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Chemical problems of the infrared sensitisation of photographic materials

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Abstract. The mechanisms of the spectral sensitisation of silver halides by infrachromatic dyes are examined. It is concluded that the effectiveness of the spectral sensitisation is determined by secondary dark oxidation reactions of the silver atoms formed — the so called dye self-desensitisation processes in which the infrachromatic dye plays the role of a catalyst — rather than by primary steps involving electron transfer from the photoexcited dye to AgHal. It is shown that processes involving the super sensitisation of infrared photographic materials constitute the inhibition of the dye self-desensitisation reactions. Supersensitisers are classified in terms of their inhibition mechanism as supersensitisers of the first and second kind. The application of supersensitisers of the first and second kind leads to a superadditive increase in light sensitivity. The modern supersensitisation methods have made it possible to develop a new generation of infrared films with improved photographic parameters. For example, the photosensitivity of an infrared film with a sensitisation maximum at 1060 nm has been increased by a factor of 100. The possibility of spectral sensitisation up to 1500 nm is demonstrated. The bibliography includes 147 references.

I. Introduction

The spectral sensitisation of silver halide (AgHal) photographic materials is one of the few examples of a highly effective spectral sensitisation process devised by man. The discovery of the spectral sensitisation of silver halides by organic dyes (Dy) is one of the most important events in the history of photography. It was achieved in 1873 by Prof. Herman Wilhelm Vogel.[1] In the course of the 120 years history of its development, the spectral sensitisation process was raised to an extremely high level of perfection. It is sufficient to state that the relative quantum yield of the spectral sensitisation in the visible region of the spectrum is close to unity, *i.e*. the photographic effectiveness of the quanta absorbed by the dye is equal to the effectiveness of the quanta absorbed by the AgHal lattice.

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The expansion of the region of spectral sensitivity into the infrared emission zone is known to encounter considerable, seemingly insurmountable, difficulties. In the first place, an appreciable decrease in the sensitisation with increase in the emission wavelength is observed.[2] Until recently there was an empirical rule, according to which light sensitivity diminishes on moving into the IR region of the spectrum approximately by an order of magnitude for each 100 nm. A particularly marked decrease in light sensitivity occurs in the region of the spectrum at wavelengths exceeding 1000 nm. The sensitivity of a photographic material with a sensitisation maximum in the region of 1000 nm is approximately 1000 times smaller than the sensitivity of the light-sensitive layers in the visible region of the spectrum. The spectral sensitivity limit corresponds to the range 1300 – 1350 nm.[3,4]

Yet another difficulty is the insufficient viability of infrachromatic photographic materials. An appreciable decrease in light sensitivity and an increase in the fogging of the light-sensitive layers is observed in the course of time, which makes them unsuitable for use a short time after their preparation. The question of the causes of the decrease in the effectiveness of their spectral sensitisation in the IR region of the spectrum has been widely discussed in the literature (see, for example, Refs 2, 5, and 6). In the dominant concept, the decrease in the light sensitivity of infrared light-sensitive layers is attributed to the energy 'deficit'. According to this concept, a light quantum absorbed by an infrared dye is significantly smaller than the quantum absorbed by AgHal and for this reason it cannot exert the same photochemical effect. Nevertheless, there are numerous experimental facts indicating the important role of secondary chemical reactions with participation of the spectral sensitiser, which determine to a large extent the effectiveness of the spectral sensitisation process.[5,6] The aim of the present review is to compare various experimental results and to analyse the theoretical approaches to the problem of infrared sensitisation.

II. The problem of the energy 'deficit'

The main problem which arises in the spectral sensitisation of wide-band semiconductors (silver halides) by organic dyes is that of the energy 'deficit'. The theory of spectral sensitisation is invoked primarily in order to explain how a lower-energy photon, absorbed by the spectral sensitiser, exerts the same photographic effect as the higher-energy quantum absorbed by the AgHal lattice. For example, the width of the forbidden band of AgBr is

2.6 eV ($\sim$500 nm absorption limit). However, the spectral sensitisation by dyes is observed in the IR region of the spectrum in the vicinity of 750–1100 nm, *i.e.* the sensitisation takes place under the influence of light quanta with a significantly smaller energy (1.6–1.1 eV).

It is noteworthy that the problem of energy 'deficit' can be readily solved within the framework of the theory of the resonance transfer of excitation energy from the dye to AgHal when the local electronic levels of the photoconductor participate in the photoprocess. Excitation energy transfer in spectral sensitisation was first examined in 1948 by Mott,[7] who put forward the hypothesis that, in the sensitised photolysis of AgBr, the light energy absorbed by the dye is consumed in the liberation of an electron at a local level in the forbidden band. This scheme was developed in detail in the 1960s in the studies of Terenin, Akimov, and coworkers[8–11] and of Kuhn, Möbius, and coworkers.[12] The possibility of spectral sensitisation *via* the excitation energy resonance transfer mechanism has been demonstrated experimentally by Akimov[11] and Kuhn and coworkers.[12] However, it was later concluded[13] that the spectral sensitisation of real AgHal emulsions is determined by electron transfer from the photoexcited dye (Dy*) to AgHal and that the contribution of the excitation energy resonance transfer does not exceed several per cent. At the present time, the electron transfer mechanism has become generally accepted.[2]

The electron transfer mechanism in the spectral sensitisation of AgHal by dyes was first examined by Gurney and Mott[14] within the framework of the band model of silver halides in 1938. According to this mechanism, the spectral sensitisation is associated with electron transfer from the photoexcited dye Dy* to the conduction band (CB) of silver halide. According to Gurney and Mott,[14] for effective sensitisation the energy level of the photoexcited electron in Dy* must be above the bottom of the conduction band of AgHal or at least close to it. In subsequent steps, the recombination of the electrons injected into the conduction band with the interstitial (or surface) Ag^+ ions, which takes place preferentially on the sensitivity centres (SC), results in the formation of a latent photographic image. The dye can return from the radical-cation ($Dy^{+\cdot}$) state to the initial state either *via* the injection of a hole into the valence band (VB) of silver halide or by the acceptance of an electron from defective surface sites, for example, from defective Br^- and I^- ions or the impurity centres (IC) formed during chemical sensitisation.

The determination of the positions of the electronic levels of the dyes adsorbed on AgHal in terms of the absolute potential scale is a fairly complex task. There exist both experimental methods for such determination and computational quantum-chemical methods. The lowest vacant level of the dye ε_{lv}, to which an electron is transferred on photoexcitation, may be characterised by the electron affinity of the dye E_{ads}. The highest occupied level ε_{ho}, from which an electron passes to ε_{lv} on photoexcitation is in its turn determined by the ionisation potential of the dye I_{ads}. Numerous attempts have been made to determine E_{ads} and I_{ads} (see James's monograph[2] and the communications quoted therein), but, owing to the difficulties arising in the interpretation of the experimental results, it is at present impossible to determine unambiguously the levels ε_{lv} and ε_{ho} of adsorbed dyes.

The energy levels of the dyes can be calculated by different quantum-chemical methods The first systematic studies on these lines were carried out by Tani and Kikuchi.[15] Electrochemical potentials and in the first place the polarographic half-wave reduction ($E^{Red}_{1/2}$) and oxidation ($E^{Ox}_{1/2}$) potentials of dyes have found extensive application in studies on spectral sensitisation for the determination of the energy levels of the dyes.[2,15–17] The potential $E^{Red}_{1/2}$ reflects the energy of the level ε_{lv} of Dy* from which an electron is transferred to the conduction band of AgHal while $E^{Ox}_{1/2}$ reflects the energy of ε_{ho}.

The polarographic half-wave reduction and oxidation potentials of dyes are at present the principal energy criteria of the electronic levels in dyes. They are frequently resorted to instead of the quantities ε_{lv} and ε_{ho}. The main reason for this is the ease of their determination. A definite relation between the positions of the electronic levels, characterised by the oxidation-reduction potentials of dyes, and the efficiency of the spectral sensitisation has been demonstrated in numerous studies. Mention should be made in the first place of the studies of Dähne,[18,19] Tani and Kikuchi,[15] Gilman,[16] and a number of other investigators (see the relevant reviews[19–23]). A definite relation between the positions of the electronic levels of dyes, characterised by the potentials, and the efficiency of the spectral sensitisation was discovered in these studies. For example, it has been shown that, as the location of ε_{lv} becomes deeper, *i.e.* in a definite range of potentials $|E^{Red}_{1/2}|$ (as a rule, $|E^{Red}_{1/2}| < 1.0$ V relative to the saturated calomel electrode), a decrease in the effectiveness of the spectral sensitisation of negative photographic materials is observed. This is associated with the fact that, starting with a certain boundary value of $E^{Red}_{1/2}$ (Dy), the levels ε_{lv} are found to be deeper than the bottom of the conduction band of AgHal, which hinders the transfer of a photoelectron from Dy* to the conduction band. The positions of the bottom of the conduction band and of the top of the valence band of AgBr have been determined[5] in terms of the electrochemical potential scale. Relative to the normal hydrogen electrode (n.h.e.), the potential of the bottom of the conduction band of AgBr is -1.1 V, while the potential of the top of its valence band is $+1.5$ V. Relative to the saturated calomel electrode (sat. c.e.), these potentials are -1.34 and $+1.26$ V respectively. The potential of the bottom of the conduction band is close to the boundary value $E^*_R = -1.37$ V established later in a study by Tani.[24]

The bathochromic shift of the absorption by cyanine dyes to the IR region of the spectrum is known to be attained as a rule when the length of the polymethine chain is increased. With increase in the length of the polymethine chain, the levels ε_{lv} become deeper and approach the levels ε_{ho}.[15] Fig. 1 illustrates the energy level diagram for thiapolymethine dyes in terms of the electrochemical potential scale relative to the AgBr bands. The potentials were taken from Shapiro *et al.*[25] Starting with the carbocyanine for which $n = 1$, the levels ε_{lv} of the dye are found to lie below the bottom of the conduction band of AgBr and are located increasingly deeper with increase in n (*i.e.* as the absorption shifts into the IR region of the spectrum). Seemingly, the problem of the effectiveness of spectral sensitisation, namely the decrease in the effective sensitisation as the level ε_{lv} of the dye assumes a deeper position $|E^{Red}_{1/2}(Dy)| < 1.34$ V relative to the sat. c.e., may be solved successfully within the framework of the energy approach to electron transfer. The energy gap (energy

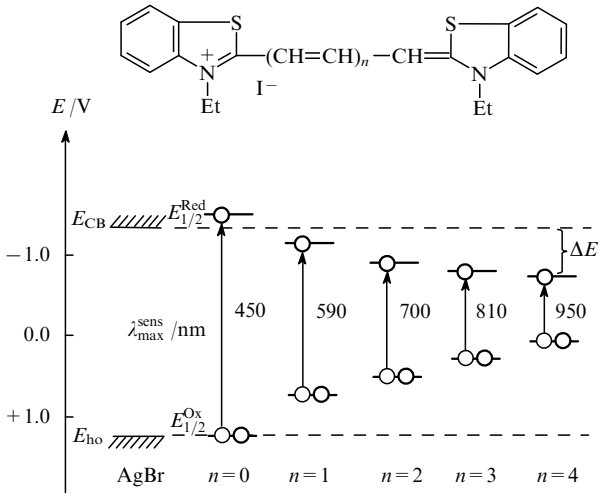


Figure 1. Energy level diagram for thiapolycarbocyanine dyes on the electrochemical potential scale (relative to sat. c.e.).

'deficit') between ε_{lv} and the bottom of the conduction band then increases. In this case, the decrease in spectral sensitivity with increase in the energy gap (ΔE) is quite reasonable, since the sensitisation rate constant k_S which determines the quantum yield of the spectral sensitisation should vary exponentially with ΔE:

$$k_S = A \exp\left(-\alpha \frac{\Delta E}{RT}\right), \quad (1)$$

where A and α are constants. This explanation of the dependence of the spectral sensitivity on $E_{1/2}^{Red}(Dy)$ can in fact be found as a rule in the literature.

Despite the agreement between the experimental results and the predictions of the theory of electron transfer from Dy* to the AgHal conduction band noted above, a certain amount of caution must be exercised in assessing the adequacy of this model. The question of the real disposition of the dye levels relative to the AgHal electron energy bands has been discussed hitherto. The mutual assignment of the levels based on photographic experiments, electrochemical data, and quantumchemical calculations, is also not unambiguous. However, the principal disadvantage of the electron transfer model considered is the absence of a dependence of the spectral sensitivity on $E_{1/2}^{Red}(Dy)$ when the light-sensitive layers are exposed *in vacuo*.

The studies by James and coworkers [26–28] of the influence of the evacuation of photographic emulsions on the effectiveness of spectral sensitisation are undoubtedly some of the most important in the field of spectral sensitisation. It was shown in these investigations that, after the removal of oxygen and water from light-sensitive layers by evacuation and the additional reductive sensitisation by hydrogen, the dependence of the sensitisation effectiveness on $E_{1/2}^{Red}(Dy)$ vanishes and many desensitising dyes, the ε_{lv} levels of which are located deep under the conduction band, become effective sensitisers. For example, spectral sensitisation has been observed for a dye with $E_{1/2}^{Red}(Dy) = -0.36$ V, for which the transfer of a photoelectron from Dy* to the AgHal conduction band is virtually impossible ($\Delta E = 1.1$ V). This was a kind of crucial experiment, which demonstrated convincingly that the effectiveness of the spectral sensitisation is determined not so much by the disposition of the dye levels relative to the AgHal bands as by the chemical reactions with participation of oxygen and water protons, which lead to the formation of secondary products (in particular, hydrogen peroxide) and which thereby divert the photoelectrons from the formation of a latent image. A similar influence of evacuation on spectrally sensitised layers has been observed also by other investigators.[28,29]

In order to account for the sensitisation by dyes the ε_{lv} levels of which are located under the AgHal conduction band, James employed a two-stage electron transfer from Dy* to AgHal,[30] according to which the electron is initially transferred not to the conduction band but to local surface capture levels located deeper (or near) the electronic level in Dy*. Such levels may be surface defects and in the first place surface Ag ions (on kink sites). Electrons are next thermally excited from the surface capture levels to the AgHal conduction band. The transfer of electrons from Dy* to local surface layers, including the silver ion levels, has also been examined by West [31] and Mitchell.[32] Gilman [16] also postulates that the number and depth of the effective electron capture levels on AgHal are more important factors, controlling the sensitising effect of the dye, than the relation between the energy levels of the dye and AgHal. The spectral sensitisation processes 'under the conduction band' with participation of surface electron traps have also been examined by Gilman.[33]

James's two-stage mechanism [30] was a logical continuation of the conclusions arising from his study [34] and also from that of Saunders and West [35] concerning the mechanism of the development process. In his earlier study,[34] James showed that, for microcrystals with subsurface sensitivity, the deep latent image undergoes latensification when the microcrystals come into contact with a number of developing substances (hydrazine, hydroxylamine, phenidone, *etc.*), capable of effecting the transfer of one electron, while Saunders and West [35] observed the formation of a latent image on AgHal single crystals at a depth of several microns under the surface when they come into contact with a normal developer. The single-stage electron transfer from developers into the bulk of AgHal is unrealistic, since, for a width of the energy gap $\Delta E = 1.3$ V between the electronic level in the developers and the bottom of the conduction band, the transfer time should be approximately 100 years.

The electron transfer from the silver atom formed on surface development of AgHal into the exposed crystals constitutes the basis of the generation of a direct negative image when a fogging developer is employed [36] and also when light-sensitive layers initially exposed in a surface developer are subjected to uniform illumination by low-intensity light.[2]

Convincing evidence for electron transfer from Dy* into the bulk of AgHal *via* the system of levels under the AgHal conduction band is provided by experiments with AgHal emulsions containing Ir^{3+} ions in microcrystals. Gilman [37] showed that a deep latent image is formed in such emulsions on spectral sensitisation by dyes with $E_{1/2}^{Red}(Dy)$ up to -0.25 V (relative to the Ag/AgCl electrode). Thermal excitation of electrons to the conduction band has been considered.

If one takes into account the appreciable oxidation potential of the Ag^+/Ag system, then the surface silver ions can be reduced by virtually any photoexcited infrared dye.[23] It is noteworthy that, even in the presence of the excess of Br^- ions actually employed in the emulsion, the AgHal surface coated by the excess bromide ions constitutes less than 20% of the entire surface,[38] *i.e.* silver ions are always present on the surface.

It is well known that the effectiveness of the spectral sensitisation of AgHal by dyes with ε_{lv} levels located under the conduction band, and in the first place by infrachromatic dyes, depends greatly on the concentration of Ag^+ ions (pAg) in the emulsion. The spectral sensitivity S_λ then increases with increase in the Ag^+ concentration.[2] The dependence of the effectiveness of infrared dyes on pAg has been studied in detail by Collier and Gilman,[39] who noted an increase in the effectiveness of spectral sensitisation for dyes having a long polymethine chain with decrease in pAg. The increase in S_λ with increase in the concentration of Ag^+ ions has been attributed to the direct phototransfer of electrons from Dy* to surface Ag^+ ions. Within the framework of the band scheme of the AgHal levels, this is equivalent to the downward bending of the bands and the approach of the bottom of the conduction band to ε_{lv} of the dye, as shown in Fig. 2. The dependence of the boundary potentials and $E_{1/2}^{Red}$ and $E_{1/2}^{Ox}$, corresponding to the injection of the dye electrons and hole into AgHal, on pAg, discovered by Berriman and Gilman,[40] is associated with this finding. Under these conditions, the injection of electrons from Dy* into AgHal is facilitated at low pAg, while the injection of holes is facilitated at high pAg.

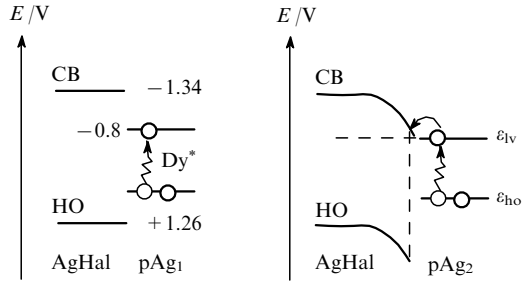


Figure 2. Schematic illustration of the bending of the AgHal bands with increase in the concentration of Ag^+ ions ($pAg_1 < pAg_2$) in a photographic emulsion during spectral sensitisation by a dye with a deep ε_{lv} level.

When the spectral sensitisation by infrared dyes is considered as a reaction of Dy* with surface Ag^+ ions, the main problem becomes not the energy 'deficit' but the effectiveness of the separation of the charges formed in the primary step and hence the probability of the recombination of the charges or their irreversible binding. It is noteworthy that this is the usual problem, characteristic of all chemical oxidation-reduction reactions, which is solved mainly by the stabilisation of the final states. In the case of silver halides, such stabilisation is possible by virtue of the rapid relaxation of the generated states as a result of the electrostatic interaction with the medium and also because of the subsequent removal of electrons through space by their relay migration *via* surface (or subsurface) silver ions or *via* impurity cations. The uniqueness of silver halides in this respect may be determined by the greater probability of the formation of silver molecules (the latent image precentres), whereupon the energy of the interatomic Ag–Ag bond is gained.

If it is supposed that the primary step consists in electron transfer to surface traps and in the first place to silver ions, the difference in the photographic effect of infrared dyes is determined not so much by the kinetics of the primary step as by the kinetics of the secondary reactions of the components of the photographic emulsion, involving the formation of silver atoms, and in the first place of the chemical processes involving the oxidation of the silver atoms and silver particles formed. The influence of chemical reactions, including reactions involving oxygen and protons, on the effectiveness of the photographic process is well known.[18] This concerns the so called processes involving the desensitisation of AgHal by dyes.

