by a light quantum ($h\nu$), is separated from the bromide ion in the crystal lattice. The electron is then bound to the silver ion, converting it to a neutral atom. If the primary result of silver halide photoexcitation is extraction of the electron from the lattice ion, i.e., an internal photoelectric effect, then spectral sensitization is an external photoelectric effect, i.e., a transfer of a electron from the photoexcited dye to the silver halide.

Earlier chemical theories considered spectral sensitization the result of some irreversible molecular changes of the sensitizer after its interaction with the AgHal. The oldest hypothesis, expressed by so many investigators that it is hardly possible to name its first author, had considered sensitization as a decomposition process of some hypothetical compounds of the dye with the silver halide.⁴ The result of such a transformation is a reduction of Ag^+ ions to the metallic silver with simultaneous formation of an oxidized, positively charged, dye radical (cation-radical, $\text{Dye}^{\bullet+}$). Sheppard and co-workers proposed a chemical explanation of the sensitization process which included the formation of a chemical complex of the dye with the silver bromide.³

Further progress of the theory of spectral sensitization was due, to some extent, to the advances in solid-state physics and photochemistry. In 1938, Gurney and

Original manuscript received February 15, 2001

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* Dedicated to the memory of Dr. T. H. James

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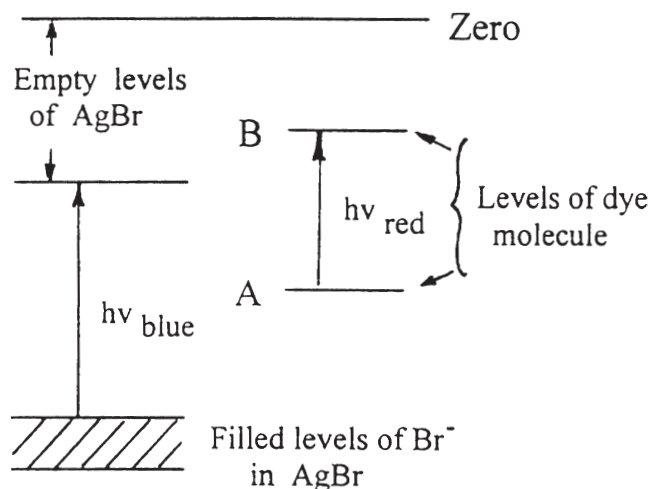


Figure 1. Scheme of the process of the spectral sensitization (from the paper of Gurney and Mott⁶).

Mott considered a mechanism of electron transfer occurring during the spectral sensitization process in the context of a zonal model of silver halides.⁶ Figure 1 illustrates the scheme of this process. According to the Gurney–Mott mechanism, a photoelectron transfers from the photoexcited level in the dye molecule to the AgBr conduction band, i.e., to the unoccupied levels lying below the zero point level (the electron level *in vacuo*). Therefore, according to Gurney and Mott, for efficient sensitization, level B of the dye must be higher than the bottom of the AgHal conduction band (CB).

Such an energy situation, however, is not common. In a number of investigations, it was shown that spectral sensitization also occurred when the photoexcited electron level was below the bottom of the conduction band.^{7,8} Hence, in the sixties, Terenin and Akimov developed a different physical concept of spectral sensitization based on resonance excitation energy transfer.^{7,8} It should be noted that spectral sensitization by resonance excitation energy transfer was first discussed by Mott as early as 1948.⁹ According to that mechanism, the light energy absorbed by the dye would be consumed by the liberation of an electron localized in the AgHal forbidden band. As indicated in Fig. 2A, the sensitization process could be accomplished by transfer of photoexcitation energy from the donor-dye to the acceptor level in the forbidden band of the photoconductor by Förster's mechanism, the result of which is the transfer of an electron from that level to the conduction band. With this type of mechanism the arrangement of the dye levels relative to the AgHal bands became unimportant. The possibility of spectral sensitization by the resonance mechanism was shown experimentally by Akimov⁸ and Buecher and Kuhn and co-workers.¹⁰

For many years, these two approaches to the initial sensitization step have coexisted, although there was active scientific discussion between the supporters of excitation energy transfer and those of electron transfer. A summary of the discussion was published,¹¹ and it might be noted that several of the authors had earlier supported the concept of energy transfer. In that study, it was clearly concluded that spectral sensitization of real emulsions was defined by electron transfer from Dye* to AgHal, and that the contribution by an energy transfer mechanism was no more than a few percent.

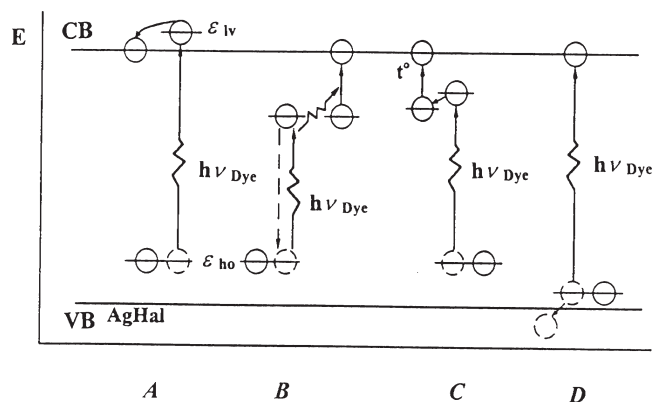
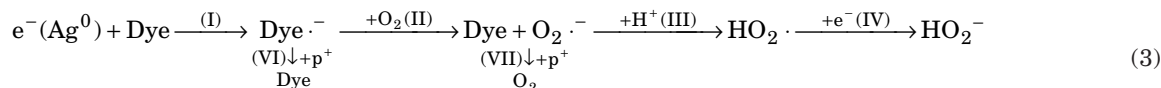


Figure 2. Scheme of processes of the spectral sensitization by electron transfer (A,C,D) and the resonance excitation energy transfer (B).

Numerous studies have shown a definite connection between dye redox potentials photographic efficiency. These results have had a fundamental importance in solving the spectral sensitization mechanism. Among these studies that should be noted are those of Daehne,¹² Tani and Kikuchi,¹³ Gilman¹⁴ as well as a number of other scientists.¹⁵ In these studies, the lowest unoccupied ϵ_{iv} , and highest occupied, ϵ_{ho} , polarographic half-wave reduction and oxidation potentials of dyes were used, as well as quantum-mechanical calculations, to establish the dyes' electron levels.

Regarding the energy transfer mechanism, the controlling factors are the positions of the ground state and excited state levels of the spectral sensitizer relative to the electronic bands of the AgHal. Some possible variants of the level inter-relationship are shown in Figs. 2A, B, C and D. Variant A, where the lowest unoccupied ϵ_{iv} level of the dye (where the electron transfers from the highest level ϵ_{ho} during photoexcitation of the dye) is higher than the bottom of the AgHal conduction band (CB), was already discussed in the Gurney–Mott mechanism (Fig. 1). In Figs. 2B and 2C the level ϵ_{iv} is localized below the conduction band so that direct transfer of an electron to the conduction band is unlikely. There is however, a good possibility that it can transfer energy or an electron to the electron-acceptor level in the forbidden band with consequent excitation of an electron into the CB. In the electron-acceptor, the ϵ_{iv} level is below the conduction band, photoelectrons from CB are formed from direct AgHal photoexcitation, and could be trapped resulting in desensitization or loss of sensitivity. Luppo–Kramer was the first to describe desensitization of AgHal by dyes and introduced the term “desensitization”.¹⁶ Finally, it is characteristic in the D variant (Fig. 2), that the position of ϵ_{iv} is equal to the conduction band, and the highest filled level ϵ_{ho} is localized near to the top of the valence band (VB), because of possible electron transfer from the VB due to photoexcitation of an electron from the ϵ_{ho} level, i.e., the hole from Dye* would be injected into the valence band. Similar processes of photoinjected holes play an important role in the spectral sensitization of direct positive processes, where, as a result, they oxidize initially formed silver centers and the photoelectrons are irreversibly trapped by desensitizer molecules (D). Indeed, in a number of publications in the 1960–1980 timeframe by Daehne, Tani, Kikuchi, Tamura, Hada, Gilman, Nelson,



James, Sturmer, Leubner and others,^{13-15,17a,18-22} established a definite relationship between the position of the dye electron levels and the efficiency of spectral sensitization. For example, it was shown that as the ϵ_{iv} level increased, desensitization increased and spectral sensitization efficiency decreased.