III. Desensitisation of silver halides by dyes

The desensitisation of AgHal by dyes is understood as the decrease in the intrinsic (blue) sensitivity of the photographic emulsion following the adsorption of dyes on AgHal microcrystals. The desensitisation of AgHal was first examined by Lüppo–Cramer,[41] who introduced the term desensitisation. Two principal desensitisation mechanisms are distinguished — electron acceptor and hole acceptor mechanisms. The desensitisation *via* the electron acceptor mechanism — type I desensitisation — is induced by dyes, including infrachromatic dyes, with a high electron affinity. After the exposure of AgHal to light ($h\nu$), the desensitising dyes capture photoelectrons from the conduction band in the ε_{lv} levels lying below the bottom of the AgHal conduction band and thereby divert them from the formation of a latent photographic image (Fig. 3). Thus the condition for the type I desensitisation is $E^{Red}_{1/2}(Dy) > E_{CB}$. This process can be represented schematically as follows:

$$[AgHal] \xrightarrow{h\nu} [AgHal]^*, \quad (2)$$

$$[AgHal]^* + Dy \longrightarrow [AgHal]^+ + Dy^{-\bullet}, \quad (3)$$

$$Dy^{-\bullet} + \text{medium} \longrightarrow \text{products}, \quad (4)$$

$$[AgHal]^+ + Dy^{-\bullet} \longrightarrow [AgHal] + Dy. \quad (5)$$

In this scheme, stage (4) corresponds to the irreversible loss of electrons as a result of the chemical interaction of $Dy^{-\bullet}$ with the components of the photographic emulsion. Stage (5) reflects the recombination of the electrons, captured by Dy, with AgHal holes.

An appreciable intensification of the desensitisation by electron-accepting dyes in the presence of oxygen and water was already noted comparatively long ago.[18,27] Blau and Wambacher[42] noted that the desensitising effect of Pinakryptol Yellow and phenosafranin is manifested only in the presence of oxygen. It was postulated that the desensitiser is more likely to be an oxidation 'transferring agent' than an oxidant proper. The influence of oxygen and moisture on emulsions containing electron-accepting dyes was also pointed out by Carrol and coworkers.[43]

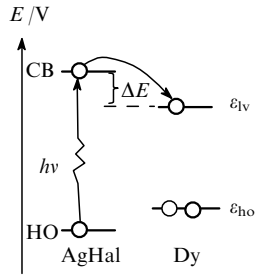


Figure 3. Schematic illustration of type I desensitisation.

The influence of oxygen and moisture on the sensitivity of spectrally sensitised emulsions was later confirmed in other studies.[26,30,40,44–51] It has been suggested[51] that the influence of oxygen on infrachromatic materials is associated with the formation of the complex $[Dy \cdot O_2]$. The studies of the influence of various emulsion factors, as well as the structure of dyes, on type I desensitisation processes have been thoroughly reviewed by Dühne.[18]

Considerable attention has been devoted to the role of oxygen and water in type I desensitisation processes in the communications of James and coworkers,[26,27,48] in which electron transfer from the AgHal conduction band *via* the dye to O_2 with formation of the $O_2^{-\cdot}$ radical-anion is discussed. The special role of water in the irreversible binding of photoelectrons with formation of hydrogen peroxide is emphasised.[48]

The following mechanism has now been adopted for type I desensitisation (Scheme 1).[5,6,17,27]

Scheme 1

$$e(Ag^0) + Dy \underset{(1)}{\rightleftharpoons} Dy^{-\cdot} \overset{O_2}{\underset{(2)}{\rightleftharpoons}} Dy + O_2^{-\cdot} \overset{H^+}{\underset{(3)}{\rightleftharpoons}} HO_2^{\cdot} \overset{e^-}{\underset{(4)}{\rightleftharpoons}} HO_2^- \overset{H^+}{\underset{(5)}{\rightleftharpoons}} H_2O_2$$

$$(6)\downarrow p^+ \qquad (7)\downarrow p^+$$

$$Dy + Hal^- \qquad O_2 + Hal^- \quad (6)$$

In the first stage of the desensitisation process, an electron from the AgHal conduction band or from a surface trap (in particular from the Ag^0 precentre of the latent image) is captured by the dye in the ground state, which is then converted into the Dy radical-anion. Next the excess electron is transferred from $Dy^{-\cdot}$ to O_2 with formation of the $O_2^{-\cdot}$ radical-anion. The superoxide radical-anion $O_2^{-\cdot}$ is known to be readily protonated, affording the radical $HO_2^{\cdot}$ with a much higher electron affinity than $O_2^{\cdot}$.[5,6] The radical $HO_2^{\cdot}$ therefore readily captures a second electron. The anion HO_2^- formed thereby is subsequently protonated, giving rise to hydrogen peroxide. In addition, there is a possibility of the recombination of the radical-anions $Dy^{-\cdot}$ and $O_2^{-\cdot}$ with holes (stages *6* and *7*).

According to the above mechanism, the dye in the ground state plays the role of an intermediate, transferring electrons from the silver atom to O_2 and the water protons, *i.e.* one is dealing with catalysis by the dye of oxidation processes with participation of oxygen and protons. The transformation of the single-stage oxidation reaction into a series of consecutive reactions in each of which the activation energy for the process is smaller than in the single-stage reaction then leads (as in any catalytic processes) to the acceleration of the overall process.

The intermediate participation of the dye in electron transfer (stage *1*) is determined by its electron affinity or, more specifically, by the depth (ΔE) of the ε_{lv} level of the adsorbed dye under the AgHal conduction band (Fig. 3). Furthermore, the effectiveness of the electron capture depends on the capture cross-section, which is a function of the charge and length of the dye molecule. Thus, other conditions being equal, the deeper the ε_{lv} level of the dye *i.e.* the smaller the absolute magnitude of $E^{Red}_{1/2}(Dy)$, the greater should be the extent of desensitisation.

The relation between the desensitising effect of dyes and the position of their lowest vacant electronic level has been pointed out independently by Bogomolov and Moshkovskii,[53] by Tamura and Hada,[54, 55] and also by Sheibe and Dörr.[56, 57] The dependence of the desensitisation on the polarographic potentials $E_{1/2}^{\mathrm{Red}}(\mathrm{Dy})$ was first noted in the study of Sheppard *et al*.[58] The authors quote a potential of -0.70 V (relative to n.h.e.) or -0.92 V (relative to the Ag/AgCl electrode) as the upper limit for desensitisation. Later these values were confirmed.[59] The same limiting potentials have been quoted by Dähne.[18, 22, 60] Desensitisation potentials in the range from -0.86 to -1.05 V (relative to the Ag/AgCl electrode) have been given in a number of studies.[17, 40, 61–64] Thus, on average the boundary desensitisation potential on the polarographic potential scale is -1.0 V (relative to the Ag/AgCl electrode). The limiting potential depends on emulsion factors and primarily on pAg. With increase in pAg and also with increase in the dye concentration, an intensification of the desensitisation is observed.[18]

In vinylogical series of polymethine dyes, the desensitising effect increases with increase in the length of the polymethine chain, which agrees with the increased depth of the $\varepsilon_{\mathrm{lv}}$ level.[15, 18, 65] The quantitative dependence of the desensitisation on the dye $\varepsilon_{\mathrm{lv}}$ has been investigated by Strurmer *et al*.[66] It was shown that the desensitisation steadily increases with increase in the depth of the $\varepsilon_{\mathrm{lv}}$ level.

The dependence of the degree of desensitisation on $E_{1/2}^{\mathrm{Red}}(\mathrm{Dy})$ has been examined in detail by Mikheeva *et al*.[67] The degree of desensitisation (*SD*) is understood as the ratio of the intrinsic sensitivity of the AgHal emulsion without the dye (*S*) to the sensitivity in the presence of the dye (S'):

$$SD = \frac{S}{S'}.$$

The linear dependence of lg *SD* on $E_{1/2}^{\mathrm{Red}}(\mathrm{Dy})$ of the general type

$$\lg SD = m\,E_{1/2}^{\mathrm{Red}}(\mathrm{Dy}) + n, \qquad (7)$$

has been discovered.[67] Here *m* and *n* are constants for constant pAg and the dye concentration. Figs 4 and 5 illustrate the dependence of lg *SD* on $E_{1/2}^{\mathrm{Red}}(\mathrm{Dy})$ for different dye concentrations and different pAg. It is striking that the linear relation is retained over a definite range of pAg and concentrations, the slope of the curves increasing with increase in pAg and the dye concentration. The boundary desensitisation level is -1.1 V (relative to sat. c.e.).

The linear dependence of lg *SD* on $E_{1/2}^{\mathrm{Red}}(\mathrm{Dy})$ has been explained within the framework of the kinetic model of spectral sensitisation processes[67] on the basis of the electrochemical potentials of the dyes and other components of the photographic emulsion, which was developed in the present authors studies.[5, 6, 17, 23] The model is based on the Marcus theory of electron transfer in polar media.[68] Since the spectral sensitisation and desensitisation of AgHal are typical oxidation-reduction reactions occurring in a polar medium, the Marcus theory is fully applicable to them. According to the Marcus theory, there is a linear relation between the free energy of formation of the transition state ($\Delta G^{\neq}$) and the thermodynamic characteristics of the elementary oxidation-reduction step:

$$\Delta G^{\neq} = -RT\ln k \approx a\,\Delta G^{0} + b \approx a\,n\,F\Delta E^{0} + b, \qquad (8)$$

where *k* is the reaction rate constant, ΔG^{0} the standard free energy change in the reaction, *a* and *b* are constants for a particular class of reactions, *n* is the number of electrons in the reaction, *F* the Faraday, and ΔE^{0} the difference between the standard potentials.

In this case, the rate of electron transfer between the components of the photographic emulsion — the molecules of Dy*, Dy, AgHal*, AgHal, and other compounds — can be expressed by kinetic equations in which the activation energy is a function of the difference between the normal oxidation-reduction potentials of the systems participating in the electron transfers. For example, the rate of passage of electrons into the conduction band or onto the AgHal surface levels, which determines the light sensitivity of

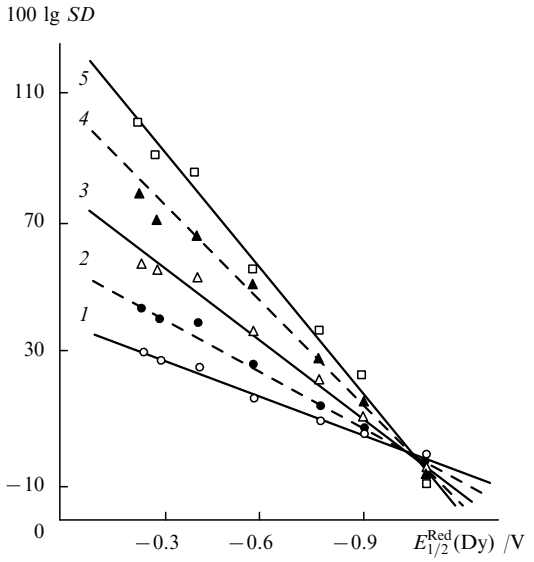


Figure 4. Dependence of lg *SD* on $E_{1/2}^{\mathrm{Red}}$ at different dye concentrations $10^{6}\,c_{\mathrm{Dy}}$ (mol per mole of AgHal) (pAg 8.0): (*1*) 1; (*2*) 2; (*3*) 4; (*4*) 8; (*5*) 10.

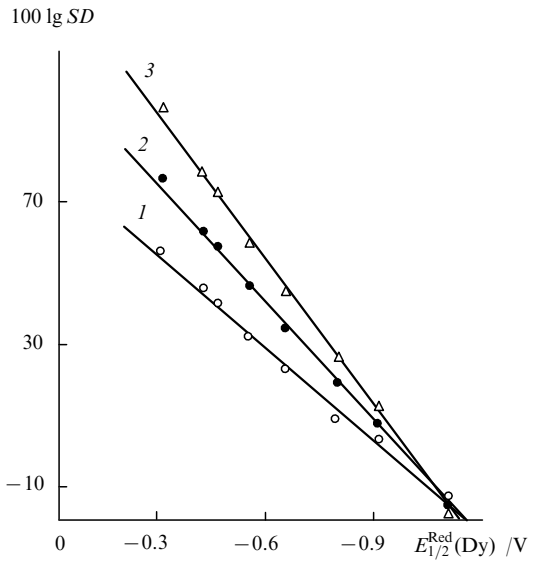


Figure 5. Dependence of lg *SD* on $E_{1/2}^{\mathrm{Red}}$ at different pAg: (*1*) 7.4; (*2*) 8.0; (*3*) 8.9. Dye concentration 2×10^{-6} mol per mole of AgHal.

the negative process, can be expressed as the sum of the rates of electron flow in individual channels of the electron transfer reactions:

$$\sum_i\left(\frac{\mathrm{d}n_{i(\mathrm{e})}}{\mathrm{d}t}\right) = \sum_i k_i c_i = \sum_i A_i c_i \exp\left(-\frac{\alpha_i \Delta E_i^{0}}{T}\right), \qquad (9)$$

where $n_{i(\mathrm{e})}$ is the number of electrons in the conduction band or on the AgHal surface, k_i the rate constant for electron transfer, c_i the concentration (or more precisely the activity) of the electron-donating (reduced) form of the *i*th system, formed after photoexcitation and capable of electron exchange with the conduction band or with the surface levels, A_i and α_i are constants for a particular class of reactions, and ΔE_i^{0} is the difference between the normal potential of the *i*th system, formed after photoexcitation, and the potential of the bottom of the conduction band E_{CB}^{0} or the electron-accepting levels ($E_{\mathrm{SL(e)}}^{0}$).

The kinetics of electron capture from the conduction band by the components of the photographic emulsion may be expressed

as the sum of the rates of the reactions, one of which is the formation of the latent image:

$$\sum_j -\left(\frac{dn_{j(e)}}{dt}\right) = \sum_j k_j c_j n_{(e)} = \sum_j A_j c_j n_{(e)} \exp\left(-\frac{\alpha_j \Delta E_j^0}{T}\right), \quad (10)$$

where c_j is the concentration of the electron-accepting (oxidised) form of the jth system and ΔE_j^0 is the difference between the potential of the bottom of the conduction band E_{CB}^0 (or $E_{SL(e)}^0$) and the normal potential of the jth system. The photographic sensitivity is determined by the ratio of the rates of the reactions involving the migration of electrons into AgHal and their irreversible binding.[5, 17]

We shall now consider the desensitisation process. According to Scheme 1, the primary stage of the desensitisation process is the capture of electrons from the conduction band or from the surface traps by the dye in the ground state. Stage *1* may be rate-determining for the overall desensitisation process. The rate constant for the protonation of $O_2^{-\cdot}$ (stage *3*) is known to be nearly diffusional, *i.e.* equal to 10^{10} cm^{-1} s^{-1}.[69] Stage *2* can also be fairly fast, since the normal potential of the $O_2^{-\cdot}/O_2$ system is -0.284 V (relative to n.h.e.),[69] *i.e.* is significantly more positive than $E_{1/2}^{Red}(Dy)$ for the majority of dyes. If it is assumed that stage *1* is rate-limiting, then the rate of capture of electrons from the conduction band by the dye is determined according to Eqn (10) (for c_{Dy} = const. and n_e = const.) by the difference between the potentials of the bottom of the conduction band E_{CB}^0 and $E^0(Dy^{-\cdot}/Dy)$. For reversible systems, the potential $E^0(Dy^{-\cdot}/Dy)$ is virtually identical with $E_{1/2}^{Red}(Dy)$. The electron capture rate constant (stage *1* in Scheme 1) can be expressed in the form

$$k_1 = A_1 \exp\left(-\alpha_1 \frac{\Delta E_1^0}{T}\right), \quad (11)$$

where $\Delta E_1^0 = E_{CB}^0 - E_{1/2}^{Red}(Dy)$. The degree of desensitisation at constant pAg should be proportional to k_1, the concentration of electrons which have emerged onto the surface of AgHal microcrystals after passing through the conduction band (c_e), and the dye concentration (c_{Dy}):

$$SD \approx k_1 c_e c_{Dy}, \quad (12)$$

For constant pAg, c_e, and c_{Dy}, we have

$$SD \sim k_1 \sim \exp\left(-\frac{\Delta E_1^0}{T}\right) \sim \exp\left(\frac{E_{1/2}^{Red}(Dy)}{T}\right). \quad (13)$$

Indeed, according to Figs 4 and 5 there is a linear dependence of lg SD on $E_{1/2}^{Red}(Dy)$.[67] It is noteworthy that the form of the dependence of lg SD on $E_{1/2}^{Red}(Dy)$ does not change if electrons are captured by the dye not directly from the conduction band but from the surface electron traps (e_S). In this case, only ΔE_1^0 changes. It may be that electrons are captured both from the AgHal conduction band and from the surface traps.

Naturally, with increase in the concentration of the desensitiser dye, there is an increase in the rate of electron capture. This explains the relation, noted by Dähne,[60] between lg SD and the dye concentration (more precisely lg c_{Dy} — see Fig. 4). The dependence of lg SD on pAg is determined by the competition between the silver ions and the dye for electron capture from the conduction band. Furthermore, Ag^+ ions may capture electrons from $Dy^{-\cdot}$ and $O_2^{-\cdot}$, formed in stages *1* and *2* (see Scheme 1), and hence can return them to the construction of the latent image. This explains the decrease in desensitisation with decrease in pAg (Fig. 5).

The quantity $E_{CB}^0 = -1.1$ V (relative to n.h.e.) or approximately -1.34 V (relative to sat. c.e.) for AgBr has been determined from experimental and calculated data.[67] Fig. 6 presents a diagram illustrating the normal oxidation-reduction potentials for the components of the silver halide emulsion. The potential diagram is extremely important methodologically, since it makes

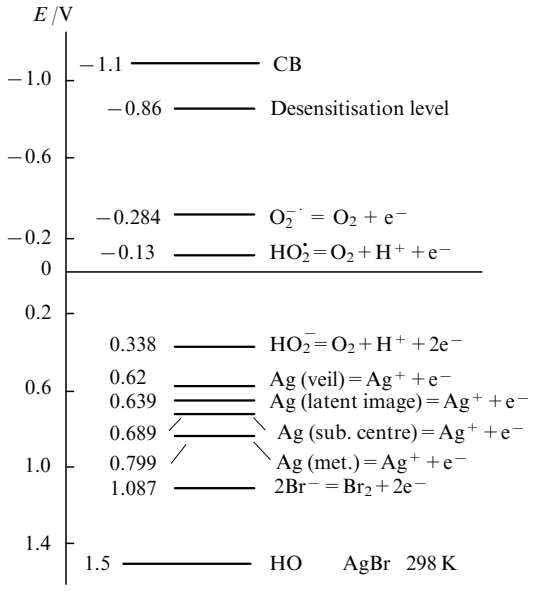


Figure 6. Oxidation-reduction potential diagram for the components of a AgHal emulsion.

it possible to compare the potentials of the electron bands of AgHal, the dyes, the photographically active silver particles, and various components of the photographic emulsion. As an example, Fig. 7 illustrates the type I desensitisation reaction path for a dye with $E_{1/2}^{Red}(Dy) = -0.6$ V (relative to n.h.e.).