Further evolution of the concepts for the spectral sensitization mechanism incorporated consideration of not only the ϵ_{iv} and ϵ_{ho} levels individually, but also the simultaneous participation of both levels in photographic process. This participation forms the basis of a modified electron transfer mechanism proposed by Tani,^{13,23,24} where not only injection of electrons from ϵ_{iv} to CB is considered, but also hole injection from ϵ_{ho} to the VB of the silver halide. Hence, the combined photographic effect is determined by the competition of these two processes.

Among the most important investigations in the spectral sensitization field are, without question, those of T. H. James and co-workers^{25,26} concerning the effect of vacuum treated photographic layers and spectral sensitization efficiency. In those studies, it was shown that after elimination of oxygen and water from the films, the spectral sensitization efficiency dependence on ϵ_{iv} drastically changed and many desensitizing dyes with ϵ_{iv} levels lying well below the conductivity band became efficient sensitizers. It was a unique *crucial* experiment that proved that spectral sensitization efficiency is defined, not so much by the position of the dyes' levels relative to the AgHal bands, as by chemical reactions where oxygen and protons of water leading are involved with the formation of secondary products (in particular, hydrogen peroxide) and, in doing so, diverting photoelectrons from latent image formation.

It should be noted that the effect of oxygen and water on photographic processes was actually detected much earlier.¹² Oxygen and moisture, after all, affect the secondary processes of desensitization by electron acceptor dyes. Even in works of Blau and Wambacher²⁷ noted that the desensitizing effects of pinacryptol yellow and phenosafranine appeared only in the presence of oxygen. Thus, the experiments of James clearly established the role of *chemical* reactions in spectral sensitization processes.

Secondary Chemical Processes of Desensitization of Silver Halides by Dyes

Let us consider in more detail, the chemical processes occurring after photoexcitation of AgHal grains in which spectral sensitizing dyes in the ground state, take part. It was mentioned above that the dyes could induce a decrease in the intrinsic (blue) sensitivity of AgHal. The problem here, however, is to address the processes of dye desensitization of AgHal grains. Desensitization processes are surface redox reactions where the dye in the ground state could be an oxidizer accepting photoelectrons, or a reducer accepting AgHal holes. Desensitization processes related to photoelectron accepting process by an electron-acceptor dye, are indicated as *type I desensitization processes*, as distinct from *type II sensitization processes* related to the hole mechanism.^{21,28-30}

Type I desensitization, illustrated below in Eq. 3, is the one best understood.^{21,26,28-30}

In Eq. 3, an electron from the conduction band, or from a surface trap, or from a latent image precenter (Ag^0), is trapped by an electron-acceptor Dye in the ground state on the ϵ_{iv} level with the formation of a $\text{Dye}^{\bullet-}$ anion-radical. Then an electron from $\text{Dye}^{\bullet-}$ is transferred to oxygen with formation of the superoxide anion $\text{O}_2^{\bullet-}$. The oxygen anion-radical, as is well known, is easily protonated with formation of a $\text{HO}_2^{\bullet}$ radical having significantly greater affinity for the electron than oxygen itself. Therefore, $\text{HO}_2^{\bullet}$ can easily capture another electron with formation of HO_2^{-} followed by subsequent protonation to hydrogen peroxide. So electrons are diverted from formation of the latent image to the formation of H_2O_2 . Hydrogen peroxide is an oxidizer and therefore could also accept electrons. Furthermore, recombination of the $\text{Dye}^{\bullet-}$ or $\text{O}_2^{\bullet-}$ electrons with holes in stages VI and VII of Eq. 3 is possible.

According to Eq. 3, the dye in the ground state acts as an intermediate electron carrier to O_2 and protons, i.e., oxidation processes catalyzed by the dye and involving the water oxygen and protons. Figuratively speaking, the photographic material after photoexcitation behaves as if it "breathes". In an oxidizing "flame", further "inflamed" by the dye, the latent image precenters are "burned away". The participation of the intermediate dye during step I of scheme (3) can be determined by a number of factors: the electron affinity of the molecule, the positive charge of the dye's chromophore, the length of cyanine dye molecule and, thereby, the significant electron trap cross-section. Here, the probability of step I should increase as the dye molecule's electron affinity increases, as indicated by the polarography half-wave reduction potential, $E_{1/2}^{\text{red}}$. In fact, as the dye electron affinity increases, i.e., as $E_{1/2}^{\text{red}}$ increases, increased desensitization is observed.¹⁷ Based on the results obtained for a series of dyes, despite their structural differences, a linear dependence of the logarithmic desensitization, $-\log \text{DD}$ on $E_{1/2}^{\text{red}}$, was found to have the general formula of Eq. 4:

$$\log \text{DD} = m \cdot E_{1/2}^{\text{red}} + n, \quad (4)$$

which holds for different dye concentrations and Ag^+ ion concentrations (pAg). Typical curves are shown in Figs. 3a and 3b.

The extremely graphic energetic pathway of type I desensitization reactions can be illustrated on an electrochemical potential scale for components of the photographic emulsion.³¹ In Fig. 4a the standard redox potentials of the components of AgBr emulsion are shown. From this figure, the potential of the bottom of the conduction band corresponds to -1.1 V (relative to the standard hydrogen electrode). The energy pathway of the desensitization reaction is shown in Fig. 4b.

In other studies, investigations to develop the kinetic model of the spectral sensitization based on dye electrochemical potentials and other components of photographic emulsion were carried out.^{15,21,29} The principle of that model, based on the Marcus theory of electron transfer in a polar environment,³² is the hypothesis that the rates of electron transfer reactions between the photoexcited AgHal and other components of the photographic film (the dye among

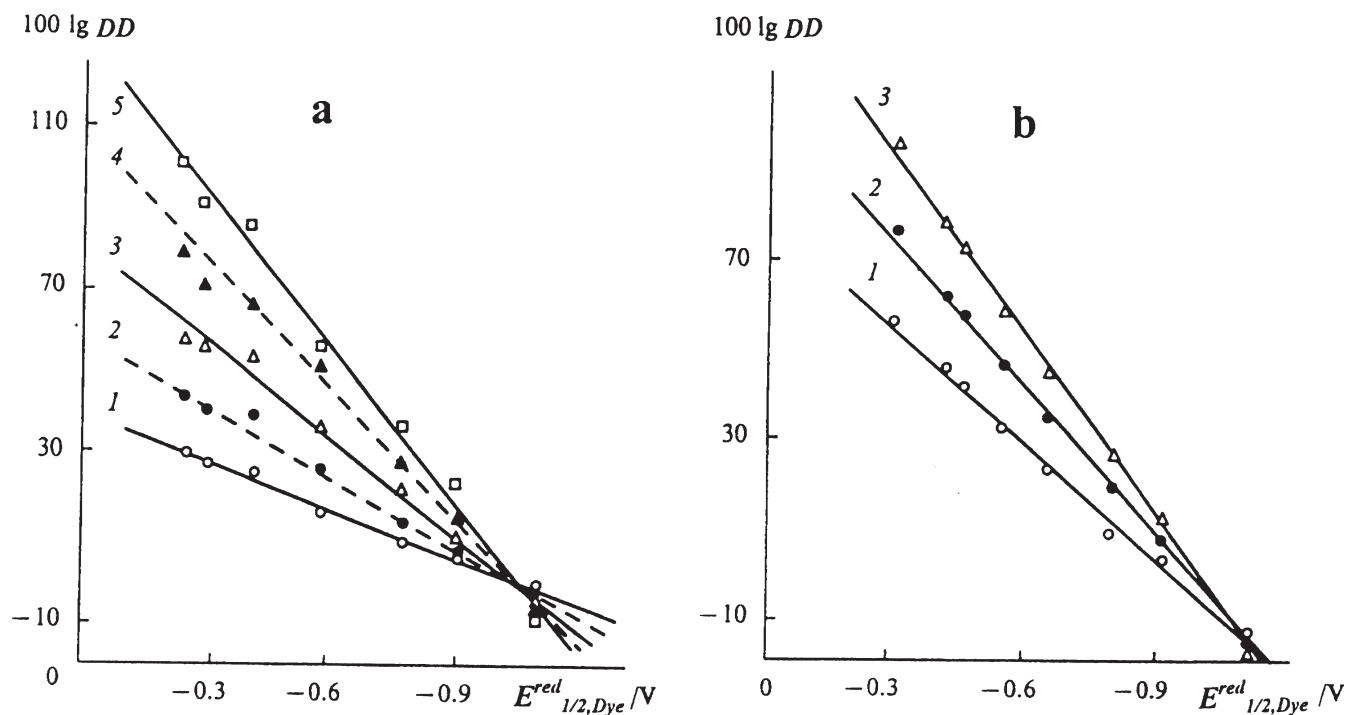


Figure 3. Dependence of $\log DD$ on $E^{\text{red}}_{1/2,\text{Dye}}$: dyes concentration (mole/mole of AgHal): 1 – 1×10^{-6} , 2 – 2×10^{-6} , 3 – 4×10^{-6} , 4 – 8×10^{-6} , 5 – 10^{-5} ; pAg = 8.0; pAg: 1 – 7.4; 2 – 8.0; 3 – 8.9; dyes concentration is 2×10^{-6} mole/mole of AgHal.

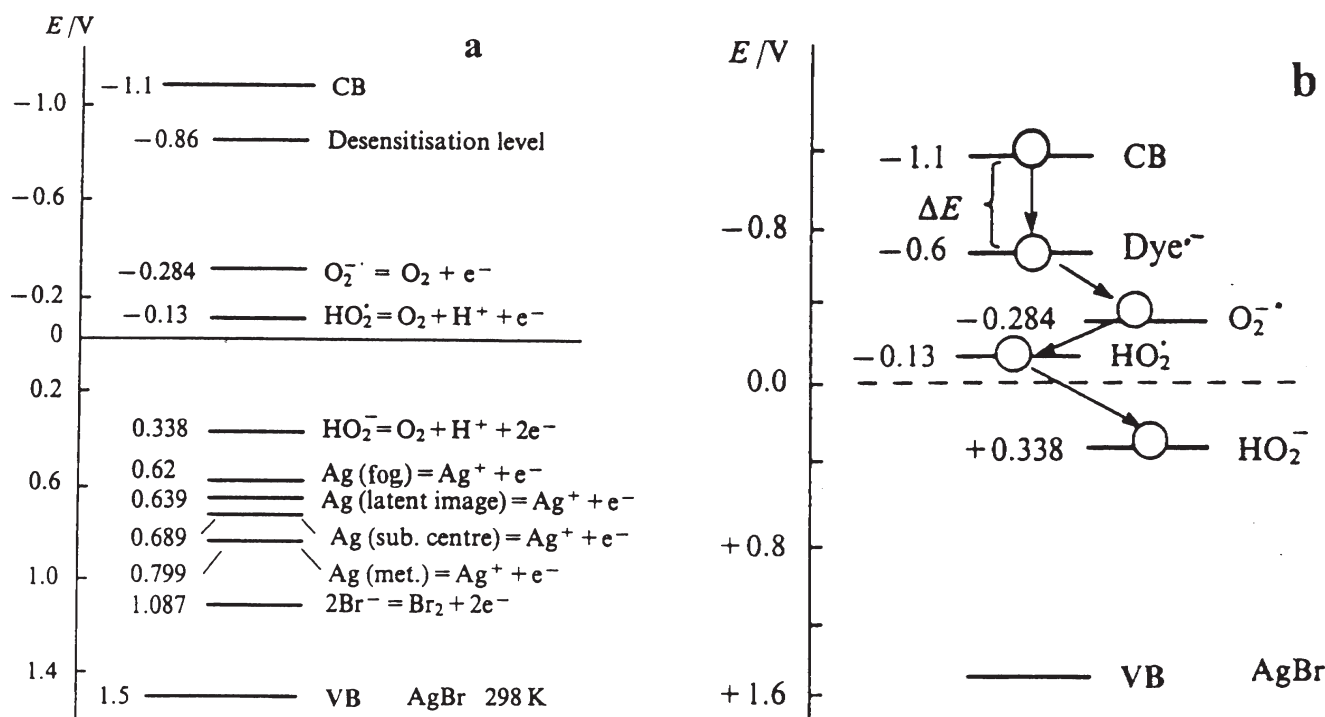


Figure 4. Oxidation-reduction potential diagram for the components of a AgBr emulsion (a) and scheme of electrons transitions in the process of desensitization of I type by electron-acceptor Dye (b); potentials are given relative to n. h. e.

them), or between the photoexcited Dye^* and other components (the AgHal among them) can be expressed as kinetic equations where the activation energy is a function of the difference between standard redox potentials of the systems taking part in electron transfer (linear free energy relationship).

$$\Delta G^\ddagger = -RT \ln k \approx a \cdot \Delta G^0 + b \approx a \cdot n \cdot F \cdot \Delta E^0 + b, \quad (5)$$

where $\Delta G^\ddagger$ is the change in the transition state free energy of, k is a reaction rate constant, ΔG^0 is the change of the reaction standard free energy, a and b are constants for specific reaction classes, n is the number of

electrons in the reactions, F is the Faraday number, ΔE^0 is the difference of the standard potentials, V.

If it is assumed that the limiting step of the process is the desensitization by electron trapping by the dye in the ground state (stage (I) of Eq. 3), then the rate constant at stage (I) can be expressed as^{15,29}:

$$k_1 = A_1 \cdot \exp(-\alpha_1 \cdot \Delta E^0_1/T), \quad (6)$$

where $\Delta E^0_1 = E^0_{CB} - E^{\text{red}}_{1/2}$. The value E^0_{CB} corresponds to the potential of the bottom of the conduction band. With everything else the same, the desensitization degree, DD, is proportional to k_1 , then

$$\text{DD} \approx k_1 \approx \exp[-(E^0_{CB} - E^{\text{red}}_{1/2, \text{Dye}})/T] \approx \exp(E^{\text{red}}_{1/2, \text{Dye}}/T) \quad (7)$$

which is consistent with the experimental results given in Fig. 3.

It is known that desensitization of AgHal is also brought about by dyes with low electron affinities ($E^{\text{red}}_{1/2} < -1.0$ V).^{15,17} Desensitization by these types of dyes, type II desensitization, is effected by the AgHal hole trapping mechanism.¹⁷ That process was considered for the first time by Carroll and by Saunders, Tyler and West.^{33,34} Type II desensitization is also an oxidation process, but in that case the dye cation-radical (Dye $\bullet^+$, hole dye), formed during oxidation of the dye in the ground state by the silver halide hole, is the oxidizer. Such processes are particularly characteristic of dyes adsorbed as polymolecular J-aggregates. Dye holes moving along the aggregate could reach the electron accepting center and recombine with the trapped electron or even oxidize the silver of the latent image. Schematically, type II desensitization can be shown as a series of successive reactions^{15,35}:



According to this scheme, AgHal, photoexcited by a "blue" photon ($h\nu_b$) oxidizes the dye to cation-radical Dye $\bullet^+$, which competes with the silver ions for trapping the photoelectron (steps 10 and 11), or oxidizes the silver found at step (10) or the latent image silver (step 12). For desensitization according to the hole mechanism it is necessary that the highest filled electron ϵ_{ho} level of the dye should be higher than the bottom of the AgHal valence band. A correlation might be observed between type II desensitization and $E^{\text{ox}}_{1/2}$ similar to the dependence of the type I desensitization with $E^{\text{red}}_{1/2}$ since the ϵ_{ho} level can be characterized by polarographic potential $E^{\text{ox}}_{1/2}$ of dye. A simple relationship between the degree of type II desensitization and $E^{\text{ox}}_{1/2}$ was not found.^{29,35,36}

The lack of a simple dependence of desensitization on $E^{\text{ox}}_{1/2}$ by the hole mechanisms for dyes, at the J-aggregate state, as a rule, is related to the rate laws for oxidation reduction processes.^{35,36} The type II desensitization rate constant:

$$k_2 = A_2 \cdot \exp(-\alpha_2 \cdot \Delta E^0_2/T) \quad (13)$$

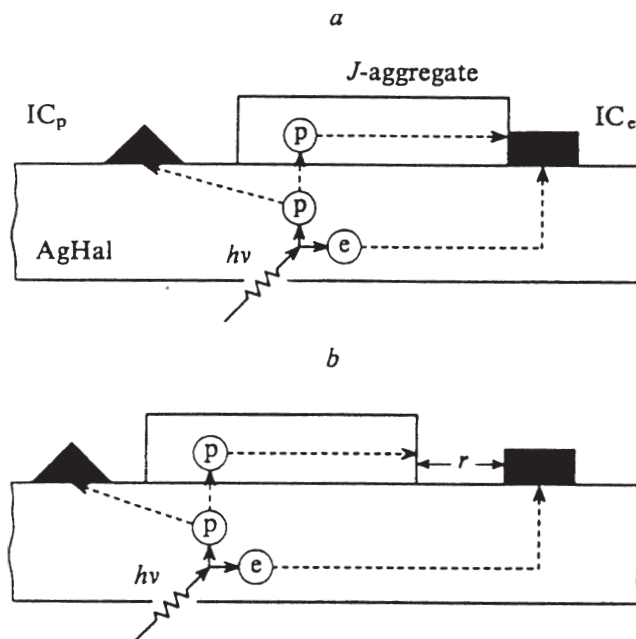


Figure 5. Schematic representation of the type II desensitization processes on the hole mechanism: a) J-aggregate is in contact with IC_e, J-aggregate separated from IC_e by a distance r ; $h\nu_b$ – photon absorbed by AgHal.

is limited primarily by the frequency factor, A_2 rather than the energy factor $\Delta E^0_2 = E^{\text{ox}}_{1/2} - E^0_{\text{VB}}$. The type II desensitization processes must depend significantly on the spatial location of J-aggregate, in which the hole is localized, relative to the impurity center in which the photoelectron is trapped. Such impurity centers (IC_e) could be products of chemical sensitization (above all, sulfur and gold-sulfur).¹⁷ Therefore, recombination rate of electrons and holes of the dye may be determined, above all, by the distance r between the dye and the IC_e. This situation is shown schematically in Fig. 5. Upon photoexcitation of the AgHal, the electron-hole pair is formed (e^- and p^+). The electron is trapped by the electron accepting center, IC_e, and the hole is trapped by either the hole accepting center, IC_p, or by the dye aggregate. Hole desensitization is a typical example of catalysis of recombination processes, where the J-aggregate plays the role of an intermediate species that promotes the reaction.