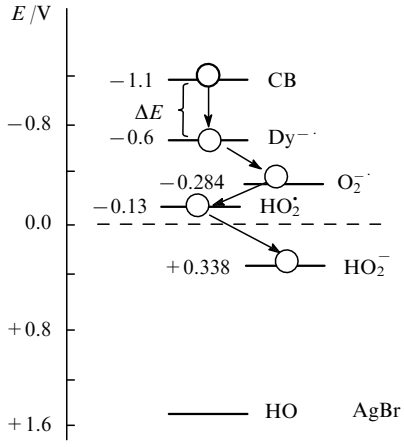


Figure 7. Energy scheme for a type I desensitisation process.

IV. Self-desensitisation of dyes

It is natural to postulate that secondary oxidative desensitisation processes should occur not only on photoexcitation of AgHal but also on photoexcitation of the dye itself — the spectral sensitiser. One is dealing with reactions involving the self-desensitisation of dyes,[2, 5, 6, 23] which is understood as the desensitising influence of the spectral sensitiser on the photoprocess in the region of its absorption. In the literature, this process had been previously called selective desensitisation in the region of spectral sensitisation.[27, 32, 70]

Unfortunately it is virtually impossible to estimate quantitatively the influence of the spectral sensitisers themselves on the spectral sensitivity, since one cannot carry out a control exposure in the same spectral zone without the dye. An indirect method is

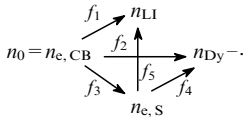
therefore used — the influence of an additionally introduced desensitiser on the spectral and intrinsic sensitivity is inferred, *i.e.* the selective desensitisation is estimated.

The difference between the desensitisation and selective desensitisation processes in the region of spectral sensitisation has been considered in a number of studies [23, 27, 70] and the greater influence of the additionally introduced desensitisers on the spectral sensitivity compared with the intrinsic sensitivity was explained by the fact that, on photoexcitation of AgHal, desensitisation is achieved by the capture of electrons from both deep electron traps (light sensitivity centres) and from shallow surface traps. On the other hand, on photoexcitation of the dye, all the photoelectrons are initially transferred to shallow surface traps, from which the capture of electrons in vacant levels of the desensitising dye is facilitated and to a greater extent the higher the value of $E_{1/2}^{\mathrm{Red}}$(Dy). In conformity with Scheme 1, the desensitisation increases the probability of stage *1* in this case, because the concentration of the electrons captured on the AgHal surface (e_S or Ag^0) is greater than on excitation of AgHal electrons into the conduction band, from which a large proportion of the electrons are immediately captured by the comparatively deep levels of the light-sensitivity centres.

The difference between the processes occurring on photoexcitation of AgHal and the dye has been inferred [71] from the amplitude and the relaxation time of the photo-e.m.f. of AgBr(I) emulsions with sulfur sensitisation. The smaller decrease in the amplitude of the photo-e.m.f. during sulfur sensitisation in the region of spectral sensitivity compared with the region of the intrinsic absorption of AgHal was explained by the fact that the impurity centres formed on chemical sensitisation capture more effectively the electrons generated in the bulk of the microcrystals than the photoelectrons formed on photoexcitation of the dye. The latter are initially captured by centres on the AgHal surface and only then pass into the conduction band. The longer growth and relaxation times the photo-e.m.f. in the region of spectral sensitisation than in the region of the intrinsic absorption of AgHal are associated with this fact.[72]

The influence of electron acceptors — pyrylocyanines with a variable electron affinity characterised by $E_{1/2}^{\mathrm{Red}}$(Dy) — on the degree of desensitisation *SD* and the degree of desensitisation SD_λ in the region of spectral sensitivity of emulsions spectrally sensitised by thiacyanines has been studied in detail.[67] Fig. 8 presents the dependence of lg *SD* and lg SD_λ on $E_{1/2}^{\mathrm{Red}}$(Dy) of the desensitisers for a coarse-grain AgBr(I) emulsion with S + Au sensitisation, containing thiadi- and thiatri-carbocyanines as spectral sensitisers. It follows from Fig. 8 that the slope of the lg $SD = \mathrm{f}(E_{1/2}^{\mathrm{Red}})$ relations is significantly greater than that of the lg $SD = \mathrm{f}(E_{1/2}^{\mathrm{Red}})$ relations, *i.e.* the influence of desensitisers on the additional sensitivity is more marked.

On desensitisation, the fate of the n_0 electrons formed in the conduction band ($n_{e,CB}$) on photoexcitation of AgHal can be represented by the following scheme:[67]



(14)

Some of the electrons (f_1) migrate to the sensitivity centres and form the latent image (n_{LI}) others (f_2) are captured directly by the dye ($n_{Dy^-\cdot}$) and are lost in accordance with Scheme 1, while a third part of the electrons (f_3) initially migrate to other surface traps ($n_{e,S}$), a proportion of which (f_4) are captured by the dye while another fraction (f_5) may be thermally excited into the conduction band and can be used in the construction of the latent image. Thus $n_0(f_2 + f_3 f_4)$ electrons are diverted from the construction of the latent image. In this case,

$$SD = \frac{n_0}{n_0 - n_0(f_2 + f_3 f_4)} = \frac{1}{1 - f_2 - f_3 f_4} = \frac{1}{f_1 + f_3 f_5}. \qquad (15)$$

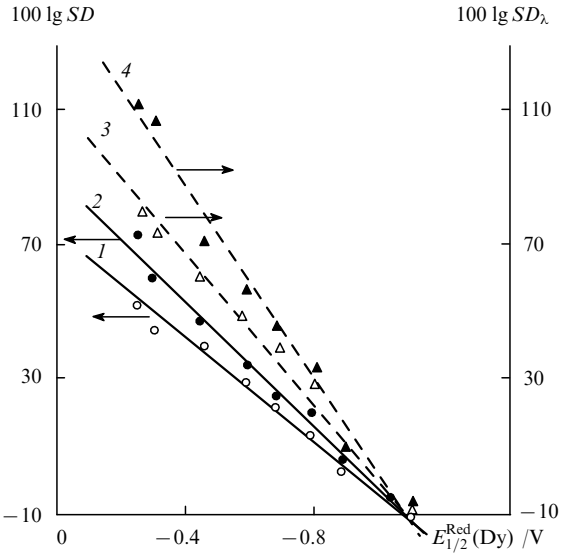
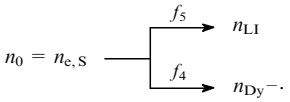


Figure 8. Dependence of lg *SD* (*1*, *2*) and lg SD_λ (*3*, *4*) on $E_{1/2}^{\mathrm{Red}}$ for emulsions sensitised by 3,3′-diethylthiadicarbocyanine iodide (*1*, *3*) and 3,3′-diethylthiatricarbocyanine iodide (*2*, *4*). Dye concentration 2×10^{-6} mol per mole of AgHal (pAg 8.0).

When the quantities f_2 and f_3 are small compared with f_1, $SD = 1$ and lg $SD = 0$.

If it is postulated that, on structural sensitisation,all n_0 electrons initially migrate to surface traps, then the scheme according to which electrons are distributed becomes different:



(16)

In this case,

$$SD_\lambda = \frac{1}{1 - f_4} = \frac{1}{f_5}. \qquad (17)$$

It follows from Eqns (15) and (17) that

$$\frac{SD_\lambda}{SD} = \frac{1 - f_2 - f_3 f_4}{1 - f_4} = \frac{f_1 + f_3 f_5}{f_5}. \qquad (18)$$

Since usually $f_1 > f_5$ in the presence of a desensitiser, we have $SD_\lambda / SD > 1$. On the other hand, the contributions of f_2 and f_4 diminish exponentially with decrease in $E_{1/2}^{\mathrm{Red}}$ of the dye:

$$f_2(f_4) \sim \exp\left(\frac{E_{1/2}^{\mathrm{Red}}}{RT}\right),$$

Therefore, at a certain limiting potential $E_{1/2}^{\mathrm{Red}}$ where f_2 and f_4 tend to zero, we have $SD_\lambda / SD = 1$. This corresponds to the observed critical potential $E_{1/2}^{\mathrm{Red}} = -1.1$ V at which the lg $SD = \mathrm{f}[E_{1/2}^{\mathrm{Red}}(\mathrm{Dy})]$ and lg$SD_\lambda = \mathrm{f}[E_{1/2}^{\mathrm{Red}}(\mathrm{Dy})]$ curves intersect (Fig. 8).

$$\Delta \lg SD = (\lg SD_\lambda - \lg SD) \sim [E_{1/2}^{\mathrm{Red}}(\mathrm{Dy}) - 1.1]. \qquad (19)$$

Thus the difference between *SD* and SD_λ can be explained within the framework of the above scheme governing the transition of electrons from Dy* to surface levels by the difficulty of the direct electron transfer to sensitivity centres on spectral sensitisation. Such transfer requires an additional energy for the excitation of electrons into the conduction band. In the absence of such energy, the probability of the capture of electrons from surface traps by the dye increases. According to Eqn (19), the difference between *SD* and SD_λ increases with increase in $E_{1/2}^{\mathrm{Red}}$(Dy).

The same type of dependence of SD and SD_λ on $E_{1/2}^{Red}(Dy)$ (Figs 4, 5, and 8) suggests that the self-desensitisation by the spectral sensitisers themselves, possessing an electron affinity, is fully realistic and may at the same time significantly exceed the desensitisation, particularly at elevated concentrations of dyes. The marked dependence of the spectral sensitivity of infrared emulsions on the concentration of the sensitiser compared with the intrinsic sensitivity is well known. It follows from Fig. 9 that the decrease in spectral sensitivity observed at certain dye concentrations is more abrupt than the decrease in the 'blue' sensitivity of AgHal. The effective self-desensitisation then requires, like desensitisation, the presence of oxygen and moisture in the light-sensitive layer. This has been confirmed by the observation [73] of an increase in the spectral sensitivity of infrachromatic layers *in vacuo* and in a moist atmosphere without oxygen whereas the simultaneous presence of oxygen and water suppressed sharply the sensitivity. The influence of water on the sensitivity of infrachromatic ultrafine-grain AgBr emulsions has been investigated.[74] It was shown that the increase in the spectral sensitivity

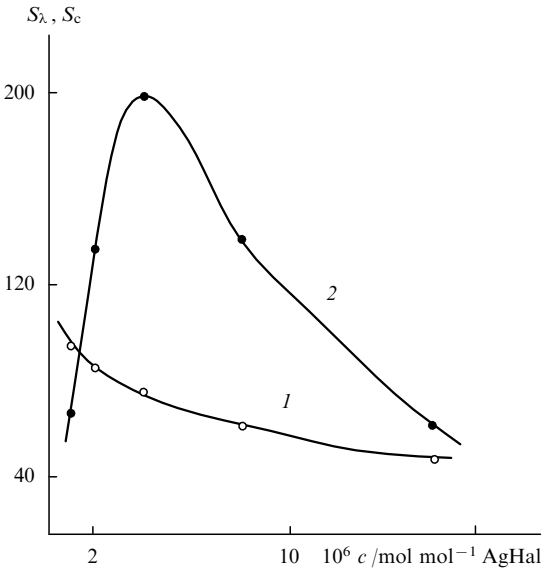


Figure 9. Dependence of the intrinsic light sensitivity S_i (*1*) and additional light sensitivity S_λ (*2*) of an emulsion sensitised by 3,3′-diethylthiadicarbocyanine iodide on the dye concentration (pAg 8.0).

of the emulsions after their drying is greater the higher the values of $E_{1/2}^{Red}(Dy)$ and pAg. The influence of an electron-accepting dye on the lifetime of the silver precentres of the latent image in the presence of oxygen and moisture has been convincingly demonstrated in a study [75] where a sharp decrease in the lifetime of the precentres under the influence of a desentising dye (phenosafranin) was observed. The regression of the latent image on an emulsion with sulfur sensitisation under the influence of a series of infrared dyes has been investigated.[6, 76] According to the results presented in Fig. 10, electron-accepting dyes accelerate significantly the regression of the latent image in conformity with Scheme 1.

The contribution of the dye self-desensitisation processes depends to a significant extent on the type of the AgHal emulsion. The decrease in self-desensitisation on emulsions of the 'core–shell' type and on an emulsion with Ir^{3+} ions in the bulk of the microcrystals may be a consequence of the lower probability of the oxidation of the latent image precentres as a result of the rapid electron transfer from these centres into the bulk of the microcrystals — onto the subsurface electron acceptance centres. This is equivalent to a decrease in the fraction of the electrons f_5 in Eqn (17). This property of the 'core–shell' emulsions and emulsions

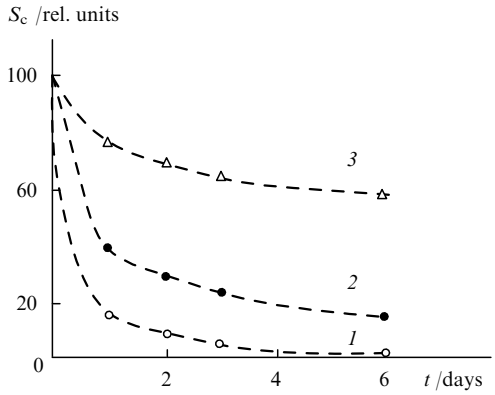


Figure 10. Variation of the intrinsic sensitivity S_i of photographic emulsions sensitised by thiapentacarbocyanine (*1*) and thiatetracarbocyanine (*2*) and in the absence of dyes (*3*) at 35 °C and 100% humidity. Dye concentration 1.8×10^{-4} mol per mole of AgHal.

with Ir^{3+} has in fact made it possible to increase significantly the concentration of spectral sensitisers and the efficiency of the spectral sensitisation itself.[37, 77–81] The decrease in the desensitisation of dyes in the region of their spectral sensitisation on a 'core–shell' emulsion has been demonstrated.[67]

As a result of the examination of the role of dye self-desensitisation processes in the establishment of spectral sensitivity, it was concluded [23] that the self-desensitisation of dyes can in essence determine the effectiveness of the spectral sensitisation itself. From this it follows that the main problem in raising the effectiveness of spectral sensitisation is that of the inhibition of the secondary dye self-desensitisation reactions.

V. Supersensitisation processes as inhibition of the self-desensitisation of dyes

There are methods for increasing the spectral sensitivity of photographic emulsions sensitised by dyes with a low level of the photoexcited electron [$E_{1/2}^{Red}(Dy) > -1.0$ V], including infrachromatic dyes.[2, 5, 82, 83] These methods known under the general term of supersensitisation, can be considered from a single standpoint of dye self-desensitisation processes within the framework of Scheme 1.[5, 6]

For the inhibition of stage *1* (Scheme 1), the dye molecules must be separated from the AgHal surface on the defects of which electrons from Dy* may be captured. One is dealing with a kind of insulation of dye molecules from AgHal, which, however, must not prevent the electron transfer from Dy*, *i.e.* a 'spacer' sufficiently permeable to photoexcited electrons and impermeable to electrons captured by traps on the AgHal surface must be created between the dye and AgHal. One can postulate *a priori* that organic substances readily adsorbed on AgHal are needed for the creation of spacers between AgHal and the dye. Such insulation is important also from the standpoint of the elimination of reactions involving the recombination of electrons with the dye radical-cations formed in the spectral sensitisation step. It may be that the separation of the dye not from the entire AgHal surface but only from the photographically active centres,where photoelectrons are located, plays an important role. In this case, the role of the organic spacers is the same as that of the AgHal shells in emulsions of the 'core–shell' type or in emulsions with deep electron capture centres created by Ir^{3+} ions.

It is essential to note that the problem of the effective charge separation in a photochemical reaction, including separation owing to the decrease in the reverse recombination of charges with the aid of the so called membranes, is general and constitutes one of the principal problems of sensitised photolysis, in particular the sensitised photolysis of water.[84, 85]

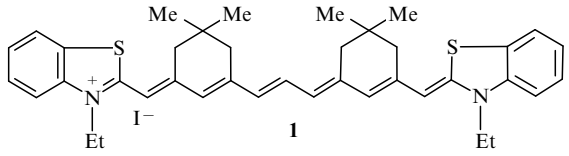
The inhibition of stages *2–5* (Scheme 1) by the insulation of the dye molecules from oxygen and water with the aid of hydrophobic organic compounds, introduced in the stage involving the preparation of photographic emulsions, is also extremely promising.[5, 23, 86] Such compounds should not be adsorbed on AgHal, but, on introduction into a water–gelatin emulsion, they should be deposited on the AgHal microcrystals owing to their hydrophobic nature and create a kind of shell protecting the dye from oxygen and water.

The use of substances adsorbable on AgHal as supersensitisers for photographic materials is well known. Riester[87, 88] showed that, when a series of sulfomercapto-derivatives of heterocyclic bases are introduced, certain dyes, including azomethine dyes, which are relatively ineffective and even desensitising under the usual conditions, become effective spectral sensitisers. According to Riester's 'glue' model, the supersensitisers (potentiators) are attached with the aid of the mercapto-group to the Ag^+ ions on the surface of microcrystals, while the sulfo-groups interact with the positively charged dye chromophores with formation of salt-like products, retaining thereby the dye molecules at a certain distance from AgHal (vaulted structure). The formation of this type of structure of the adsorbed dye promotes, according to Riester, a more effective excitation energy or electron transfer from Dy* to AgHal and also a decrease in desensitisation as a result of the capture of photoelectrons by the dye. This agrees with the conclusions reached by O'Brien,[89] who believes that the sensitisation efficiency is greater when the dye is fixed at a distance of 10–20 Å above the AgBr surface.

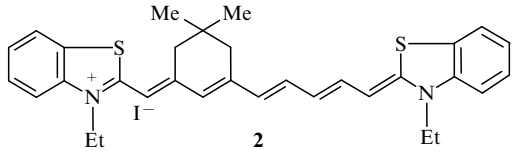
Carrol and Johnson[90] and also Vompe and coworkers[91, 92] described the supersensitising effect of bistriazinylamino-derivatives of stilbene-*o*,*o*′-disulfonic acid on infrachromatic dyes. The alkyl derivatives of 4-hydroxy-6-methyl-1,3,3*a*,7-tetraazaindene (for example, the 2-heptyl derivative)[93, 94] and various triarylphosphines[95–98] also exert supersensitising and antifogging effects.

It is essential to note that Gilman's supersensitisation mechanism,[82] adopted in the literature, the operation of which requires that the supersensitiser should be oxidised more readily than the dye, is inapplicable in this instance, since supersensitisers of the above type are as a rule more difficult to oxidise than the dyes.[83] Thus the mechanism of the action of supersensitisers of this type on infrachromatic emulsions is obscure and the search for the latter is purely empirical. However, it is striking that the above compounds are adsorbed on AgHal[99, 100] and may therefore play the role of 'insulators' between the dye and AgHal.

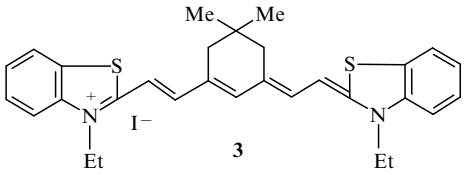
As an illustration of the action of supersensitisers of different structures, we shall present data obtained on an ultrafine-grain (d = 0.05 μm) transparent AgBr(I) emulsion.[101, 102] The use of a transparent emulsion makes it possible to measure the absorption spectra of light-sensitive layers in the IR region. The emulsion was sensitised by penta-, tetra-, and tri-carbocyanine dyes with structures **1**, **2**, and **3**.



1

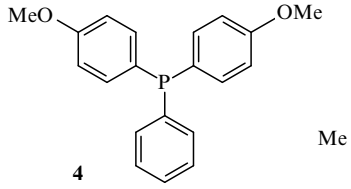


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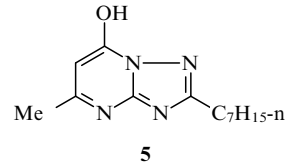


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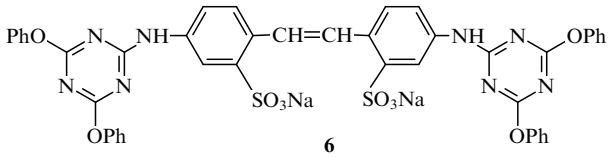
Di-(*p*-anisyl)phenylphosphine **4**, 2-heptyl-4-hydroxy-6-methyl-1,3,3*a*,7-tetraazaindene **5**, the disodium salt of *p*,*p*′-bis(4,6-diphenoxy-1,3,5-triazin-2-yl-amino)stilbene-*o*,*o*′-disulfonic acid **6**, and *C*,*N*-diphenylnitrone **7** were used for supersensitisation. The supersensitisers **4**–**6** are compounds adsorbable on AgHal, while the nitrone **7** is weakly adsorbable.



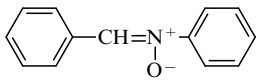
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6



7

In the first place, it was shown in experiments without supersensitisers that the intensity of the principal bands of the dyes depends on pAg: with decrease in pAg, the absorption and the stability of the adsorbed dye increase.[5, 102] This is manifested particularly clearly on the pentacarbocyanine **1**. It follows from Fig. 11*a* that an appreciable increase in absorption by the dye occurs when pAg changes from 7.6 to 5.6, whereupon the absorption band maximum undergoes a hypsochromic shift. The increase in absorption and in the stability of the dye when a fused emulsion is allowed to stand may be attributed to the formation of complexes of the type $[Dy \cdot Ag_S^+]$ on the AgHal surface.[23, 83, 103] This may be the cause of the hypsochromic shift of the absorption band, since the polymethine structure of the dye should be disturbed with a consequent hypsochromic shift of the absorption on formation of a bond between a methine carbon atom of the chain and Ag_S^+. The stabilisation of the dye is also induced by the Tl^+, Cd^{2+}, Pb^{2+} Bi^{3+}, Al^{3+}, and Th^{4+} cations. It is striking that, with increase in the charge on the cation, the concentration of the compound which leads to an increment in the absorption by Dy and in the stabilisation of the latter diminishes steadily.[104] The stabilising effect of inorganic cations is associated with the formation of the complexes $[Dy \rightarrow M^{n+}/AgHal]$ on the AgHal surface, as a result of which there is a decrease in the probability of the donor–acceptor interaction of the adsorbed dye with the components of the dispersion medium (water, gelatin, *etc.*), resulting in the decolorisation of the dye.[103]

With decrease in pAg, the spectral sensitivity S_λ increases (Fig. 11*b*) and, with increase in the wavelength of the absorbed light, the increase in spectral sensitivity becomes more marked (the 'fan' effect). Owing to experimental limitations, measurements at the sensitisation maximum have not been made. The increment in the long-wavelength sensitivity exceeds, even after correction for the increase in the intrinsic sensitivity of the emulsion, the increment in adsorption. A similar picture has been observed for the tetra- and tri-carbocyanines **2** and **3**.[102]

The introduction of compounds **4** and **7** and their mixture into an emulsion with the pentacarbocyanine **1** also induces an increase

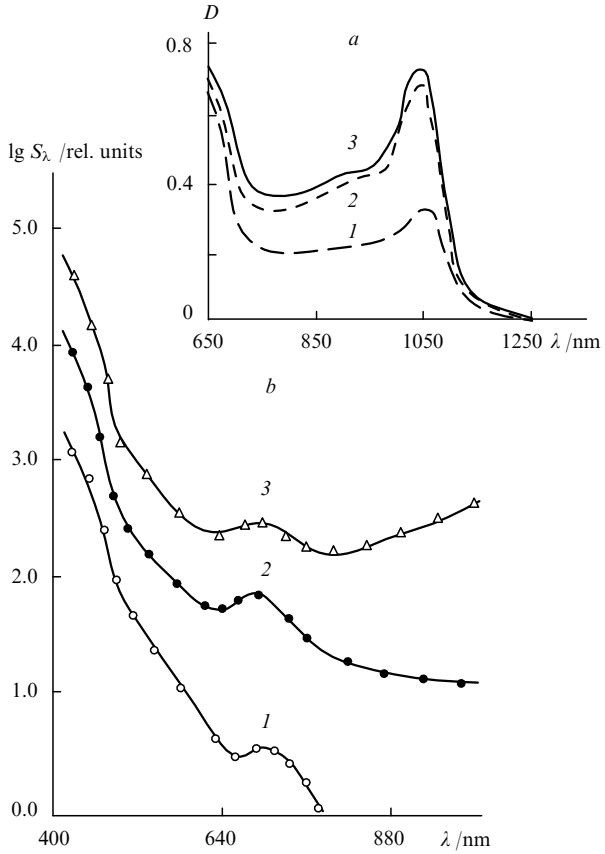


Figure 11. Absorption spectra (*a*) and spectral sensitivity curves (*b*) for emulsions sensitised by dye **1** at different pAg: (*1*) 7.6; (*2*) 5.6; (*3*) 4.6. Dye concentration — 2×10^{-4} mol per mole of AgHal.

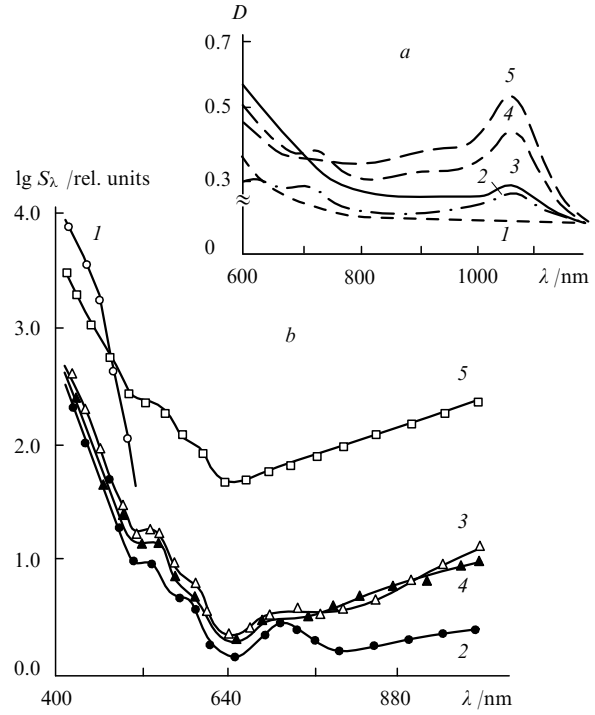


Figure 12. Absorption spectra (*a*) and spectral sensitivity curves (*b*) for emulsions without a dye (*1*), with dye **1** (*2*), and with dye **1** in the presence of supersensitisers **7** (*3*), **4** (*4*), and **4** + **7** (*5*) at pAg 5.6. Concentration of dye **1** — 4×10^{-4} mol per mole of AgHal and concentration of supersensitisers — 1×10^{-2} mol per mole of AgHal.

in absorption and in the spectral sensitivity of the light-sensitive layers (Fig. 12). It is striking that di(*p*-anisyl)phenylphosphine causes a bathochromic shift of the dye absorption band (Fig. 12*a*). The increase in spectral sensitivity is illustrated in Fig. 12*b*. An analogous picture of the growth of absorption and sensitivity following the introduction of supersensitisers has been observed for emulsions sensitised by tetra- (Fig. 13) and tri-carbocyanines (Fig. 14). Like compound **4**, compounds **5** and **6** induce a bathochromic shift of the principal absorption band of the dye. The results of the supersensitising effects of the additives **4**–**7** are summarised in Table 1.

The observed increment in the additional sensitivity under the influence of supersensitisers in most cases exceeds the increment in absorption. Thus the action of these compounds is to some extent analogous to the action of silver ions (pAg) noted above. It is noteworthy that the addition of supersensitisers induces an increase in the intrinsic sensitivity (for dyes **1** and **2**, owing to the decrease in the desensitisation of the dyes). After correction for the intrinsic sensitivity, the supersensitising effect of the additives **4**–**6** is manifested in all the cases listed in Table 1, while compound **7** has an effect only in a certain range of pAg (see experiments *2*, *5*, *9*, and *14* in Table 1).

The increase in absorption and partly also the increase in sensitivity in the presence of supersensitisers are apparently associated with the increase in the adsorption and stability of the adsorbed dye. This can be accounted for by the decrease in the donor–acceptor interaction of the adsorbed dye with the components of the dispersion medium (water, gelatin, *etc*.) and by the insulation of the reaction centres of the dyes by organic (including hydrophobic) compounds.[103] This question will be examined below.

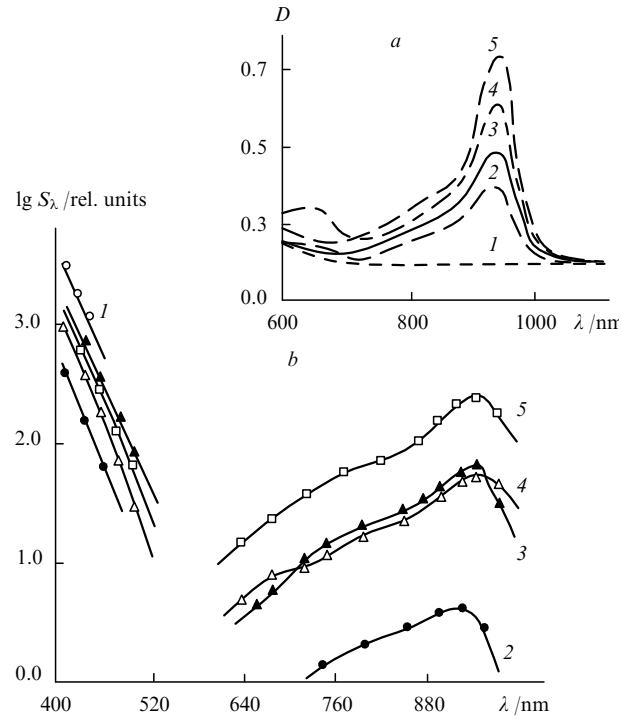


Figure 13. Absorption spectra (*a*) and spectral sensitivity curves (*b*) for emulsions without a dye (*1*), with dye **2** (*2*), and with dye **2** in the presence of superdensitisers **7** (*3*), **5** (*4*), and **7** + **5** (*5*) at pAg 7.6. Concentration of dye **2** — 2×10^{-4} mol per mole of AgHal and concentration of supersensitisers **5** and **7** — 3×10^{-3} and 1×10^{-2} mol per mole of AgHal.

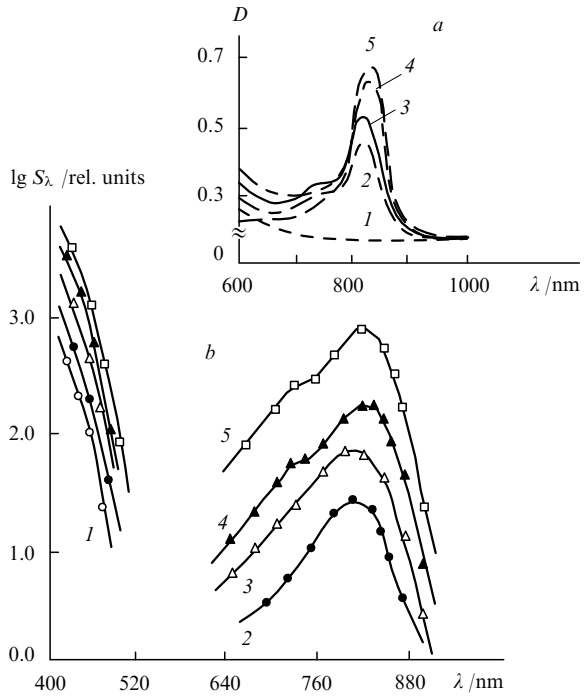


Figure 14. Absorption spectra (*a*) and spectral sensitivity curves (*b*) for emulsions without a dye (*1*), with dye **3** (*2*), and with dye **3** in the presence of supersensitisers **7** (*3*), **6** (*4*), and **6** + **7** (*5*) at pAg 9.0. Concentration of dye **3** — 2×10^{-4} mol per mole of AgHal and concentration of supersensitisers **6** and **7** — 1×10^{-2} mol per mole of AgHal.

Table 1. The influence of supersensitisers (S) on the absorption and light sensitivity of infrared light-sensitive layers.

No. of experiment	Dy	S	λ /nm	pAg	$\frac{D(\mathrm{Dy+S})}{D(\mathrm{Dy})}$ (see [a])	$\frac{S_\lambda(\mathrm{Dy+S})}{S_\lambda(\mathrm{Dy})}$ (see [b])	$\frac{nS_\lambda(\mathrm{Dy+S})}{S_\lambda(\mathrm{Dy})}$ (see [c])
1	**1**	**4**	980	7.6	see [d]	13	4.8
2	**1**	**7**	980	7.6	see [d]	1.6	0.6
3	**1**	**4**+**7**	980	7.6	see [d]	32	9.5
4	**1**	**4**	980	5.6	4.0	4.3	3.8
5	**1**	**7**	980	5.6	1.7	4.6	3.6
6	**1**	**4**+**7**	980	5.6	5.7	100	11
7	**2**	**4**	935	9.0	12	93	40
8	**2**	**5**	935	9.0	7.0	8.9	5.6
9	**2**	**7**	935	9.0	4.3	2.5	0.4
10	**2**	**4**+**7**	935	9.0	13	590	47
11	**2**	**5**+**7**	935	9.0	15	710	83
12	**2**	**4**	935	7.6	1.9	11	7.1
13	**2**	**5**	935	7.6	2.1	15	12
14	**2**	**7**	935	7.6	1.5	13	5.9
15	**2**	**4**+**7**	935	7.6	2.3	83	22
16	**2**	**5**+**7**	939	7.6	2.7	63	19
17	**3**	**6**	825	9.0	1.6	7.1	2.0
18	**3**	**7**	825	9.0	1.2	2.8	1.2
19	**3**	**6**+**7**	825	9.0	1.7	28	6.6

[a] Ratio of the optical densities of photographic emulsions with a dye and a supersensitiser and with the dye alone. [b] Ratio of the spectral sensitivities of photographic emulsions with a dye and a supersensitiser and with the dye alone. [c] Correction introduced to take into account the intrinsic sensitivity of AgHal (S_{420}); $n = S_{420}(\mathrm{Dy})/S_{420}(\mathrm{Dy+S})$. [d] For experiments *1–3*, the values of *D* are not quoted because they are very low.

It is necessary to deal in greater detail with the effect of supersensitiser compositions. The compositions are responsible for a greater increase in absorption than the individual supersensitisers. This increase is in a number of instances close to the additive value or less than that (Table 1). On the other hand, the increment in additional sensitivity, even after correction for ΔS_{420} is in many instances superadditive, *i.e.* exceeds (sometimes considerably) the sum of the effects due to the individual supersensitisers. Superadditivity is manifested particularly clearly at high values of pAg (pAg 9.0 for dye **2** and pAg 7.6 for dye **1**). Thus the increase in the additional sensitivity greatly exceeds the increment in the absorption by the emulsions. It is striking that the use of compositions consisting of supersensitisers **4**–**6** does not induce a superadditive effect. Such an effect is observed only when these supersensitisers are employed together with the nitrone **7**.

Since the supersensitisers alter only slightly the position of the absorption maximum due to the adsorbed dyes, one may conclude that these compounds hardly affect the positions of the energy levels of the dyes. The existence of a superadditive effect for compositions comprising supersensitisers of two types — adsorbed (compounds **4**–**6**) and weakly adsorbed (compound **7**) on AgHal[99] — constitutes definite evidence for the different mechanisms of the action of these compounds.

Special mention should be made of the fact that the relative quantum yield of the spectral sensitisation (φ_r^{420}) for light-sensitive layers containing the pentacarbocyanine **1** and the **4** + **7** composition (pAg 5.6) in the region of $\lambda = 1000$ nm is 0.14.[5] This value is only a few times smaller than the yields φ_r^{420} for fine-grain photographic materials sensitised towards visible light despite the twofold decrease in the active light quantum.

The superadditive effect of the **4** + **7** and **5** + **7** supersensitiser compositions has been investigated in greater detail on a coarse-grain ($d = 1$ μm) highly sensitive AgBr(I) emulsion sensitised by the pentacarbocyanine **1** at pAg 7.2 and 7.8.[105] The supersensitisation was investigated over a wide range of light-sensitive layer exposure times — 10^2–10^{-11} s. For times of the order of 10^{-5}–10^{-11} s, a YAG : Nd laser with $\lambda = 1060$ nm was used for the exposure, while for times of 5×10^{-2}–1.6×10^2 s the emulsions were exposed in a FSR-41 sensitometer behind an interference light filter with $\lambda = 1050$ nm. The supersensitisation coefficient (*K*) was characterised by the ratio of the spectral sensitivity of the emulsion with the given supersensitiser (or with a supersensitiser composition) to the light sensitivity of the emulsion without supersensitisers. The results of these studies are presented in Table 2.

It follows from Table 2 that the introduction of supersensitisers into spectrally sensitised light-sensitive layers leads to an

Table 2. Dependence of the infrared emulsion supersensitisation effect on the supersensitisers employed and on the duration of exposure.

No. of experiment	Exposure time /s	pAg 7.2				
		K_4	K_5	K_7	K_{4+7}	K_{5+7}
1	1.6×10^2	10	6.0	6.0	33	25
2	9	11	7.0	8.5	50	26
3	5×10^{-2}	16	10	14	120	50
4	10^{-5}	17	7.0	10	100	50
5	1.2×10^{-8}	15	6.0	10	100	50
6	3×10^{-11}	12	4.0	8.5	125	60
7	1.6×10^2	10	10	8.0	70	70
8	9	13	10	12	100	70
9	5×10^{-2}	16	11	14	160	180
10	10^{-5}	16	10	6.0	200	100
11	1.2×10^{-8}	20	12	7.0	250	110
12	3×10^{-11}	17	8.0	4.5	330	170

appreciable increase in sensitivity, but the degree of supersensitisation is different under these conditions: the greatest supersensitisation effect is observed for di-(*p*-anisyl)phenylphosphine **4**. A superadditive effect is characteristic of supersensitiser compositions, especially at pAg 7.8. The highest degree of supersensitisation has been determined for the **4** + **7** composition. It is stiking that the coefficient K changes comparatively little (not more than by a factor of 2–3) over a wide range of exposure times, covering 13 orders of magnitude. This is possible if the supersensitisers have little effect on the primary step of the photochemical reaction and their action is manifested on slower secondary stages of the process involving the formation of the latent photographic image.