If self-organization of the dye molecules as a J-aggregate on the surface of the AgHal grain is hindered then it begins at the surface defects, including the IC_e. As a result of the contact of the J-aggregate with IC_e ($r \rightarrow 0$) frequency factor A_2 and recombination rate increase, resulting in significant desensitization by the dye. On the other hand, if J-aggregation is accomplished easily and aggregate formation is possible not only on the AgHal defects, but also on other sites, then the probability of the contacts of aggregates with IC_e decreases, r grows (Fig. 5b) and, as a consequence, both the frequency factor A_2 and the recombination rate decreases. In the case of tunneling transfer of the Dye $\bullet^+$ hole to IC_e, the pre-exponential term, $A_2 = f \exp(-2r)$, is strongly dependent on r .^{35,36} Hence, the rate constant of type II desensitization must also strongly depend on r . This approach provides one explanation for the complicated dependence of hole desensitization on dye structure.

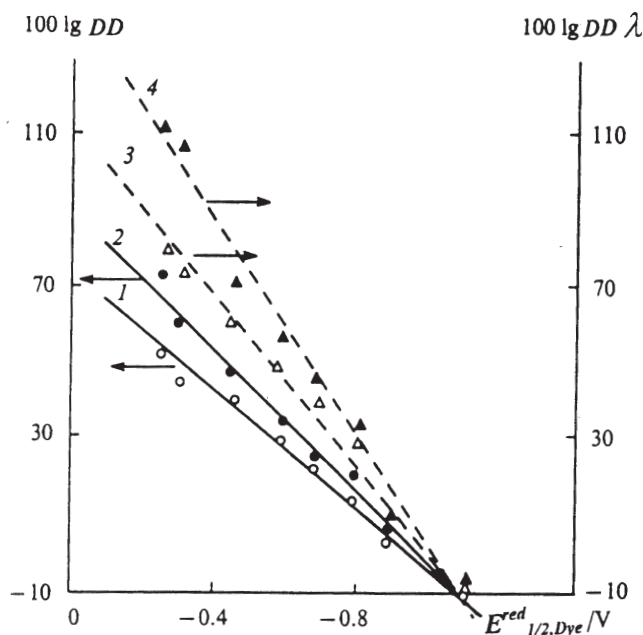


Figure 6. Dependence of $\log DD$ (1,2) and $\log DD_\lambda$ on $E_{red}^{red}/2$ of desensitizer for emulsions sensitized by 3,3'-diethylthiadicarbocyanine iodide (1,3) and 5,5'-diethylthiatricarbocyanine iodide (2,4). Dye concentration 4×10^{-6} mole/mole of AgHal, $pAg = 8.0$.

Processes of Self-Desensitization

It is obvious that secondary oxidation processes of desensitization take place not only from photoexcitation of AgHal but also with the spectral sensitizers themselves. The cases in point are the self-desensitization reactions of dyes.^{17,21,28,29} By this we mean that the desensitizing effect of the spectral sensitizer on the photographic process in the spectral region of its absorption. Unfortunately, it is impossible to estimate quantitatively the effect of the dyes themselves on the spectral sensitivity since it is impossible to do a controlled exposure in the same spectral region without the dye. So an indirect method is used: the effect on the spectral and intrinsic sensitivity of emulsion when a second desensitizer is added. Similar to the desensitization processes, self-desensitization is divided into type I and type II.^{28,29}

The effect of pyrylocyanines acceptors, with various electron affinities characterized by $E_{red}^{red}/2$, on the desensitization degree (DD) and the desensitization in the spectral sensitivity region DD_λ of emulsions sensitized by thiapolycarbocyanines, have been studied in detail.³¹ Figure 6 shows the dependence of $\log DD$ and $\log DD_\lambda$ on $E_{red}^{red}/2$ for desensitizers in a coarse-grained AgBr(I)-emulsion with S and Au-sensitization and thiadi- and thiatricarbocyanine spectral sensitizers. As can be seen in Fig. 6, the slopes of the dependence $\log DD_\lambda = f(E_{red}^{red}/2)$ are significantly higher than that of $\log DD = f(E_{red}^{red}/2)$, i.e., the effect of desensitizers on spectral sensitivity is quite significant.

Differences in the desensitization and selective desensitization processes and the greater effect of additionally added electron-acceptor type desensitizers on the spectral sensitivity compared to intrinsic sensitivity were explained by Meyer and Nesawibatkó.³⁷ In this case, desensitization of photoexcited AgHal is accom-

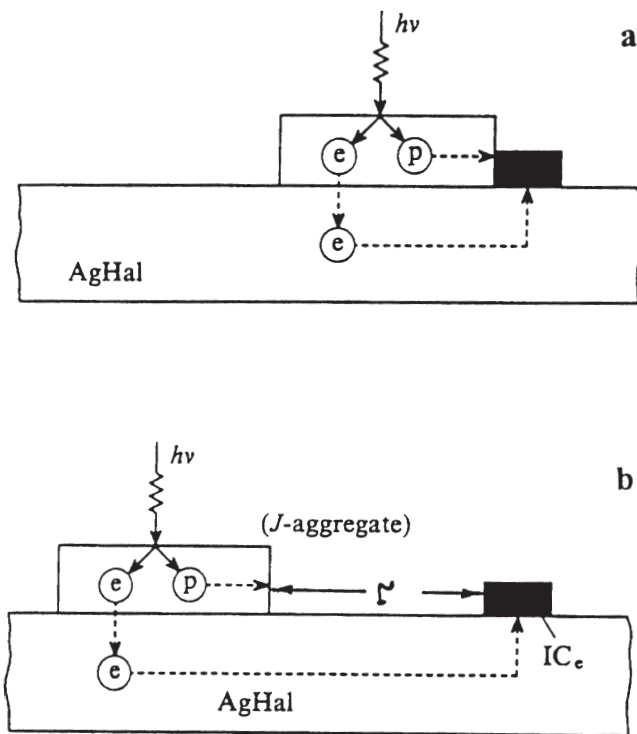


Figure 7. Schematic representation of II type self-desensitization of dyes: J-aggregate is in contact with IC_e , b) J-aggregate separated from IC_e by a distance r .

plished by electrons accepted both from deep electron traps (sensitivity centers) and shallow surface traps, while all electrons from Dye photoexcitation are initially captured in shallow surface traps, from which electron capture to vacant Dye levels is facilitated.

A singular nature of the dependencies of DD and DD_λ on $E_{red}^{red}/2$ (compare Figs. 3 and 6) allows one to conclude^{21,28-30} that type I self-desensitization by spectral sensitizers themselves is quite possible and could significantly exceed desensitization. Moreover, self-desensitization actually could define of sensitization by electron-acceptor type dyes. The scheme of type I self-desensitization processes is similar to the scheme (3) of type I desensitization, the only difference being that in the case of the dye cation-radical, $Dye^{\bullet+}$, a hole, p^+ , is created. Similarly, type II self-desensitization processes via the hole mechanism define the efficiency of the silver halide spectral sensitization by dyes having a low electron affinity, which as a rule, forms J-aggregates.^{21,28-30,35,36}

Similar to type II desensitization processes, type II self-desensitization is also defined by the topography of J-aggregates, i.e., by the distance between the J-aggregate and electron-acceptor impurity center, IC_e . This process is illustrated in Fig. 7. Type II self-desensitization is especially probable at the contact point of the J-aggregate with IC_e (Fig. 7a). It must be emphasized that the type II desensitization process has more steps than self-desensitization. On photoexcitation of AgHal, a fraction of the holes could be trapped on the grain surface by dye with formation of dye holes, and another fraction could be trapped by hole accepting impurity centers— IC_p . (see Fig. 5). The process of type II self-desensitization is more simple because the dye hole inevitably appears during spectral sensitization, i.e., at the point of electron transfer from the photoexcited

dye to the AgHal (Fig. 7). Hence, the number of dye holes can be greater. Thus, the probability of self-desensitization can be greater than the probability of desensitization and, as a result, its effect on the spectral sensitivity can exceed the effect of desensitization on the intrinsic sensitivity of the emulsion. The well known experimental fact of decreasing spectral sensitivity with increasing J-aggregate dye concentration beyond an optimum level can also be explained in the context of dye self-desensitization. Because of the increase in AgHal grains surface coverage by J-aggregates, the distance between them and IC_e has to decrease and, as a result, the rate of recombination processes has to increase. It was concluded, for example, that from an investigation of the role of self-desensitization processes in the spectral sensitivity of AgHal materials, that the spectral sensitization process of negative silver halide emulsions is defined by the kinetics of secondary reactions rather than by the primary photoreaction,²¹ i.e., by the dye self-desensitization reaction. Therefore, the theory of the spectral sensitization of such materials must be, primarily, the theory of self-desensitization of dyes.

Supersensitization as Inhibition of Secondary Oxidizing Processes

Because of the significant contribution of self-desensitization processes in spectral sensitization efficiency, inhibition of those secondary oxidizing processes acquires great significance. A case in point is supersensitization of photographic materials.²⁸

For type I self-desensitization processes, retardation of reactions in steps (I-VII) of scheme (3) appears to be quite promising.^{21,28-30} In order to inhibit step I, dye molecules must be separated from the AgHal surface, where electron trapping from Dye* at defects can occur. A case in point is a peculiar kind of dye separation from the AgHal that, however, must not hinder electron transfer from Dye*, i.e., a kind of interlayer between the dye and AgHal must be created that should be sufficiently penetrable for photoexcited electrons (possibly via the tunneling mechanism) yet unpenetrable for electrons trapped on the AgHal surface. Such isolation is also important in terms of elimination of electron recombination reactions with cation-radicals. In order to inhibit the reactions with O₂ and protons in steps (I), (III) and (V) in scheme (3), isolation of dye molecules from O₂ and H₂O by hydrophobic organic compounds, added during the production of the photographic emulsions is promising. Finally, in order to eliminate the recombination steps (VI) and (VII), an acceptor for the dye holes, formed during the spectral sensitization process, is necessary.

A priori it can be imagined that for formation of "interlayer" between the AgHal and dye it is required that the organic components adsorbed very well on the AgHal, but, on the other hand, compounds that inhibit reactions in steps (II), (III) and (V) should not strongly adsorb on the AgHal microcrystals. However, the latter must be quite hydrophobic, i.e., be able to precipitate on the AgHal grains, once added to the water-gelatin medium, and make a kind of shell that protects the dye from O₂ and H₂O. The use of compounds, adsorbed on AgHal as supersensitizers of photographic materials is well known. Among these there are Riester's potentiators, containing mercapto groups,³⁸ bis-triazinylamino derivatives of stilbene-o,o'-disulfo acid,^{39,40} alkyl derivatives of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene,⁴¹ and various triarylphosphines.⁴² C,N-diarylnitrones were investigated in detail⁴⁴ as hydrophobic compounds^{29,30,43}, the

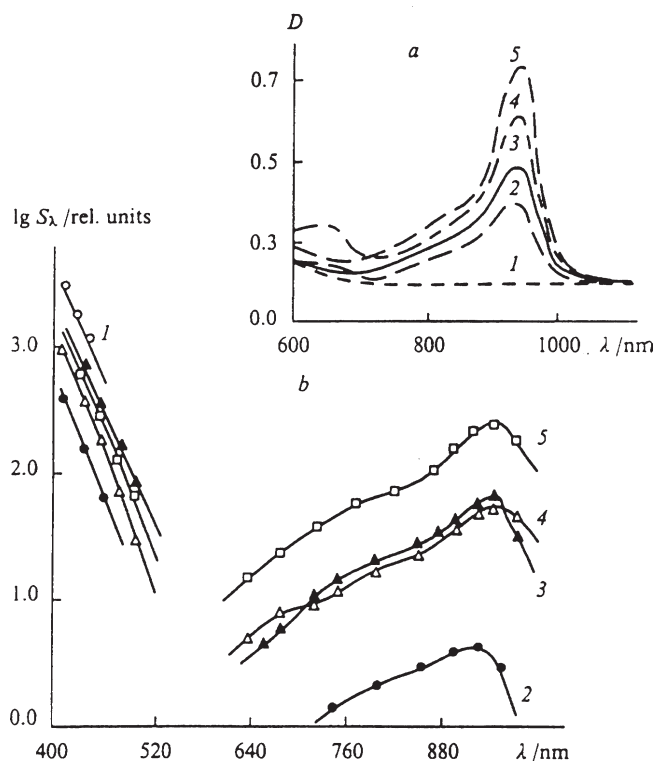


Figure 8. Absorption spectra (a) and spectral sensitivity curves (b) of the layers, sensitized by 3,3'-diethyl-9,11-(β,β-dimethyltrimethylene)-thiatetracarbocyanine iodide: 1- without dye, 2- with dye (Dye), 3- S-1 + Dye, 4 - S-2 + Dye, 5 - S-1 + Dye + S-2.

photographic effects of which were discovered in NIIKHMIFOTOPROEKT in 1975. It was shown that the addition of both adsorbing supersensitizers (supersensitizers of the 1st type) and hydrophobic compounds (supersensitizers of the 2nd type) causes a significant increase in the spectral sensitivity of the films sensitized by thia-tri-, tetra-, penta- and hexacarbocyanines.^{43,44} In Fig. 8, as an example, curves of spectral sensitivity and absorption are shown for a film sensitized with thia-tetracarbocyanine. Addition of 2-heptyl-4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (S-1, curve 3, Fig. 8) and C. N-diphenylnitron (S-2, curve 4) each cause an increase in spectral sensitivity and some increase in the absorption band intensity of the adsorbed dye. It is characteristic that spectral sensitivity increase significantly exceeds absorption increase.⁴³ Increase in absorption and, as a result, partial increase of sensitivity in the presence of the supersensitizer, are probably related to the adsorption increase and stability of the adsorbed dye.⁴³

The composition of the supersensitizers defines the superadditive sensitivity (curve 5, Fig. 8). An analogous pattern was observed for films sensitized by thia-tri-, penta- and hexacarbocyanines.⁴⁴ The superadditivity effect for compositions of two types of supersensitizers, adsorbed and weakly adsorbed on AgHal, may be considered the result of the compounds effect on the subsequent steps of the self-desensitization process shown in scheme (3). The concept is illustrated by Fig. 9 where it is seen that one supersensitizer (S-1) separates dye from the AgHal and the other (S-2) forms a shell isolating dye from environment. The portion of electrons

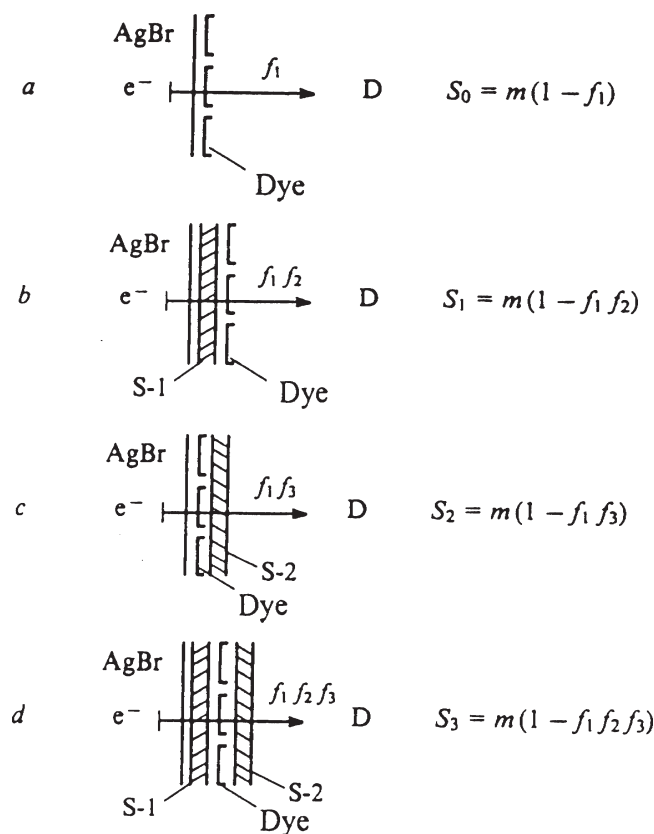


Figure 9. Scheme of supersensitization processes of photographic layers sensitized by electron-acceptor dye (a), single supersensitizers of first type, S-1 (b) and second type, S-2 (c) and their composition S-1+S-2 (d).