The results obtained for mixtures of supersensitisers are of special interest. The coefficients of supersensitisation by compositions greatly exceed the sum of the coefficients for the individual compounds and in certain cases are almost equal to or even exceed the product of the parameters for the individual substances (Table 2). Similar results have been obtained for a monodisperse AgBr(I) emulsion with cubic microcrystals (l = 0.25 m).[76]

As already mentioned, the superadditive effect of compositions may be a consequence of the different mechanisms of the action of the compounds constituting the composition and the fact that in most cases the coefficients are closer to the product than to the sum of the individual parameters can be regarded as a result of the supersensitising effect of the substances in the consecutive stages of the self-desensitisation process presented in Scheme 1. Since compound **7** does not possess a specific affinity for AgHal and is poorly adsorbed on the latter,[99] microcrystals and it most probably inhibits the self-desensitisation in stages *2–4* and *7* by insulating the dye molecules from oxygen and water. Thus its effect is similar to that of evacuation.[23,83] The nitrone is a hydrophobic compound, so that, after its introduction into a water–gelatin emulsion, it can be deposited on the AgHal may generate a kind of shell around them, promoting thereby the removal of oxygen and water from the surface of the crystal. The supersensitising effect of compounds **4**, **5**, and **6** may be associated with the inhibition of stage *1*, *i.e.* when adsorbed on AgHal,[99,100] these compounds may separate the dye from AgHal and hence prevent the capture of electrons. One cannot rule out also a decreased probability of the direct electron transfer from Dy* to the dye in the ground state under the influence of these compounds.[106]

The different effects of supersensitisers are schematically illustrated in Fig. 15, where it is shown that one supersensitiser (S-1) separates the dye from AgHal and the impurity centres formed in the course of chemical sensitisation, whilst the other (S-2) creates a shell insulating the dye from the medium.[5,6]

We shall now consider the result of the effect of the supersensitiser composition assuming that the supersensitisers inhibit the electron loss reactions in two consecutive stages (for example,in stages *1* and *2* of Scheme 1) of the dye self-desensitisation process. The transfer of electrons from AgHal to the desensitiser D (for example to O_2) mediated by the dye is shown schematically in the same Fig. 15. Here f_1 is the designation of the fraction of electrons lost in the presence of the dye, $f_1 f_2$ represents the fraction of electrons lost in the presence of the dye and the supersensitiser S-1 separating the dye from AgHal, $f_1 f_3$ is the fraction of electrons in the presence of the dye and the supersensitiser S-2 separating the dye from the desensitiser D, and $f_1 f_2 f_3$ designates the fraction of electrons in the presence of the dye and the two supersensitisers S-1 + S-2 subject to the condition that the supersensitisers inhibit the loss of electrons in two consecutive stages.

If the light sensitivity of the photographic emulsion (S) is proportional to the number of electrons remaining on AgHal and forming the latent photographic image, then the supersensitisation coefficients can be formulated as follows:

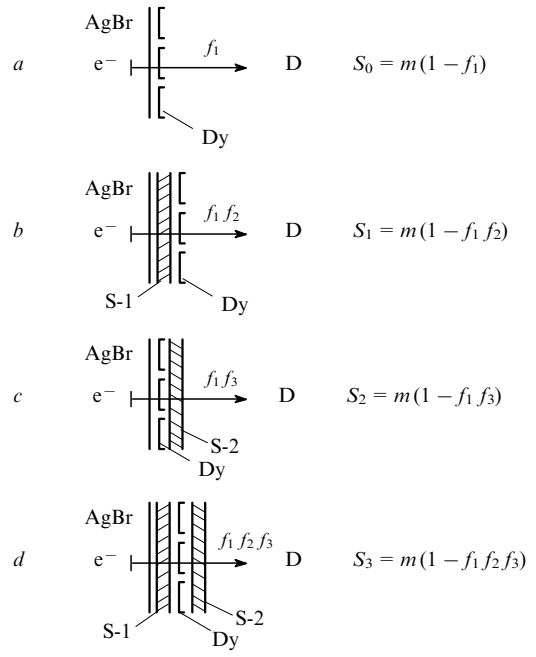


Figure 15. Schematic illustration of the processes involving the supersensitisation of photographic emulsions spectrally sensitised by a dye (*a*), by individual organic supersensitisers S-1 (*b*) and S-2 (*c*), and by the S-1 + S-2 composition (*d*).

$$K_1 = \frac{S_1}{S_0} = \frac{1 - f_1 f_2}{1 - f_1}, \qquad (20)$$

$$K_2 = \frac{S_2}{S_0} = \frac{1 - f_1 f_3}{1 - f_1},$$

$$K_3 = \frac{S_3}{S_0} = \frac{1 - f_1 f_2 f_3}{1 - f_1}.$$

We shall consider several limiting cases:

1. $K_3 = K_1 K_2$.

We find from Eqns (20)

$$K_1 K_2 = \frac{(1 - f_1 f_2)(1 - f_1 f_3)}{(1 - f_1)(1 - f_1)} = \frac{1 - f_1 f_3 - f_1 f_2 + f_1{}^2 f_2 f_3}{(1 - f_1)^2}. \qquad (21)$$

We adjust the quantities $K_1 K_2$ and K_3 to a common denominator:

$$K_3 = \frac{1 - f_1 f_2 f_3 - f_1 + f_1{}^2 f_2 f_3}{(1 - f_1)^2}. \qquad (22)$$

Hence it follows that $K_3 = K_1 K_2$ if $f_2 + f_3 - f_2 f_3 = 1$. This is possible if the coefficients f_2 and f_3 or one of them are close to 1. In the latter case, one of the supersensitisers is appreciably less effective than the other.

2. $K_3 < K_1 K_2$

This case holds if $f_2 + f_3 - f_2 f_3 < 1$ or f_2 and $f_3 < 1$. This is a real case if both supersensitisers are active.

In the most general case where several (i) photosensitisers operate consecutively, we have

$$K_{i(i \to \infty)} = K_{\max} = \frac{1 - f_1 f_2 \cdots f_i}{1 - f_1} = \frac{1}{1 - f_1}, \qquad (23)$$

i.e. the limiting value of the supersensitisation coefficient is determined by f_1. If f_1 = 0.9 then $K_{\max}$ = 10 and, if f_1 = 0.99, we have $K_{\max}$ = 100. The last value is close to those obtained for the **4** + **7** supersensitiser composition at pAg 7.2 (Table 2).

3. $K_3 > K_1K_2$

This case occurs for $f_2 + f_3 - f_2f_3 > 1$ or for f_2 and $f_3 > 1$. It is unrealistic, because the number of electrons lost exceeds the number present initially.

If it is assumed that the light sensitivity of emulsions with the **4** + **7** supersensitisers is close to the limiting value and that the supersensitisation coefficient is close to K_{max}, we arrive at the conclusion that, in emulsions without supersensitisers, only one photoelectron out of the 100 formed ($f_1 = 0.99$) is used to form the latent image. The fact that in a number of instances the coefficient of supersensitisation by compositions exceeds the product of the coefficients for the individual substances may be associated with the change in the absorption of light by the dye under the influence of the supersensitisers. Thus phenomenological examination of the processes involving supersensitisation by mixtures of substances confirms the possibility of their acting in two consecutive stages of the self-desensitisation of dyes.

1. Supersensitisers of the first kind

We shall deal in greater detail with the effect of supersensitisers of the first kind, *i.e.* those adsorbable on AgHal. The adsorption of triarylphosphines on AgHal is undoubtedly associated with the ability of these compounds to form complexes with silver ions *via* the lone pair of $3s^2$ electrons on the phosphorus atom.[107] Thus the adsorption of phosphines in the presence of silver ions on the AgHal surface is apparently associated with the formation of a complex with these ions. On the other hand, in the presence of an excess of Hal^- ions on the AgHal surface, there is a possibility of either the desorption of these ions under the influence of the phosphines or of the adsorption of the phosphine with formation of a complex with the subsurface silver ions (another adsorption model).[100, 109]

In the presence of an excess of halide ions, the surface of microcrystals in AgHal emulsions is known to be negatively charged and at a certain depth under the surface there is a region of a positive space charge generated by the interstitial silver ions.[2] There is a dynamic equilibrium between the surface silver ions and the subsurface interstitial ions. It may be that, when phosphines are introduced into the emulsion, the silver ions are 'drawn' from the region of the subsurface charge to the surface and complexes are formed with these ions.[5]

The interaction of triaryl derivatives of Group V elements having the general formula XAr_3, where X = P, As, or Sb, with the surface of AgHal microcrystals has been investigated by IR spectroscopy and by measuring the ionic conductivity.[110] According to IR and Raman spectra, vibrations ($\nu = 158\ cm^{-1}$) having the same frequency as the vibrations of the $P \rightarrow Ag^+$ bond in the complex $AgBr \cdot PPh_3$ are observed when PPh_3 is adsorbed on AgBr. Spectroscopic data led to the conclusion that the adsorption of the phosphine on AgBr results in the formation of a chemical bond between a surface Ag ion and the phosphorus atom of the PPh_3 molecule. This leads in its turn to a shift of the vibrational frequencies of the C–P bond sensitive to the nature of the complex-forming agent. Similar changes in the IR spectra have been observed also for $AsPh_3$ and $SbPh_3$. The compounds XAr_3 decrease the longitudinal ionic conductivity of sputtered AgBr layers, whereupon a definite relation is observed between the conductivity and stability constants of the silver complexes $AgBr \cdot XAr_3$.[110] Measurements of the ionic conductivity of AgBr(I) emulsion layers by the dielectric loss method have shown that the adsorption of PPh_3 shifts the frequency maximum (f_{max}) on the dielectric loss curve to lower frequencies. Since the conductivity of AgHal is proportional to f_{max} according to Sillars,[111] the observed shift of f_{max} indicates a decrease, following the addition of the phosphine, of the ionic conductivity generated by interstitial silver ions.

When silver complexes are formed on the surface of AgHal microcrystals, the surface charge changes. The interaction of the supersensitiser **4** with AgHal has been investigated by the luminescence method.[108] The adsorption of organic substances on AgHal alters the surface charge, which influences in its turn the mechanism of the luminescence of paired iodine centres. Thus, if the surface charge of the AgBr(I) microcrystals is negative or the surface is uncharged, then, by irradiating an excited specimen with long-wavelength light at 77 K, it is possible to achieve a luminescence flash at the wavelength corresponding to the green luminescence band of the paired iodine centres. On the other hand, if the surface charge is positive by virtue of the excess of silver ions, a flash is not observed. It has been shown[100] that, when di-(*p*-anisyl)phenylphosphine **4** is introduced into a AgBr(I) emulsion prepared using poly(vinyl alcohol) as the binder, the green-band luminescence flash diminishes.

Additional evidence for the influence of the compounds XAr_3 on the surface charge of AgHal microcrystals has been obtained in experiments on a primitive coarse-grain AgBr(I) emulsion without chemical sensitisation.[112] In such emulsions, the subsurface sensitivity exceeds the surface sensitivity as a result of the positive space charge generated by the interstitial silver ions. The introduction of triphenylstibine into the emulsion leads to a sharp increase in the surface sensitivity owing to a redistribution of the surface charge, which is illustrated in Fig. 16. The subsurface sensitivity was determined after the successive etching of layers in a 1% $Na_2S_2O_3$ solution and on developing the specimens (after etching) in a glycine surface developer.

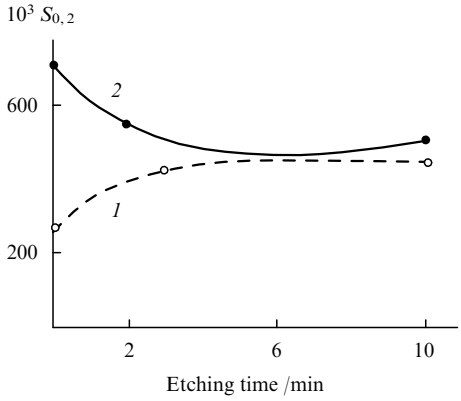


Figure 16. Dependence of the surface and subsurface sensitivity of light-sensitive layers based on a primitive AgBr(I) emulsion without additives (*1*) and containing triphenylstibine (*2*) on the etching time in 1% $Na_2S_2O_3$ solution. Triphenylstibine concentration 5×10^{-4} mol per mole of AgHal. Development — 8 min in a surface glycine developer.

The influence of adsorbed organic compounds on the surface charge has been considered in a number of studies. Thus the change in the sign of the AgHal photo-e.m.f. under the influence of gelatin has been explained[113] by the redistribution of charges on the surface of microcrystals. It has been shown[114] that, under certain conditions, the binding of the interstitial silver ions by the adsorbed gelatin leads to the appearance of a positive charge on the AgBr(I) surface. Tani[115] explained the decrease in the bending of the electron bands of AgHal on the surface by the decrease in the subsurface positive charge under the influence of a series of stabilisers and antifogging substances — derivatives of tetraazaindenes and benzotriazole.

The appearance of a positive charge on the surface of AgHal microcrystals when triarylphosphines are adsorbed promotes the adsorption of infrachromatic dyes, which leads to an increase in the absorption and in the stability of the adsorbed dye, as happens with increase in the concentration of silver ions in the emulsion. This has been demonstrated in relation to the pentacarbocyanine **1** (cf. curves *2* and *4* in Fig. 12*a*). The stability of dye **1** in aqueous gelatin solutions and in the adsorbed state on the AgBr(I) emulsion at different pAg as well as the influence of di-(*p*-anisyl)phenylphosphine **4** on the stability of the adsorbed dye

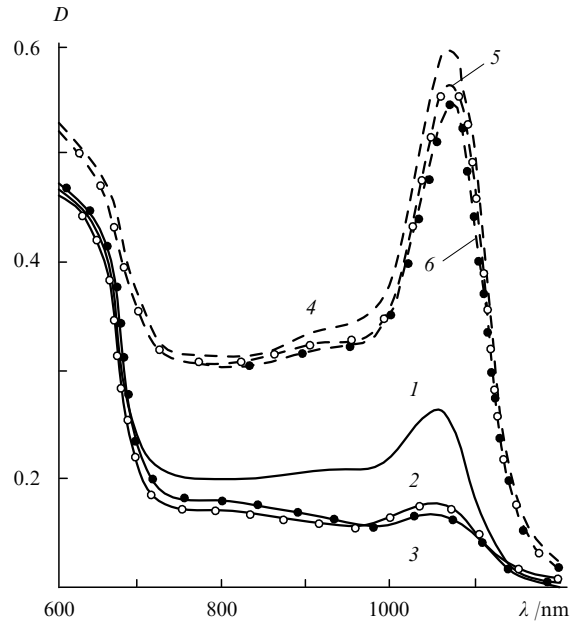


Figure 17. Absorption spectra of the pentacarbocyanine dye **1** in ultrafine-grain AgBr(I) emulsion at pAg 7.6 (*1–3*) and in the presence of supersensitiser **4** (*4–6*) as a function of the period during which the emulsion is allowed to stand at 40 °C: (*1*) and (*4*) after 5 min; (*2*) and (*5*) after 18 min; (*3*) and (*6*) after 30 min. Concentration of dye **1** 2.5×10^{-4} mol per mole of AgHal; concentration of supersensitiser **4** 1×10^{-2} mol per mole of AgHal.

have been investigated in detail.[103] Fig. 17 illustrates the increase in the absorption (cf. curves *1* and *4*) and in the stability of the adsorbed dye **1** (cf. curves *1–3* and *4–6*) under the influence of the phosphine **4**.

The observed bathochromic shift of the absorption of infrachromatic dyes under the influence of phosphines and the increase in the stability of the infrared dye can be accounted for by the formation of a ternary complex between the silver ions, the supersensitiser, and the dye [$Ag^+ \cdot S \cdot Dy$].[5]

It has been shown [110] that, when PAr_3 is adsorbed on AgBr, a new variable-composition organosilver bromide phase of the type $AgBr \cdot PAr_3$ may be formed in addition to the local chemical bond $Ag^+ - P$. Thus the dye may be adsorbed not on AgBr but on the organosilver bromide phase. In any case, both under conditions involving the participation of the ternary complex and on adsorption of the dye on the organosilver bromide phase, a spacer consisting of organosilver complexes is created between AgHal and the dye.

It is noteworthy that the action of phosphines differs from that of Riester's potentiators,[87, 88] which bind the surface silver ions *via* their mercapto-groups in the form of salts and thereby compensate their positive charge. Neutral (from the standpoint of the electrical charge) phosphines only partially compensate the charge of the silver ions in the complex, increasing the overall surface concentration of the silver ions and hence promoting the adsorption of the dye and the interaction of the photoexcited infrared dye with silver ions. The spacer should not prevent electron transfer from Dy* *via* the silver ions to AgHal, but it may inhibit significantly the secondary reactions involving the oxidation of the generated silver atoms by dye molecules in the ground state. Indeed, in the presence of di-(*p*-anisyl)phenylphosphine, the desensitisation of silver halides by infrared dyes diminishes.[102] Such insulation of the strongly fogging infrared dyes from AgHal leads to a sharp diminution in the fogging of infrared emulsions in the presence of triarylphosphine.

It may be expected that the effect of uncharged complex-forming agents examined above is definitely associated with the complex-forming capacity of the silver ions. To test this hypothesis, a study was made of a series of triphenyl derivatives having the general formula XPh_3, where X = N, P, As, Sb, or Bi. The photographic effect of this series of compounds had not been investigated previously on coarse-grain AgBr(I) emulsions sensitised by tricarbocyanine.[116] It has been shown that the maximum supersensitisation effect is attained in the case of triphenylphosphine, which is followed by triphenylarsine and triphenylstibine; triphenylamine and triphenylbismuthine hardly influence the photographic properties of emulsions.

The effect of compounds of the above series has been investigated on an ultrafine-grain AgBr(I) emulsion ($d = 0.05$ μm) sensitised by the pentacarbocyanine **1**.[109] The introduction of these compounds as well as di-(*p*-anisyl)phenylphosphine **4** leads to an increase in the absorption by the adsorbed dye. In terms of their effect, the test compounds can be arranged in the sequence N < Bi < P < As ≈ Sb. The absorption curves for the emulsions are presented in Fig. 18. In conformity with the data of Akhmedzyanov *et al.*,[116] it was established that NPh_3 and $BiPh_3$ do not have a positive photographic effect, whereas PPh_3, $AsPh_3$, and $SbPh_3$ induce an increase in the spectral sensitivity in the long-wavelength band. At pAg 8.6, the supersensitisation coefficients for compounds in the series PPh_3, $AsPh_3$, and $SbPh_3$ are 2.1, 2.9, and 5.8 respectively.

In order to estimate the complex-forming capacities of the

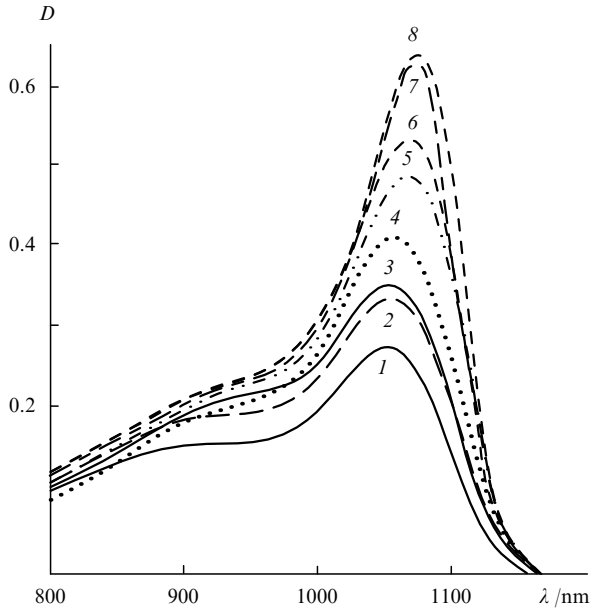


Figure 18. Absorption spectra of ultrafine-grain AgBr(I) emulsion sensitised by dye **1** at pAg 7.6: (*1*) without additives; (*2*) NPh_3; (*3*) additional amount of $AgNO_3$; (*4*) $BiPh_3$; (*5*) PPh_3; (*6*) $P(CH_3OC_6H_4)_2Ph$; (*7*) $SbPh_3$; (*8*) $AsPh_3$. Concentration of dye **1** 3×10^{-4} mol per mole of AgHal; concentration of additives 1×10^{-2} mol per mole of AgHal.