transferred through the dye to the desensitizer (D) is indicated as f_1 . In the presence of supersensitizer S-1, which separates the dye from the AgHal, the portion of lost electrons decreases to $f_1 \cdot f_2$. In the presence of a hydrophobic S-2, the electrons lost are equal to $f_1 \cdot f_3$. The smallest loss $f_1 \cdot f_2 \cdot f_3$, should be expected for a composition of supersensitizers S-1 and S-2 working sequentially. If sensitivity, S , of the photographic layer is proportional to the number of electrons remaining on the AgHal, and then forming the latent image, then $S_0 = m(1-f_1)$, $S_1 = m(1-f_1 \cdot f_2)$ and $S_3 = m(1-f_1 \cdot f_2 \cdot f_3)$. Thus, the maximum sensitivity must correspond to the composition of supersensitizers. Figuratively speaking, the supersensitization situation is similar to a pipe where the electron flow is from the AgHal to the desensitizer, with two taps regulating the flow. The reducing function of nitron, or of a product of its hydrolysis, is discussed in Ref. 44. As a consequence of thenitron reducing properties, either dye hole capture in steps (VI) and (VII) of scheme (3), or latensification of the latent image, an increase in the stability of the latent image is possible.⁴⁵ The important supersensitizing role of another reducing agent, ascorbic acid in infrared films has been reported by Muentner and co-workers.⁴⁶⁻⁵⁰

There are at least three possible routes that inhibit type II self-desensitization processes, i.e., three methods of supersensitization.^{17,28-30,51} These routes are illustrated in Fig. 10. The first is the classic Gilman method of supersensitization,^{17,52} which consists of a compound that is more easily oxidized than the dye accepting the dye hole. Supersensitization conditions for the Gilman

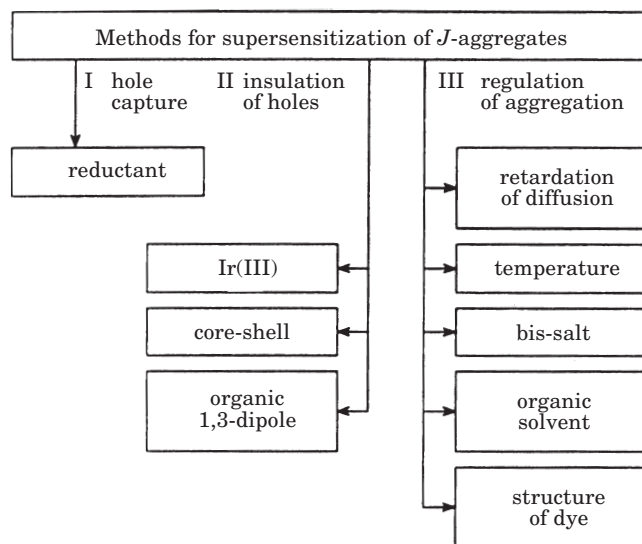


Figure 10. Principal methods of supersensitization of J-aggregating dyes.

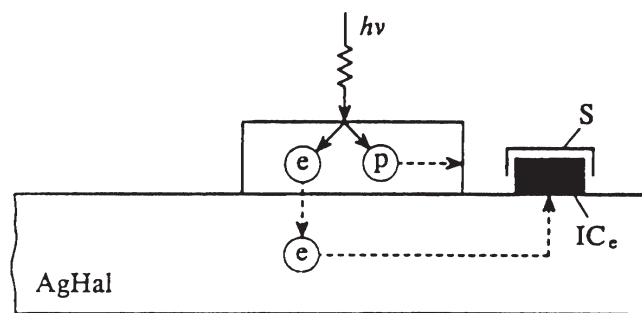
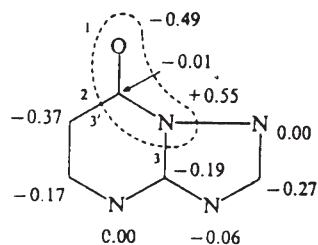


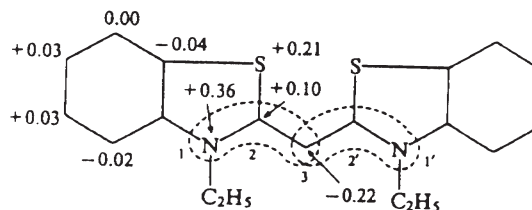
Figure 11. Schematic representation of the "isolation" supersensitization mechanism by retardation of II type self-desensitization of by supersensitizer S adsorbed on IC_e .

strategy can be expressed as $E_{1/2,S}^{ox} < E_{1/2,Dye}^{ox}$. For AgBr: $E_{1/2,S}^{ox} < E_{1/2,Dye}^{ox}$ and $E_{1/2,S}^{ox} < 0.8$ V (relative to s. c. e.).⁵³ The Gilman reduction mechanism of supersensitization is so well known, we need not consider the details here.

The second method of supersensitization consists in "isolation" of the dye hole from IC_e .^{28,29,35} Essentially, this is a selective adsorption of organic compounds on Ag_2S - or (Ag,Au)S-centers, so that the J-aggregates are isolated from the IC_e . The result, schematically illustrated in Fig. 11, decreases the probability of recombination processes. Insulators, as a rule, are not very oxidizing compared to dyes-sensitizers, i.e., they cannot work by the reduction mechanism. A necessary condition for selective adsorption of organic compounds on Ag_2S - and (Ag,Au)S-centers is the presence of 1,3-dipoles^{35,51} in the structures. A well known stabilizer, 4-hydroxy-6-methyl-1,3,3a,7-azaindene (TAI), that supersensitizes J-aggregates, is a typical compound of this type.⁵⁴ According to the quantum-mechanical calculations, TAI exhibits the characteristic 1,3-dipole, as indicated in Fig. 12. Thiamonomethinecyanine dyes (TMMC), which exhibit significant supersensitizing activity, also have clearly defined 1,3-dipolar fragments in their structures.⁵⁴ It is typical that in the thiamonomethinecyanine dye, there are two 1,3-dipoles. The π -charge distribution, shown in Fig. 12 may be the source



TAI



TMMC

Figure 12. Diagram of distribution of π -electron density in TAI and thia-monomethinecyanine molecules (TMMC). On the diagram 1,3-dipoles are marked.

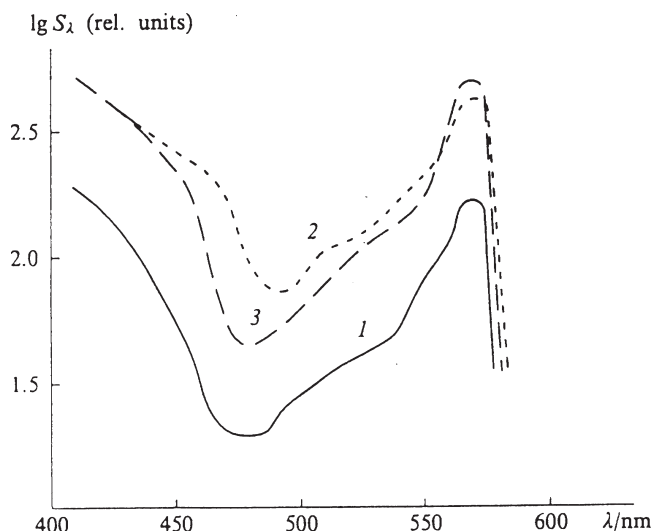


Figure 13. Curves of spectral sensitivity of AgBr emulsion, sensitized by 1,1',3,3'-tetraethyl-5,5'-dichloroimidacarbocyanine iodide (2×10^{-4} mole/mole AgBr) without supersensitizer (1) and in the presence of selenamonomethinecyanine (2) and thiamonomethinecyanine (3); concentration of the supersensitisers – 4×10^{-4} mole/mole of AgBr.