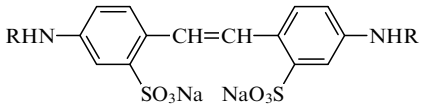
compounds, the changes in the pAg of the emulsions were measured after the introduction into the latter of equal molecular amounts of the above substances (10^{-2} mol per mole of AgHal). The initial pAg 7.6 changed to 7.8, 7.8, 8.5, 8.6 and 8.65 after the addition of NPh_3, $BiPh_3$, PPh_3, $AsPh_3$, and $SbPh_3$ respectively, while the initial pAg 6.6 changed to 6.95, 6.95, 7.9, 7.9, and 8.2. Thus the absence of a photographic effect by NPh_3 and $BiPh_3$ is associated with their weak complex-forming capacity. The compounds $AsPh_3$ and $SbPh_3$ have approximately the same complex-forming capacities in relation to silver ions in solution, but PPh_3 is a stronger complex-forming agent.[117] The observed increase in the supersensitising activity in the series $PPh_3 < AsPh_3 < SbPh_3$ is apparently associated with the different adsorbabilities of these

compounds on AgHal, which are determined by the molecular geometry. Hence it follows that these two properties must be considered jointly.

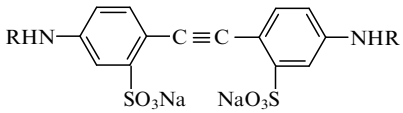
The specificity of the action of the compounds XPh_3 (X = N, P, As, Sb) as well as $(PhC{\equiv}C)_nPPh_{3-n}$ has been attributed [110] to the structure of the surface organosilver bromide complexes. The structure of the complex formed — the stoichiometric composition, the phase state, the type of crystal lattice, and the structure of the electron bands — should determine the effectiveness of the interaction with it of the spectral sensitiser in the ground and photoexcited states. For example, when PPh_3 is adsorbed on a AgBr emulsion with cubic microcrystals at pAg 7.5 and on a coarse-grain AgBr(I) emulsion with cubooctahedral microcrystals at pAg 8.5, two different surface complexes, differing in their IR spectra, are formed. The vibrational frequencies of the *q*-modes in these spectra are close to those of the bond vibrations in the complexes $Ag_2Br_2 \cdot PPh_3$ and $AgBr \cdot PPh_3$ (1099 and 1095 cm^{-1} respectively). On spectral sensitisation at the wavelength corresponding to the absorption band of the infrared dye, a decrease in the intensity of the band with $\nu = 1099$ cm^{-1} is observed, while the band with $\nu = 1095$ cm^{-1} changes little under these conditions.[118] This indicates different photochemical reactivities of the surface complexes.

A similar picture has been observed for supersensitiser **4**. On the basis of Ahrland's data,[117] it was concluded that organosilver complexes may participate in the primary step of the spectral sensitisation by the infrared dye, undergoing photochemical decomposition with formation of a silver atom. Furthermore, the photographic activity of the complexes is manifested in secondary dark stages as a result of the inhibition of the recombination and oxidation reactions of silver atoms.

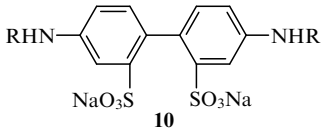
We shall now consider the activity of another supersensitiser of practical importance — the disodium salt of bistriazinylaminostilbene-*o*,*o*′-disulfonic acid **6**. The increase in the adsorbability of dyes under the influence of supersensitiser **6** has been demonstrated [99, 100] and is illustrated in Fig. 19, which presents the isotherms for the adsorption of penta- and tetra-carbocyanines on AgBr powder without a supersensitiser and in the presence of compound **6**. The interaction of a series of derivatives of aromatic diamino-compounds having the general formula RHN–Ar–NHR with cyanine dyes in solutions and on the AgHal surface has been investigated in detail.[119, 120] In order to establish the nature of the interaction of the supersensitisers and spectral sensitisers in adsorption on AgHal, the principal types of interaction were examined in the above studies stage by stage: (1) dye–supersensitiser, (2) supersensitiser–substrate, and (3) dye–supersensitiser–substrate. The following supersensitisers were investigated:



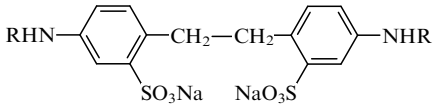
8



9



10



11

The peripheral groups R were 1,3,5-triazinyl and acyl substituents. The studies were carried out on quino-4,4′-cyanines with different lengths of the polymethine chain and also on thiapolycarbocyanine dyes.[121]

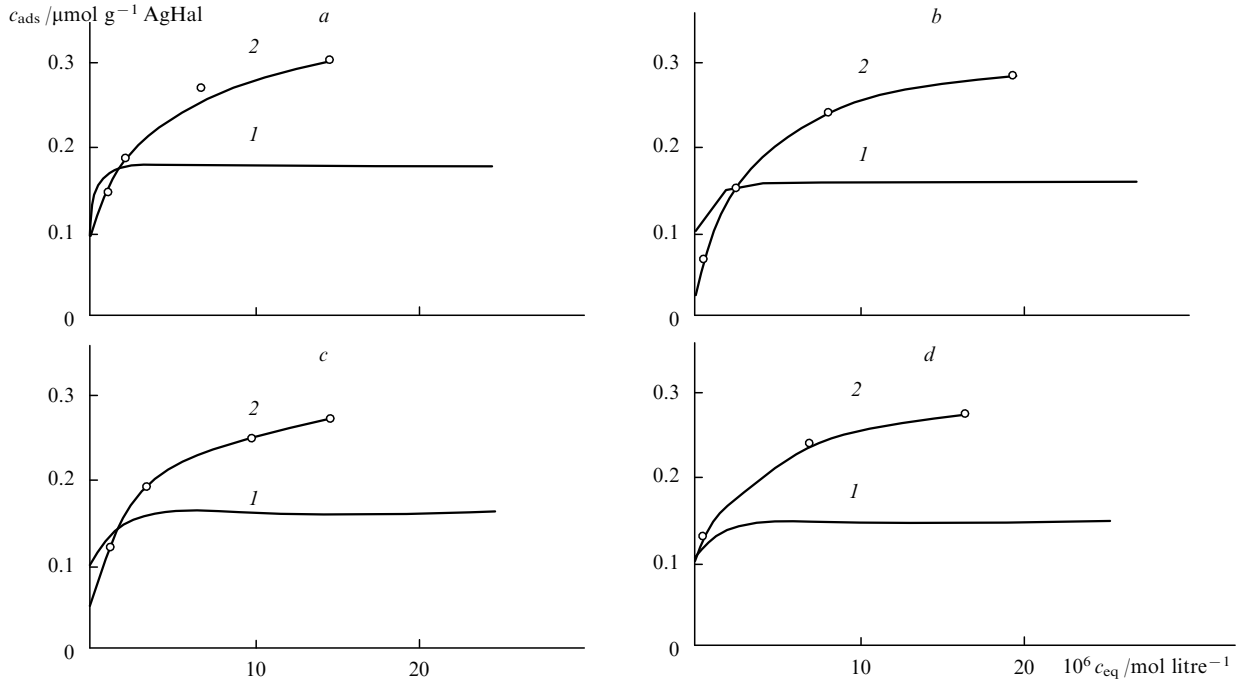


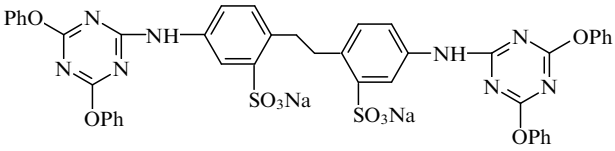
Figure 19. Isotherms for the adsorption of penta- and tetra-carbocyanines on a AgBr preparation from alcoholic solutions (*1*) and after preliminary adsorption of supersensitiser **6** (*2*) at 25 °C; dye: (*a*) 3,3′-diethylthiatetracarbocyanine iodide; (*b*) 3,3′-diethyl-9,11-(β,β-dimethyltrimethylene)thiatetracarbocyanine iodide; (*c*) 3,3′-diethylthiapentacarbocyanine iodide; (*d*) 3,3′-diethyl-9,11,9′,11′-bis(β,β-dimethyltri-methylene)thiapenta-carbocyanine iodide; c_{ads} = amount of adsorbed dye; c_{eq} = equilibrium concentration of dye.

It has been shown [120] that in solutions the interaction in the dye – supersensitiser system is in the nature of the π – π interaction of the two planar systems of the dye and the supersensitiser. A condition for the effective interaction of the π-system of the dye with the π-system of the compound RHN – Ar – NHR is both the presence in the supersensitiser structure of a central π-conjugated Ar skeleton and of auxochromic fragments R capable of π-conjugation with the central skeleton *via* the nitrogen atoms of the amino-groups. A bathochromic shift of the stretching vibrations of the NH groups and also a change in the profile of the absorption bands due to the SO_3^- groups [120] were observed in the IR spectra of supersensitisers adsorbed on AgBr microcrystals. This led to the conclusion that the nature of the adsorption centres is the same: NH and SO_3^- groups. The IR spectra of *p*,*p*′-bis(4,6-diaminophenyl-1,3,5-triazin-2-yl-amino)stilbene-*o*,*o*′-disulfonic acid **6a**, adsorbed on AgBr microcrystals had been obtained earlier [122] in the frequency range 700 – 1700 cm^{-1}.

It was concluded that the test compounds do not form a strong chemical bond with the silver ions. This conclusion was confined by the small influence of supersensitisers of the above type on the ionic conductivity of sputtered AgBr layers.[120]

It has been concluded [120] that the SO_3^- and NH groups participate in the interaction of compounds **8** – **11** with AgHal, the main π-system of the molecules being hardly involved. The interaction *via* the SO_3^- groups should be most probably regarded as the substitution of halide ions on the AgHal surface by $ArSO_3^-$ ions and not as the binding of interstitial or surface silver ions by analogy with the adsorption of compounds of the type of triarylphosphines. One may imagine that, in the adsorption of compound **6**, and similar derivatives, the molecule assumes an orientation such that its aromatic component is separated from AgHal by SO_3^- groups. In the case of compound **6**, the planar π-conjugated part of the molecule is arranged parallel to the AgHal surface and is at a definite distance from the latter. Conventionally this constitutes the 'table on two SO_3^- legs' model. The NH groups can also serve as 'supports'. It is noteworthy that this model resembles the Riester potentiators model.[87, 88]

The observation of the interaction of the nonplanar supersensitiser **12** with the dye on the AgHal surface should be regarded as the most important result of the above study.[120]

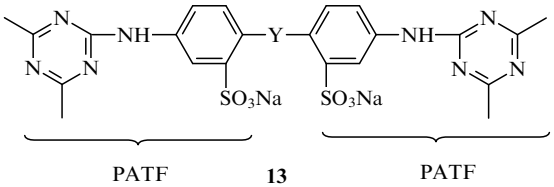


12

Like supersensitisers with π-conjugated aromatic fragments Ar, compound **12** induced a bathochromic shift of the absorption maximum of the adsorbed infrared dyes, an increase in the absorption intensity, and a supersensitisation effect comparable other in magnitude to that of compound **6**. On the other hand, it has been found that compound **12** does not interact with the dye in solution.

In order to account for the photographic activity of this sensitiser and the bathochromic shift of the absorption maximum of the dye, it is necessary to postulate a flattening of the molecule of compound **12** following adsorption on AgHal. Consequently, the situation on AgHal changes significantly compared with that in solution, *i.e.* the π – π interaction between the supersensitiser and the dye becomes possible in the dye – supersensitiser – AgHal ternary system. In this case, a decisive factor for the dye – supersensitiser interaction may be not only (and perhaps not so much) the planarity of the entire molecule of compound **12** but also the geometrical correspondence between certain parts of the two interacting systems. Such a part in the molecule of compound **12** may be the phenylaminotriazinyl fragment (PATF), which interacts with AgHal *via* the SO_3^- and NH groups according to IR spectra.[120]

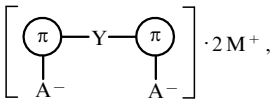
It has been postulated [120] that, in more general terms, a molecule having the following structure should be photographically active:



13

Y = $-(CH=CH)_n-$, $-(C\equiv C)_n-$, $-(CH_2-CH_2)_n-$, where n = 1, 2, 3.

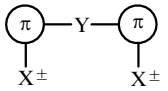
in which the two phenylaminotriazinyl fragments are disposed at a certain distance specified by the bridging group Y. This distance between the two π-systems is apparently in fact the principal factor determining the photographic activity of the supersensitisers. The geometrical requirements which must be met by the supersensitiser may be determined both by the AgHal lattice constant and by the structure of the supersensitising dye. It is probably quite unnecessary that PATF should be the anionic π-fragment. Other compounds can also assume the role of such π-fragments.[5] In a general form, the structure of the supersensitiser can be represented as follows:



14

where A^- is the acid group, π the conjugated system, Y the bridging group, and M^+ the cation. Thus one is dealing with bisanionic structures of supersensitisers consisting of two π-systems with negative charges localised on the acid groups and linked to one another *via* the bridging Y group.

A certain analogy between the supersensitisers of the class under consideration and the bridged bisquaternary salts of heterocyclic bases used for the supersensitisation of orthochromatic and panchromatic dyes, as a rule in the *J*-aggregated state, is striking.[123 – 125] Therefore, continuing the generalisation, one may put forward the hypothesis that there is a single principle underlying the supersensitising activity of bridged compounds containing at least two cationic or anionic fragments:



15

where $X^{\pm}$ is a group with a localised positive or negative charge. The specificity of the activity of particular supersensitisers having structure **15** may be associated with the following structural features of the dyes: (1) the overall charge on the spectral sensitisers (cationic, betaine, anionic), (2) the distribution of the π-charge density in the molecule, (3) the polarisability of the molecule, (4) the electron-donating or electron-accepting capacity of the π-system, *etc.*[120] Since infrared dyes are as a rule used in the form of cations, the suitability of the bisanionic compounds **14** as supersensitisers may be associated with purely electrostatic factors.

The question naturally arises what is the mechanism of the supersensitising activity of the test compounds. The photographic activity of compounds of the given class can apparently be usefully considered within the framework of the insulation model, according to which the supersensitiser creates a 'spacer' of molecular dimensions between the dye and AgHal.[5, 6] This is illustrated conventionally in Fig. 20. The insulation model is in essence similar to Riester's model,[88] but there are also significant differences associated with the mechanism of the interaction in the dye – supersensitiser – AgHal system. The insulating spacer prob-

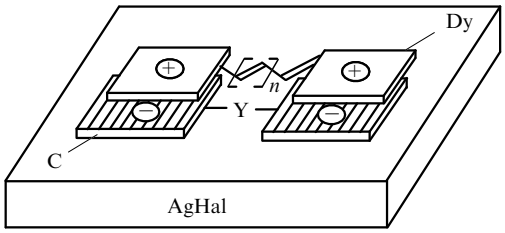
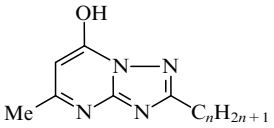


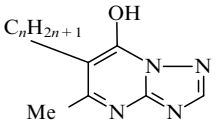
Figure 20. A model of the adsorption of a supersensitiser and dye on AgHal.

ably does not prevent electron transfer from the excited Dy* molecule to AgHal (apparently *via* a tunnelling mechanism), but it does prevent the reverse capture of photoelectrons by the dye radical-cations formed or by neighbouring electron-accepting Dy molecules in the ground state in accordance with Scheme 1.

The activity of the supersensitiser 2-heptyl-4-hydroxy-6-methyl-1,3,3*a*,7-tetraazaindene **5**, which induces an increase in the absorption by the dye adsorbed on AgHal (Fig. 13, Table 1), is caused not only by the presence of the tetraazaindene ring but also to a large extent by the presence of the long (C_7H_{15}) alkyl group. It has been shown [94, 126] that the supersensitising activity of alkyl derivatives of tetraazaindene and 1,2,4-triazole increases with increase in the length of the aIkyl group from C_1 to C_7, *i.e.* with increase in the hydrophobicity of the compounds. The supersensitising activity of 2-alkyl (compound **16**) and 5-alkyl (compound **17**) derivatives of tetraazaindene on emulsions sensitised by thiapenta- and thiatetra-carbocyanines **1** and **2** has been investigated.[127]



16



17

$n = 1-11$.

In the series of compounds investigated, the hydrophobicity increased steadily on passing from C_1 to C_{11} alkyl substituents. The 2-alkyl derivatives **16** showed the greatest photographic activity, especially on emulsions sensitised by the pentacarbocyanine **1**. The results obtained are presented in Fig. 21. The supersensitisation effect increases the spectral sensitivity by a factor of 11. It is striking that an abrupt jump in the effectiveness of the sensitisation is observed on passing from $n = 4$ to $n = 6$. On further increase in the length of alkyl group from $n = 6$ to $n = 11$, the effectiveness changes little.

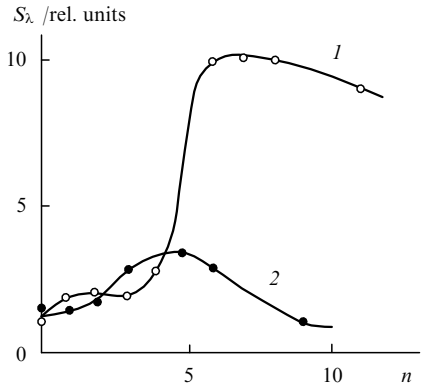


Figure 21. Dependence of the spectral sensitivity of photographic emulsions sensitised by the thiapentacarbocyanine **1** on the number of carbon atoms in the alkyl groups of compound **16** (*1*) and **17** (*2*).

The effectiveness of 5-alkylated derivatives **17** is appreciably smaller than that of compound **16** (cf. curves *2* and *1* in Fig. 21). The increase in the spectral sensitivity of emulsions with the tetracarbocyanine **2** is smaller than for emulsions with the pentacarbocyanine **1**, but the nature of the activity of the supersensitisers remains the same.[127] The supersensitisation by compounds **16** and **17** can be partly due to the increase in the adsorbability of the supersensitisers with increase in the length of the alkyl substituent, which has been observed, for example, for a series of *N*-alkyl derivatives of cations.[2] Comparison of the results obtained for 2- and 5-alkyl derivatives of tetraazaindene permits the conclusion that the photographic activity of supersensitisers is determined not only by their hydrophobicity but also by the disposition of the hydrophobic groups in the molecule. It is also possible that the higher photographic activity of the 2-alkyl derivative **16** is associated with the location of the alkyl substituents at the photographically active fragment of the molecule.[127]

The mechanism of the action of supersensitisers of the first kind, *i.e.* those absorbable on AgHal, has been investigated in model electrochemical experiments. The inhibition of electron transfer to oxygen and protons by supersensitisers has been demonstrated extremely clearly in experiments designed to investigate the influence of these compounds on the polarographic oxygen reduction waves in aqueous alcoholic media.[128] In this case, the mercury dropping electrode and not photoexcited silver halide served as the source of electrons for oxygen. Under the usual conditions, in aqueous media, oxygen is reduced at the mercury electrode to hydrogen peroxide in accordance with Scheme 2.[129]

Scheme 2

$$O_2 + e^- \overset{(1)}{\rightleftharpoons} O_2^{-\cdot} + H^+ \overset{(2)}{\rightleftharpoons} HO_2^{\cdot} + e^- \overset{(3)}{\rightleftharpoons}$$
$$\rightleftharpoons HO_2^- + H^+ \overset{(4)}{\rightleftharpoons} H_2O_2 .$$

Under these conditions, the reversibility of stages *1–3* depends on the pH of the medium. It was shown that the introduction of di-(*p*-anisyl)phenylphosphine **4** into the solution shifts the half-wave oxygen reduction potential towards more negative values and diminishes the height of the wave (cf. curves *1* and *3* in Fig. 22). The shift of the wave is caused by the inhibition of electron transfer in stage *1* (Scheme 2) owing to the formation on the electrode of an insulating film preventing electron transfer to oxygen. Calculation of the electron transfer rate constant showed that, in the presence of the phosphine **4**,the rate of transfer diminishes by a factor of 3000. Compound **5** induces a smaller effect. In its presence, the rate falls by a factor of 400 (cf. curves *2* and *3* in Fig. 22).