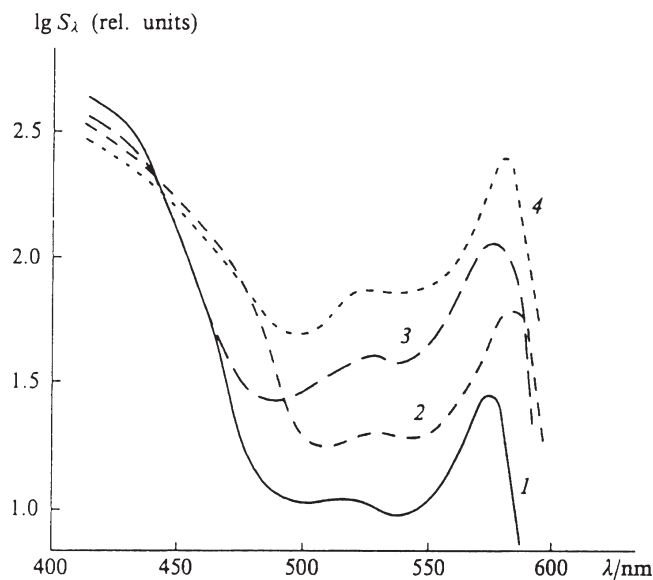


Figure 14. Curves of spectral sensitivity of AgBr emulsion, sensitized by quino(2,2')cyanine (2×10^{-4} mole/mole AgBr) without supersensitizer and in the presence of selenamonomethinecyanine (4×10^{-4}) (2); 2-(*p*-dimethylaminostyryl)benzothiazole (0.5×10^{-4}) (3) and composition of the supersensitisers ($4 \times 10^{-4} + 0.5 \times 10^{-4}$) (4).

of the TMMC supersensitizing activity at concentrations significantly lower than TAI. The supersensitization effect from monomethinecyanines in photographic films sensitized by 1,1',3,3'-tetraethyl-5,5'-dichloroimidacarbocyanine iodide J-aggregates is shown in Fig. 13.^{51,54}

According to the isolation mechanism, compounds can act as supersensitisers if they are more difficult to oxidize than the dye sensitizers, i.e., $E_{1/2,S}^{ox} > E_{1/2,Dye}^{ox}$.^{28–30,35} A necessary condition of supersensitization activity of that type of compound is a correlation between the length of the 1,3-dipole and the distance between the Ag^+ and S^{2-} ions in the Ag_2S -particle lattice (about 2.5 – 2.6 Å).⁵⁵ The correlation of the charges ensures specific adsorption of the organic compounds on the Ag_2S - and (Ag,Au)S-centers by the “lock and key” model.

The isolation of J-aggregates from Ag_2S -centers is effected in emulsions with internal sensitivity centers, in “core-shell” emulsions and in emulsions with Ir^{3+} -ions^{56–58} (see Fig. 10). Because of photoelectron capture deep in the AgHal grains, electron-hole recombination processes are hindered, and type II self-desensitization is significantly diminished.

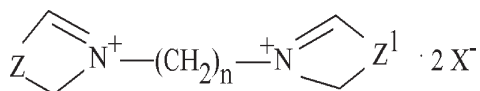
It is characteristic that the simultaneous involvement of the two type II self-desensitization methods causes a superadditive increase in light sensitivity. This effect is illustrated in Fig. 14. Addition of sensitizing quino(2)cyanine J-aggregates in the film, based on 2-(*p*-dimethylaminostyryl)benzothiazole, which operates by Gilman's mechanism of hole capture ($E_{1/2,S}^{ox} = 0.60$ V; $E_{1/2,Dye}^{ox} = 0.94$ V), results in an increase in spectral sensitivity. Increased sensitivity is also observed in the case of the difficultly oxidizable selenamonomethinecyanine ($E_{1/2}^{ox} = 1.21$ V). For a composition containing both the selenamonomethinecyanine and an easily oxidizable styryl base, showed significantly exceeded effects than for the individual compounds (compare curves 2, 3, and 4, Fig. 14).

The superadditive effect of supersensitization provides definitive evidence for a different mechanism of supersensitization of photographic films by the two types of compounds which interfere, in turn, with consecutive steps of dye-hole self-desensitization. This occurs by either capture of the initial dye holes by easily oxidizable supersensitizer followed by isolation of the remain-

ing hole from the photographically active centers by the difficult oxidizable compound, or the reverse.

The third method of supersensitization consists of controlling J-aggregation. Control can be accomplished by the addition of organic compounds to the emulsion, which promote aggregation or take part in "recrystallization" of the aggregates, thereby favoring the formation of better regulated structures of J-polymers.^{35,51} The self-association process of dyes in J-aggregates seems to have a number of analogies with crystallization processes and therefore includes at least two stages: nucleation followed by growth of the ordered structure. Aggregation of cyanine dyes occurs, in reality, at surface defects on the microcrystalline AgHal grain. Hence, the nucleation step must be defined by, in addition to the structure of the dye molecule, the number and types of surface defects, as well as by supersaturation of the dye solution. The growth stage of J-aggregates is determined basically by the supersaturation of the sensitizer solution. The level of defects of the grain surface is directly related to their habit and to the type of chemical sensitization, the process of which can form new defects and impurity centers. The analysis of the factors influencing J-aggregation can be found in reviews.^{17,59}

Organic or inorganic compounds added to the photographic emulsion during grain growth, chemical, and spectral sensitization, could affect J-aggregation at the aggregate nucleation step, changing the number and types of surface defects, or at the aggregate growth step. The absence of contact between the J-aggregate and IC₀ (increase of r) can be a result of these processes, as can be the formation of more ordered, built J-aggregate structures, i.e., more uniform. It could decrease the probability of excitation energy dissipation between various J-aggregates, separated by the energy level sets. Controllers of J-aggregation include bis-quaternary salts of heterocyclic bases having the following general formula.



where Z and Z¹ are groups of atoms that form pyridine, quinoline or benzimidazole rings, $n > 2$, X⁻ is an anion.

The use of bis-quaternary salts of nitrogen-containing heterocycles has been known for some time.⁶⁰ The effect of bis-quaternary salts of benzimidazole has been investigated in detail by Lifshits and co-workers,^{61,62} and the effect of α -picoline has been reported by Shchelkina and Shapiro.^{35,51,63} The addition of bis-quaternary salts in the photographic emulsion at concentrations comparable to the J-aggregating dye concentrations enhances the dye's tendency to J-aggregate, and leads to a bathochromic shift of the band maximum as well as an increase in the spectral sensitization efficiency. Figure 15 illustrates the effect of decamethylene-bis-(α -picolinium) dibromide on J-aggregation of 3,3',9-triethyl-4,5,4',5'-dibenzothiacarbocyanine bromide. Addition of bis-salt promotes J-aggregation of the dye (compare curves 1 and 2, Fig. 15). It is possible that the adsorption of the bis-salts on the AgHal grains, the result of the specific alignment of paired positive charges, localized on the nitrogen atoms, to the paired negative charges of halide ions on the AgHal surface, generates a surface potential topology that promotes the formation of J-aggregates not only on defects but at other sites as well, and, overall, favors the growth of more highly ordered aggregate structures.

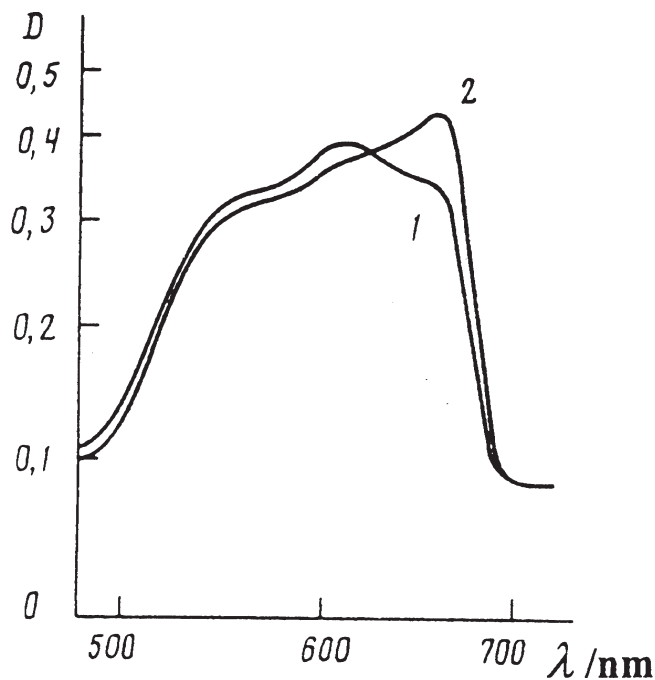
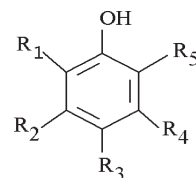


Figure 15. Absorption spectra (a) of the AgBr-layers (cubic microcrystals $l = 0,17 \mu m$), sensitized by 3,3',9-triethyl-4,5,4',5'-dibenzo-thiacarbocyanine bromide without (1) and with decamethylene-bis- (α -picolinium) dibromide (2); concentrations of the dye and bis-salt 2×10^{-4} mole/mole of AgBr.

Furthermore, it is well known that J-aggregation is promoted by replacement of the alkyl groups on the nitrogen of the cyanine dyes with sulfo-alkyl groups, i.e., transition to a betaine dye structure.^{17,64} It seems likely that the presence of di-polar betaine structure in anionic dyes could promote both the nucleation stage of J-aggregate on a di-polar AgHal grain surface (Ag⁺ and Hal⁻ ions) as well as the subsequent growth of the aggregates themselves.

It is known that, upon J-aggregation, various weakly active photographic compounds do exhibit some activity, for example, ketones, nitriles, quinoline derivatives,⁶⁵ aromatic alcohols^{35,51} etc. During investigation of photographic activity of phenol, when added to the emulsion together with the dyes, we found a significant effect on the position of the J-bands absorption (bathochromic shift) and on the efficiency of spectral sensitization.⁶⁶ Other phenols of the general formula.



where R₁ – R₅ = H or alkyl groups exhibit a similar effect.⁶⁶

As a rule, bathochromic shift of the J-bands is associated with a decreased dye package angle or with an increase in the number of sensitizer molecules forming an aggregate.¹⁷ Both parameters must be dependent on the rate of aggregation. Rapid aggregation results in a chaotic formation of many dissimilar aggre-

gates on the AgHal surface defects. The effect of phenol, for example, has been shown to be obtained even when it is added to the emulsion after the formation of the J-aggregates.⁶⁶ It has been suggested that the effect of aromatic alcohols is a so-called "recrystallization" or, in common photographic terms "digestion" of J-aggregates.⁶⁶ In that case, phenols play the role of an environment (a solvent) promoting recrystallization. One of the results of this process can be the formation of a more ordered J-aggregate structure with bathochromic shifted absorption bands, isolated from the impurity centers ($r > 0$). The second result is an increase of photographic activity of the aggregates.

J-aggregates, before the addition of the spectral sensitizer, can promote the formation of many new defects on the AgHal grain surface, which stimulates growth of J-aggregates on sites not associated with impurity centers. Such multiple defects are formed, for example, on AgHal grains prepared with variable halide composition, especially, AgBr(I) emulsions. Hence, J-aggregation, as a rule, is facilitated up to a certain iodide ion concentration limit in AgBr(I) emulsions.¹⁷ In the same way, the effect of thiocyanate and cyanide ions on J-aggregation can be explained.¹⁷ J-aggregation can be controlled by decreasing the rate of dye addition to the solution (diffusion retardation, Fig. 10). This can be accomplished by addition of poorly water soluble dyes, as water sols, or by re-adsorption of the dyes from the surface of an inert substrate (SiO₂, etc.) to the AgHal. Increasing the melt emulsion temperature at the dye addition favors the formation of more ordered and extended J-aggregates.^{17,67}

Summary

All of the data summarized above clearly demonstrate that secondary *chemical* oxidation processes, or in photographic terminology, desensitization processes, play a very important role in spectral sensitivity. In this case, desensitization in the region of the dye absorption, self-desensitization of the dye, significantly exceeds the desensitization in the region of silver halide absorption and, in fact, can limit the observable spectral sensitization efficiency. Oxidation mechanisms of dye self-desensitization could be different and defined by the position of the dye energy levels relative to the AgHal energy bands as well as relative to the local surface levels. It is characteristic that a dye in the secondary processes can play the role of an oxidation catalyst. Therefore, in a general sense, it may be concluded that the catalytic oxidation reactions of photographically active particles involve vacant molecular orbitals of π -conjugated systems, examples of which are polymethine dyes and their cation radicals.

Supersensitization processes, to a great degree, amount to retardation of secondary reactions of self-desensitization. The inhibition routes of oxidizing processes could be quite diversified, controlled by spectral sensitizer properties and the type of photographic emulsions, and therefore, compounds could have very different structures. The use of various supersensitizers and their compositions enable secondary oxidizing processes to be totally eliminated, the limiting value of the relative quantum yield of spectral sensitization can be nearly achieved. This accomplishment was shown in an infrared photographic film example.^{29,44,68} The efficiency of spectral sensitization in IR region, $\lambda \approx 1000$ nm, was increased by about 100 times, and was brought closer to the values obtained in the visible region.

It is necessary to call attention to the following point. In the majority of research on spectral sensitization,

beginning with the classic work of Gurney and Mott,⁶ the emphasis was on the initial step of spectral sensitization, which affects the efficiency of the entire spectral sensitization process. The efficiency of this first step was considered in the physical context of the relationship between the electron levels of the excited dye and the AgHal electron bands. While secondary chemical reactions were taken into account with this type of approach, they were assigned only a minor role. That is, the secondary chemical reactions depended, to a large degree, on the extent of those primary process. The accumulated experience over time, up to now, however, strongly points to chemical processes playing a major role.

The fundamental difference between AgHal based photographic processes and photoprocesses in other wide-band semiconductors, consists in the fact that, in the wake of the photophysical step of charge separation, a chemical step follows that results in the formation of atoms, silver particles, and halogen. In that second chemical step, adsorbed molecules, capable of reacting with the primary photoproducts, among them spectral sensitizers, takes on great significance.

Now it is obvious that the relative quantum yield of spectral sensitization, ϕ_r , is determined both as a quantum yield of the primary photographic process of an electron transfer from Dye* to AgHal (ϕ_{sens}), and the quantum yield of secondary dark processes of the latent image formation (ϕ_{li}). This relationship can be expressed as⁶⁹:

$$\phi_r = \phi_{sens} \cdot \phi_{li}.$$

Based on the experimental data, it is possible to conclude that the value of ϕ_r depends to a large degree, on ϕ_{li} , i.e., on the dark processes of latent image formation. The catalytic processes of dye self-desensitization, in essence, can determine the spectral sensitivity of photographic materials.⁶⁹

For most contemporary ortho-, pan-, and in particular, infrared dyes, the photoexcited electron energy level is located below the bottom of the AgHal conduction band.^{29,30,35,44} Consequently, the first step in spectral sensitization could be considered to be a surface redox reaction of the photoexcited dye with silver ions, which is essentially equally probable for many dyes.^{21,28,29}

The difference in the photographic efficiency of dyes is due to different probabilities of self-desensitization. A vivid example of this is efficiency of photographic activity of infrared dyes, at $\lambda_{max} = 1060$ nm, approaching that of dyes absorbing in the visible. This efficiency is the result of inhibition of self-desensitization despite a nearly two-fold decrease of active light quanta and the deeper ($\Delta E \approx 0.5$ V) photoexcited dye level.^{29,68}

It now is easy to observe that in considering the first step as a surface chemical reaction we return to the first chemical hypotheses of the spectral sensitization.^{3,4} The essential difference in these theories lies in the fact that the emphasis of the new chemical view is transferred, in the first step of separation of the photogenerated products, from electrons, or silver atoms, to holes. In this regard, photography is not particularly unique in the photochemistry field. The problem of charge separation is central in fields such as photosynthesis,⁷⁰ sensitized photolysis, and, in particular, sensitized photolysis of water.^{71,72}

Spectral sensitization processes take place on the AgHal microcrystal surfaces where dyes are adsorbed. The unique ability of cyanine dyes to J-aggregate, that resulted in their universal application as spectral sensitizers to black-and-white and color photographic materials, is defined, probably, by the efficiency of the

initial separation of photogenerated charges between the molecules taking part in the J-aggregates. A certain analogy can be drawn between the artificially created human process of spectral sensitization and the natural processes of spectral sensitization in photosynthesis, which have been perfected over many millions of years of evolution. The first step in the spectral sensitization in the reactive center during photosynthesis consists of charge separation in bacterial chlorophyll molecule dimers.⁷⁰ According to modern concepts, the location of the J-aggregates relative to electron and holes acceptors on the AgHal surface also greatly defines the efficiency of charge separation in a photographic process, and is related to that spectral sensitivity. Hence, the J-aggregate topography on the real AgHal grain surface is crucially important, particularly with respect to investigations of crystals with new forms. Until now, control of the charge separation process was more sporadic than deliberate. There is now no doubt that designed control of J-aggregation is the essence of the challenge in spectral sensitization of photographic materials. ▲

Acknowledgment. The author wishes to thank Drs. David R. Whitcomb and Lilia P. Burleva for their assistance in preparation of the English version of this article.

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