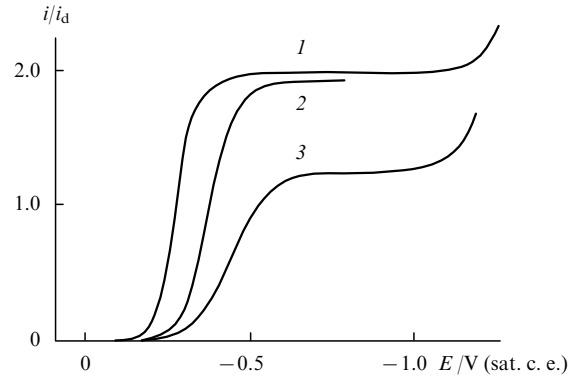


Figure 22. Polarographic curves for the reduction of oxygen in an air-saturated aqueous propanol solution at pH 13.0: (*1*) without supersensitiser; (*2*) with supersensitiser **5**; (*3*) with supersensitiser **4**. Concentration of supersensitisers 6.2×10^{-4} mol per mole of AgHal.

The decrease in wave height in the presence of the phosphine **4** down to virtually the one-electron value is associated with the inhibition of stage *2* by the insulating film. Oxygen is then reduced to $O_2^{-\cdot}$ and not to hydrogen peroxide. The effect of the phosphine **5** is smaller in this stage than that of the phosphine **4**. In terms of their inhibiting effect on electron transfer and the inhibition of the protonation of $O_2^{-\cdot}$, the supersensitisers XPh_3 (X = P, As, Sb) may be arranged in the sequence [128] $SbPh_3 > AsPh_3 > PPh_3$. The average ratio of the pore area in a film comprising the compounds XPh_3 on the electrode to the area occupied by one molecule is 0.30, 0.32, and 0.42 for $SbPh_3$, $AsPh_3$, and PPh_3 respectively, *i.e.* the density of the insulating film diminishes in the sequence $SbPh_3 > AsPh_3 > PPh_3$. Thus the functions of certain supersensitisers of the first kind involve not only the creation of an 'insulating spacer' but also the formation of a hydrophobic spacer inhibiting secondary processes involving water protons.

2. Supersensitisers of the second kind

We shall now proceed to the consideration of supersensitisers of the second kind, *i.e.* compounds which are poorly adsorbable on AgHal and the activity of which is apparently associated mainly with their hydrophobic nature. The secondary oxidation reactions with participation of oxygen and water in stages *2–4* and *7* (Scheme 1) are in fact inhibited precisely because of the hydrophobic nature of the supersensitisers. The activity of *C*,*N*-diphenylnitrone **7**, which supersensitises infrared light-sensitive layers both individually and in compositions with supersensitisers of the first kind, has already been considered above. The supersensitising effect of nitrones was discovered in 1975 at the State Research and Design Institute of the Chemical-Photographic Industry (GOSNIIKhIMFOTOProekt). *C*,*N*-Diphenylnitrone is weakly adsorbed on AgBr.[99] According to IR spectroscopic data (in the frequency range 400–4000 cm^{-1}), no changes are observed in the vibrational spectrum of the nitrone **7** after its adsorption on AgBr.[76] The weak interaction of nitrones with AgHal is also indicated by their small influence on the ionic conductivity of AgBr emulsions.[76]

In order to test experimentally whether organic hydrophobic compounds do really inhibit reactions involving electron loss by silver halide, a study was made of the influence of a series of substances (*C*,*N*-diphenylnitrone, azobenzene, azoxybenzene) on the luminescence of spectrally sensitised AgBr microcrystals.[130] If such compounds are able to insulate the surface of the emulsion microcrystals from interaction with oxygen and water, then one may expect an increase in the concentration of electrons in the conduction band and on the surface capture levels and hence an increase in the intensity of the low-temperature luminescence of microcrystals and dyes, arising on recombination of electrons with the holes of AgHal and the dyes respectively.

Measurements of the low-temperature (77 K) luminescence of a fine-grain AgBr emulsion have been carried out with excitation by light corresponding to the region of the intrinsic absorption by AgBr (λ = 365 nm). Fig. 23*a* presents the luminescence spectra of the emulsion before and after the introduction of solutions of the nitrone **7**. It follows from the results presented in the figure that the nitrone **7** increases the intensity of the orange luminescence of the AgBr microcrystals. Furthermore, the intensity of the optical luminescence flash, stimulated by infrared light, increases. Similar results have been obtained for azobenzene and azoxybenzene.

It is striking that the increment in the luminescence intensity under the influence of the supersensitisers investigated corresponds to an increase in the photographic activity of the compounds. Thus the facts described agree with the hypothesis that hydrophobic substances on the surface of emulsion microcrystals prevent the liberation of photoelectrons into the medium and hence increase the intensity of the recombination luminescence and the light sum localised in deep traps.

The fluorescence and phosphorescence bands of the dyes are observed in the luminescence spectra of silver bromide emulsions sensitised by thiacarbocyanines and thiadicarbocyanines: with

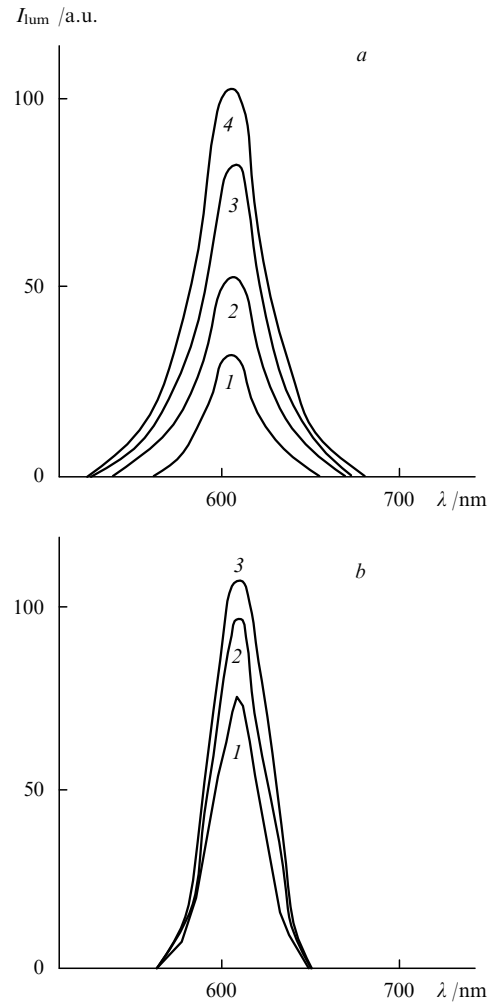
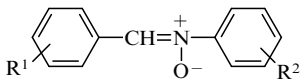


Figure 23. Luminescence spectra of a AgBr emulsion: (*a*) before (*1*) and after (*2–4*) introduction of compound **7** at different concentrations (10^{-3} mol per mole of AgHal) (*2*) 1; (*3*) 5; (*4*) 10; (*b*) before (*1*) and after the introduction of azobenzene (*2*) and azoxybenzene (*3*) at a concentration of 10^{-3} mol per mole of AgHal.

λ_{max} = 615 and 740 nm in the former case and with λ_{max} = 770 and 900 nm in the latter. The luminescence appears as a result of the recombination of free electrons with holes localised by dye molecules. As was to be expected, the addition of the nitrone **7** to spectrally sensitised emulsions leads to an increase in the intensity of the low-temperature recombination luminescence, which is due to a sharp decrease in the probability of the capture of photoelectrons by molecular oxygen and moisture.[130]

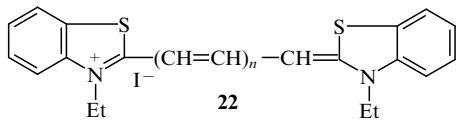
Akhmerov *et al.*[131] investigated in detail by luminescence and photographic methods the activity of nitrones having the general formula



7, **18** – **21**

R^1 = H, R^2 = H (**7**); R^1 = *o*-Cl, R^2 = H (**18**); R^1 = H, R^2 = *p*-Me (**19**); R^1 = *p*-OMe, R^2 = *p*-Me (**20**); R^1 = *o*-Cl, R^2 = *p*-Me (**21**).

The studies were performed on a fine-grain AgBr emulsion spectrally sensitised by thiapolycarbocyanines **22** with different lengths (*n*) of the polymethine chain.



22

The activity of the nitrones was compared with their hydrophobicity estimated from the partition coefficients (K_{part}) of the substances in the 1-octanol – water two-phase system.[127] A correlation between the hydrophobicity of the nitrones and their ability to increase the intensity of the low-temperature luminescence of AgBr and the dyes was demonstrated. Fig. 24 presents the dependence of the intensity (μ_1) of the orange luminescence of AgBr on the hydrophobicity of the nitrones. The luminescence intensity increases with increase in hydrophobicity. Fig. 25 illustrates the dependence of the effectiveness of the activity of nitrones on the length of the polymethine chain of the thiapolycarbocyanines **22**. For all the nitrones, an increase in the intensity of the luminescence of the dyes (μ_2) with increase in chain length is observed, the effectiveness of the nitrones being greater the greater their hydrophobicity (cf. curves *1*–*4* in Fig. 25). The figure also illustrates the effect of the supersensitisation (Δ lg S_λ) of the light-sensitive layers with thiapolycarbocyanines by the nitrone **21** (curve *5* in Fig. 25). The results can be accounted for within the framework of Scheme 1 by the self-desensitisation of the dyes. Indeed, with increase in the length of the polymethine chain of the dyes, their vacant level under the AgBr conduction band becomes deeper and hence there is an increase in the probability of electron capture in stage *1* of Scheme 1. The effectiveness of the insulating spacer, which prevents electron transfer from $Dy^{-\cdot}$ to oxygen and the water protons, should therefore increase with increase in the length of the polymethine chain, which agrees with experimental results. The increase in effectiveness with increasing hydrophobicity of the compounds can also be explained within the framework of the supersensitisation scheme examined above.

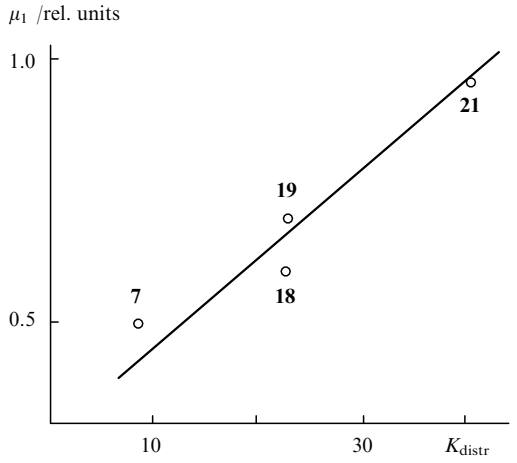


Figure 24. Dependence of the intensity of the orange luminescence of a AgBr emulsion on the hydrophobicity of the nitrones **7**, **18**, **19**, and **21**. Concentration of nitrones — 3×10^{-3} mol per mole of AgHal. $\mu_1 = (I-I_0)/I_0$ (I_0 and I are the intensities of the AgBr luminescence in the absence and presence of the nitrone respectively).

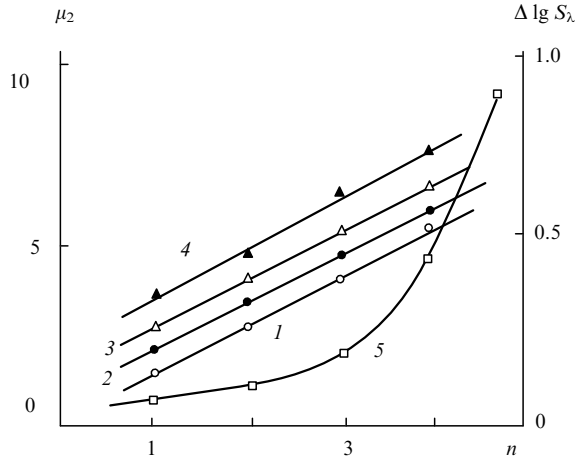


Figure 25. Dependence of the intensity of the luminescence of dyes (*1*–*4*) and of the increase in spectral sensitivity (*5*) for a AgBr emulsion sensitised by thiapolycarbocyanines **22** after the introduction of the nitrones **18**–**21** [(*1*) **18**; (*2*) **19**; (*3*) **20**; (*4*) **21**] on the length (n) of the polymethine chain of the dyes. Concentration of dyes — 5×10^{-5} mol per mole of AgHal; concentration of nitrones — 3×10^{-3} mol per mole of AgHal. $\mu_2 = (I-I_0)/I_0$ (I_0 and I are the intensities of the fluorescence of the dyes at the maximum in the absence and presence of a nitrone respectively); $\Delta\lg S_\lambda = \lg(S_\lambda/S_\lambda^0)$ (S_λ^0 and S_λ are the spectral sensitivities in the absence and presence of a nitrone respectively).

The hydrophobic properties of nitrones are manifested by a shift of the polarographic half-wave reduction potential of oxygen and also by a decrease in wave height (Fig. 26).[128] The increase in the hydrophobicity of the nitrones, associated with the introduction of chlorine atoms into the benzene ring, is accompanied by the inhibition of electron transfer to the oxygen and the protonation of $O_2^{-\cdot}$. In terms of its influence on the inhibition of the electron transfer from the electrode to the oxygen, the nitrone **21** is close to di-(*p*-anisyl)phenylphosphine **4**, while in terms of the inhibition of the protonation of $O_2^{-\cdot}$ it is 2.5 times more effective than the latter.[128]

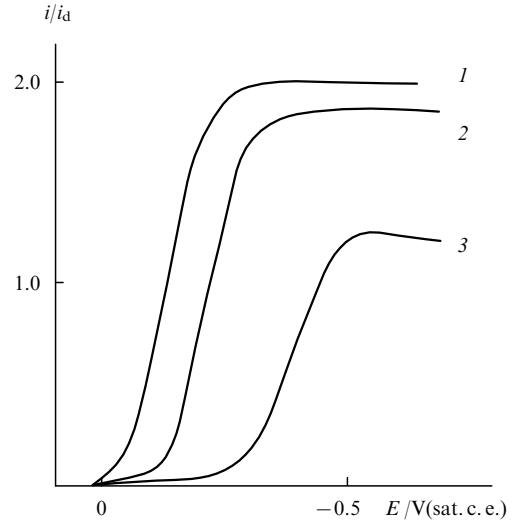


Figure 26. Polarographic curves for the reduction of oxygen in an air-saturated 10% aqueous propanol solution at pH 11.0; (*1*) without supersensitiser; (*2*) with the nitrone **7**; (*3*) with the nitrone **21**. Concentration of supersensitisers — 6.2×10^{-4} mol per mole of AgHal.

According to Scheme 1, the probability of the dye self-desensitisation processes increases with increase in the concentration of the electron-accepting dye and in its electron affinity. The effectiveness of the supersensitisation by nitrones inhibiting the loss of photoelectrons should therefore also increase with increasing concentration of the dye and of its affinity. Fig. 27 presents the dependence of the supersensitisation coefficients (K_s) on the dye concentration for photographic emulsion6 sensitised by the thiapentacarbocyanine **1** and containing the supersensitiser **4** of the first kind and its compositions with supersensitisers of the second kind — the nitrones **7** and **21**.[76] According to Fig. 27, with increase in the concentration of the dye **1** the supersensitisation effect produced by the phosphine **4** diminishes (straight line *1*),

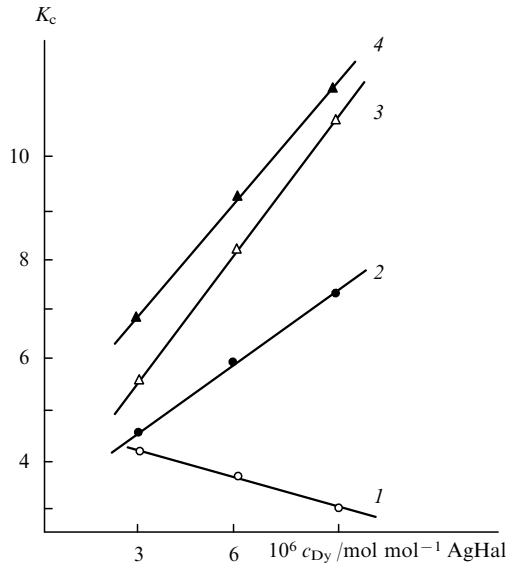
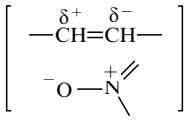


Figure 27. Dependence of the coefficient of the supersensitisation of photographic emulsions sensitised by the thiapentacarbocyanine **1** and containing supersensitisers **4** (*1*), **4** + **7** (*2*, *3*),and **4** + **21** (*4*) on the dye concentration. Concentrations of supersensitisers (mol per mole of AgHal): 9×10^{-4} of compound **4**, 5×10^{-3} (*2*) and 1×10^{-2} (*3*) of compound **7**, and 2.5×10^{-3} of compound **21**.

while that by the additionally introduced nitrone **7** (or **21**) actually increases (straight lines *2*–*4*). This clearly demonstrates the difference between the mechanisms of the supersensitisation by the two types of substances.

The photographic activity of nitrones has been attributed [132] to a certain combination in its molecule of the hydrophobic aryl rings and the polar oxyazamethine group. Calculations showed [133] that the length of the N–O bond (1.406 Å) is close to that of the C–C bond in the polymethine chain of cyanines; this makes possible quadrupole interactions of the type



with the alternating charges of the chain. As a result of such interaction, part of the polymethine chain of the dye may be insulated by the nitrone from oxygen and water.

The acceleration of the regression of the latent image centres by the molecules of infrared dyes in the ground state in conformity with Scheme 1 (Fig. 10) was already examined above. It is essential to emphasise that stable latent image centres (LIC), consisting of at least four (or more) silver atoms and formed in the course of the exposure of the light-sensitive layers, are oxidised in model investigations whereas in a real spectral sensitisation process mainly silver atoms with a low stability (precentres of the latent image) are oxidised in the course of the desensitisation. Nevertheless, model studies are useful for discovering the general rules governing the oxidation of silver particles.

The influence of supersensitisers on the regression of LIC has been investigated on a monodisperse AgBr(I) emulsion with sulfur sensitisation.[76, 132] The activity of supersensitisers of the first kind (compounds **4** and **6**) and second kind (compound **7**) and of their compositions has been investigated. Fig. 28 presents curves for the regression of LIC, characterising the variation of the intrinsic (S_i) and spectral (S_λ) sensitivity of photographic emulsions at 35 °C and 100% humidity. According to the results, the phosphine **4** retards somewhat the decrease in S_i and S_λ for the light-sensitive layers (curves *1* and *2* in Figs 28*a* and 28*b*). A similar picture is observed in the presence of supersensitiser **6** (cf. curves *1* and *3*). It is striking that the hydrophobic compound (the nitrone **7**) inhibits the regression of LIC to a greater extent than compounds **4** and **6**. Special mention should be made of the considerable decrease in the degree of regression (by a factor of 7–10) in the presence of a composition comprising supersensitisers of the first kind (compound **4**) and second kind (compound **7**) (cf. curves *1*–*4* and *5* in Figs 28*a* and 28*b*). Thus model studies on the regression of LIC agree with the hypothesis that oxidation reactions involving dyes in the ground state are inhibited by supersensitisers of the first and second kind.

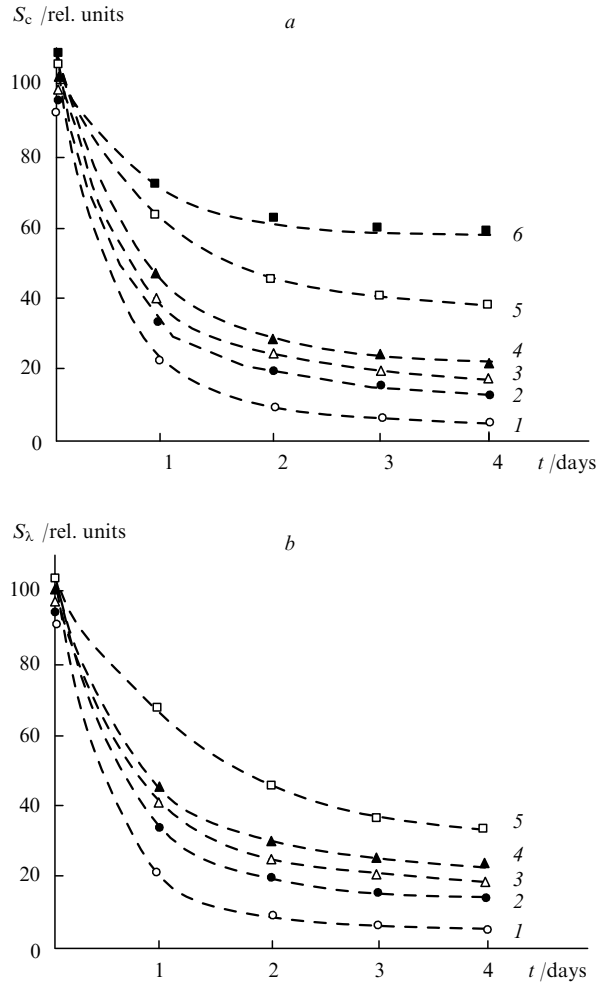


Figure 28. Variation of the intrinsic (S_i) (*a*) and spectral (S_λ) (*b*) sensitivities of photographic emulsions sensitised by the thiacarbocyanine **1** individually and in the presence of supersensitisers at 35 °C and 100% humidity: (*1*) dye **1**; (*2*) **4** + **1**; (*3*) **6** + **1**; (*4*) **1** + **7**; (*5*) **4** + **1** + **7**; (*6*) without a dye. Dye concentration 18×10^{-6} mol per mole of AgHal; concentrations of supersensitisers (mol per mole of AgHal): 3×10^{-4} of compound **4**, 5×10^{-3} of compound **6**, and 1×10^{-2} of compound **7**.

The method involving the evacuation of photographic emulsions before exposure [134] has been used [76] to obtain additional experimental proof of the role of oxygen and moisture in dye self-desensitisation processes and also of the inhibiting influence of supersensitisers on these secondary processes. As was to be expected, on exposure *in vacuo* of a photographic emulsion sensitised by the thiapentacarbocyanine **1**, the spectral sensitivity of the emulsion increased by a factor of 2.7 (Table 3), while after the admission of air it fell again and virtually reached the initial value.

A supersensitiser of the first kind (compound **4**) increased the spectral sensitivity of an emulsion of this type by a factor of 4. On

Table 3. The influence of evacuation on the photographic sensitivity of infrared emulsions (pAg 7.6).

Exposure conditions	S_λ(**1**)	D_0(**1**)	S_λ(**4**+**1**)	D_0(**4**+**1**)	S_λ(**1**+**7**)	D_0(**1**+**7**)	S_λ(**4**+**1**+**7**)	$D_{0(4+1+7)}$
Before evacuation	1.0	0.35	4.0	0.25	5.0	0.48	11.0	0.35
In vacuo	2.7	0.25	6.0	0.30	7.5	0.60	11.0	0.35
After admission of air	1.2	0.38	4.5	0.25	6.0	0.60	11.5	0.50

Note. The values of S_λ behind a KS-14 light filter are quoted in relative units based on the criterion of density $D = D_0 + 0.85$.

evacuation of emulsions, S_λ increased by a further factor of 1.5 and on subsequent admission of air it fell and virtually attained the initial value. The nitrone **7** also induced an increase in spectral sensitivity (by a factor of 5). It is striking that the joint activity of supersensitisers **4** and **7** exceeded the influence of evacuation. Thus their activity is not restricted solely to the inhibition of the reactions with oxygen and water. However, on exposure of evacuated light-sensitive layers containing the nitrone, their sensitivity nevertheless increased by a further factor of 1.5. This result as well as the decrease in S_λ for light-sensitive layers with supersensitiser **7** after the admission of air apparently indicate the incomplete inhibition of secondary reactions with participation of oxygen and water by the nitrone **7**.

Attention should be drawn to the fact that neither evacuation nor the introduction of individual supersensitisers ensured the maximum increment in the light sensitivity of photographic emulsions. A superadditive increase in the spectral sensitivity of an emulsion was attained only when supersensitisers **4** and **7** were employed jointly. There was then no evacuation effect. Thus the experimental data presented confirmed the hypothesis that oxygen and moisture influence the self-desensitisation reactions of electron-accepting dyes and indicate the ability of supersensitisers to inhibit secondary reactions involving oxygen and water protons.

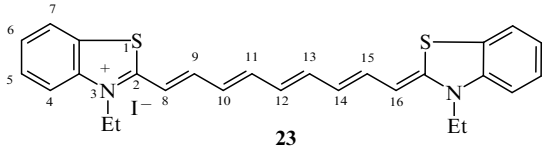
Whereas the greater influence on S_λ compared with evacuation, in the case of the supersensitiser of the first kind **4** can be accounted for by the formation of a 'spacer' between the dye and AgHal, which effectively inhibits the self-desensitisation reactions in stage *1* of Scheme 1, another explanation is possible for nitrones.

In experiments on the regression of the latent image during the storage of exposed specimens with *C*,*N*-diphenylnitrone at an elevated temperature and humidity, the appearance of a sensitometric wedge on the undeveloped emulsions has been observed.[76, 132] The formation of visual densities is definite evidence for the occurrence of processes involving the intensification of the latent image. Thus the nitrone has a reducing function. The nitrone **7** belongs itself to the class of compounds which are difficult to oxidise, but its hydrolysis product — phenylhydroxylamine — has reducing properties. A 'reductive' mechanism, involving the latensification of the latent image, can therefore be considered as a variant of the supersensitising activity of nitrones. This results in a decrease in the probability of stage *1* (Scheme 1). The supersensitisation of infrared photographic materials by reductants has been discussed.[135, 136] According to the authors of these publications, the infrared dye is oxidised on the surface of AgHal to radical-cations, which intensify the desensitisation processes by electron capture. The reductant (for example, ascorbic acid) reduces the radical-cations to the dye, promoting a decrease in desensitisation.

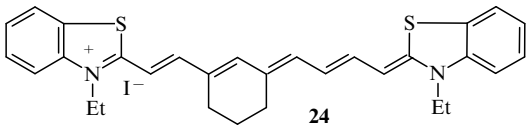
When secondary chemical dye self-desensitisation chemical processes are considered, attention is concentrated on the inhibition of stages *1*–*5* (Scheme 1). The recombination reactions of the electrons captured by the dye and oxygen with the dye holes (stages *6* and *7*) have been examined to a significantly lesser extent. On the other hand, the recombination processes can also contribute to the self-desensitisation of dyes. It may be that the role of supersensitisers of the first and second kind consists also in the inhibition of the recombination processes. In particular the reducing function of nitrones may involve the acceptance of a dye hole and hence the inhibition of stages *6* and *7* (Scheme 1), *i.e.* nitrones or their hydrolysis products can function in accordance with Gilman's hole capture mechanism.[82] The difference between the approaches of the present author and Lenhard *et al.*[135] to the 'reductive' mechanism of supersensitisation concerns only the question of the origin of the infrared dye radical-cations; thus Muenter [135] believes that the radical-cations are formed in a dark process during the oxidation of the dye on the AgHal surface, whereas the present author believes that it occurs during the spectral sensitisation photochemical reaction.

VI. Self-supersensitisation of infrared dyes

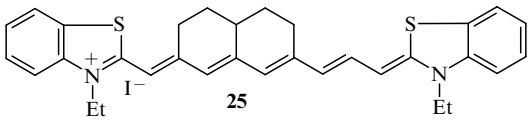
Infrachromatic dyes with saturated cyclic groups in the polymethine chains belong [137, 138] to the class of highly effective spectral sensitisers. The photographic effectiveness of such dyes has been attributed in a number of studies [139–141] to hydrophobic protection by the saturated cyclic groups of the polymethine chain of the dyes against oxygen and water protons. The increase in the photographic activity of the infrachromatic dyes as hydrophobic alkyl groups accumulate in the chain has been demonstrated in relation to the thiatetracarbocyanines **23**–**26**.[139, 141]



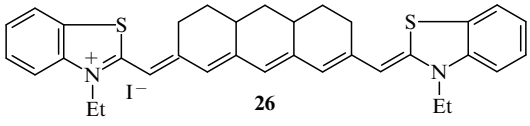
23



24



25



26

Table 4 presents results obtained on a monodisperse AgBr(I) emulsion with cubic microcrystals ($l = 0.27$ μm). The photographic activity of cyanines has been studied both individually and in the presence of supersensitisers of the first (the phosphine **4**) and second (the nitrone **7**) kind . The spectral (S_λ) and intrinsic (S_i) sensitivities of the photographic emulsions are quoted in relative units. The sensitivity of the emulsion without a dye has been adopted as unit S_i, whilst the sensitivity of photographic emulsions sensitised by dye **23** unsubstituted in the chain adopted as unit S_λ.

Table 4. The influence of the cyclic groups in the polymethine chain of thiatetracarbocyanines on the effectiveness of spectral sensitisation.

No. of experiment	Supersensitiser + dye	S_λ(KS-14)	S_i (S3S-22)
1	Unsensitised emulsion	–	1.0
2	**23**	1.0	0.3
3	**4** + **23**	2.0	0.4
4	**4** + **23** + **7**	3.5	0.5
5	**24**	2.0	0.4
6	**4** + **24**	5.0	0.45
7	**4** + **24** + **7**	7.0	0.55
8	**25**	4.0	0.5
9	**4** + **25**	10.5	0.55
10	**4** + **25** + **7**	20	0.6
11	**26**	6.0	0.5
12	**4** + **26**	18	0.6
13	**4** + **26** + **7**	40	0.6

Note. The values of S_λ and S_i have been obtained at pAg 7.4 from the criterion of density $D = D_0 + 0.85$ at a colour temperature of the light source of 2850 K.

It follows from Table 4 that, with increase in the number of cyclic groups in the polymethine chain of the dyes from one (dye **24**) to two (dye **25**) and three (dye **26**), the spectral sensitivity due to the individual dye increases relative to the unsubstituted thiatetracarbocyanine **23** by factors of 2, 4, and 6 respectively (cf. experiments *2*, *5*, *8*, and *11* in Table 4). The desensitising activity of the dyes diminishes in the same series of compounds (by a factor of 1.1–2.0) (cf. the values of S_i obtained in experiments *2*, *5*, *8*, and *11*). It is striking that the influence of cyclic groups on S_λ is significantly greater than on S_i.

The introduction of the supersensitiser of the first kind **4** promotes an increase in the spectral sensitivity of emulsions, which becomes more marked as cyclic groups accumulate in the chain (cf. the values of S_λ obtained in experiments *3*, *6*, *9*, and *12* in Table 4), as a result of which the sensitivity of the emulsions with the **26** + **4** composition exceeds by a factor of 18 the sensitivity of those with the thiatetracarbocyanine **23** alone. Under the same conditions, the intrinsic sensitivity increases only by a factor of 2. The supersensitising activity of the nitrone **7** is also determined by the number of hydrogenated bridges in the polymethine chain and reaches a maximum for dye **26** with three rings. Similar results have been obtained also on emulsions with the supersensitiser of the first kind **6**.[141] The regular features of the influence of cyclic groups in the chain are retained in the series of substituted thiapentacarbocyanines.[132, 141] The greater influence of supersensitisers and cyclic groups on S_λ than on S_i confirms the difference, already discussed, between the dye desensitisation and self-desensitisation processes. According to the data presented, the supersensitising activity of cyclic groups in the dye chains is retained also in emulsions containing the supersensitisers of the first kind **4** and **6**, which themselves reduce the self-desensitisation of dyes as a consequence of the insulation of the latter from AgHal and promote thereby a more effective manifestation of the inhibiting activity of the hydrophobic saturated rings. The additional increase in spectral sensitivity in the presence of the hydrophobic supersensitiser of the second kind **7** can also be accounted for by the increase in the protective functions of the hydrophobic bridging groups in the presence of *C*,*N*-diphenylnitrone. The hydrophobic nitrone probably insulates additionally from oxygen and water the part of the dye chain which is not protected by the cyclic groups. This can explain the increase in the effectiveness of the nitrone as rings accumulate in the chain, because the hydrophobic protective effects are then, as it were,added together. A contribution by the 'reductive' mechanism is possible.

It has been suggested [132, 141] that the photographic activity of dyes with bridging groups should be manifested when the groups are in those positions in the polymethine chain where there is an excess π-electron density of the dye molecule which has captured an electron (in $Dy^{-\cdot}$). The probability of electron transfer to oxygen is a maximum at precisely these sites. When these sites are shielded by saturated groups, which hinder the approach of oxygen and especially water molecules, the probability of the dye self-desensitisation reactions should diminish. According to the molecular diagram (Fig. 29) of the distribution of π-electron density, constructed on the basis of LCAO MO quantum-chemical calculations in the Hückel approximation, the excess electron density in $Dy^{-\cdot}$ is concentrated in the 9-, 11-, 13-, and 15-positions in the polymethine chain of the thiatetracarbocyanine. Indeed, the introduction of two or three hydrogenated bridges at sites with the highest -electron density (the 9-, 11-, and 13-positions for dye **25** and the 9-, 11-, 13-, and 15-positions for dye **26**) leads to a significant increase in the spectral sensitivity of the photographic emulsions. The value of S_λ for photographic emulsions with dye **24**, containing a saturated excess group in other positions in the chain (10, 12), where there is no excess electron density, is greater by a factor of 2 than for emulsions with the unsubstituted dye **23**. Presumably in this case the hydrophobic protection by the cyclic group extends not only to the sites to which it is attached but also to the neighbouring 11-position.

The distribution of π-electron density in the thiapentacarbocyanine molecule is also illustrated in Fig. 29. The highest π-electron density in $Dy^{-\cdot}$ is concentrated in the 9-, 11-, 13-, 15-, and 17-positions in the outer polymethine chain. According to experimental data,[132, 141] the introduction of the β,β-dimethyltri-

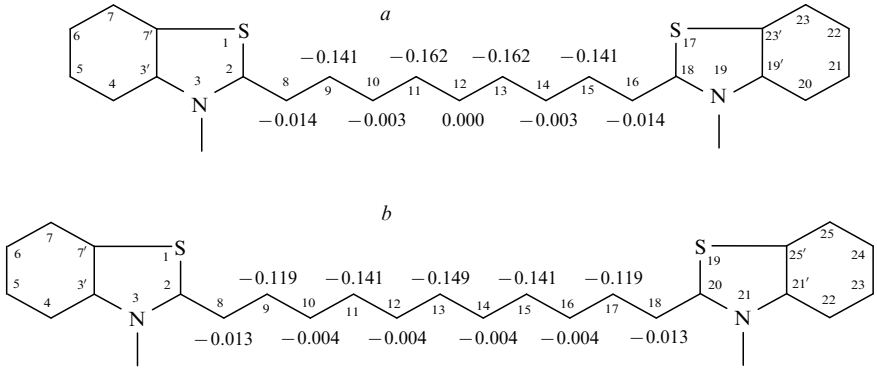


Figure 29. Molecular diagrams for the distribution of π-electron density in the polymethine chain of thiatetracarbocyanine (*a*) and thiapentacarbocyanine (*b*).

methylene hydrophobic bridges in the 9- and 11-positions and in the 9-, 11-, 15-, and 17-positions (dye **1**) also increases the photographic activity of these dyes in the presence of supersensitisers compared with the thiapentacarbocyanine unsubstituted in the chain.

It is striking that cyclic bridging groups in the chains of thiatetra- and thiapentacarbocyanines decrease the catalytic effect of the dyes on the oxidation of latent image centres, *i.e.* the regression of LIC at elevated temperatures and humidities. Fig. 30 presents data taken from Mikheeva [132] for the thiatetracarbocyanines **23**–**26**. The decrease in catalytic activity with increase in the number of rings in the chain is associated with the hydrophobic protection of the chain, already discussed, and hence with the inhibition of the reactions presented in Scheme 1. Thus, if it is assumed on the basis of the results that cyclic groups do indeed play the role of the hydrophobic protectors of the chain, one may speak of a new phenomenon — the self-supersensitisation of infrared dyes under the influence of saturated bridging groups.[141] It is essential to note that one is dealing with the self-supersensitiaation of dyes different from that considered by Collier,[142] according to which the self-supersensitisation of *J*-aggregates of dyes is effected by dyes in the molecular form *via* the hole-acceptance mechanism.

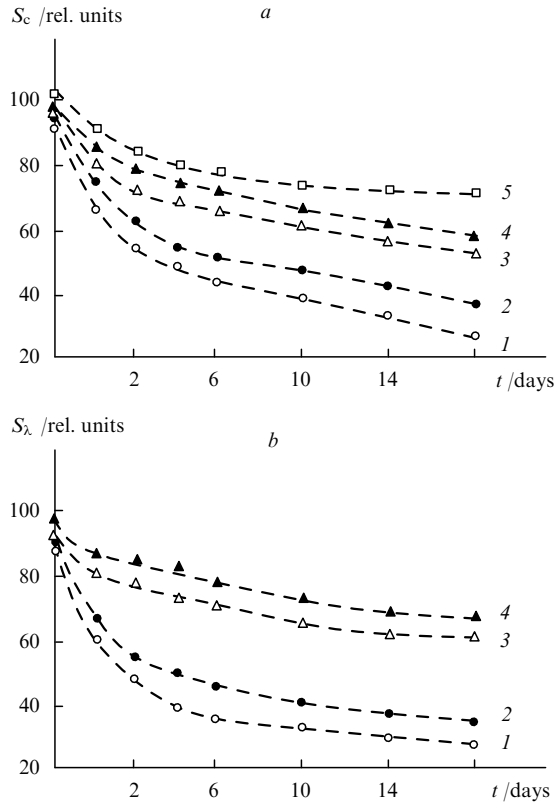


Figure 30. Variation of the intrinsic (S_i) (*a*) and spectral (S_λ) (*b*) sensitivities of photographic emulsions sensitised by the thiatetracarbocyanines **23** (*1*), **24** (*2*), **25** (**3**), and **26** (*4*) and of photographic emulsions without a dye (*5*) (28 °C, 78% humidity).

VII. Conclusion

The data examined indicate convincingly that the secondary chemical oxidation processes, or, in photographic terminology, the desensitisation processes play a very important role in the establishment of the sensitivity of infrared photographic materials. The desensitisation in the region of absorption by the dye (self-desensitisation) then exceeds the desensitisation in the region of absorption by the silver halide. The self-desensitisation can actually determine the effectiveness of the spectral sensitisation itself. The oxidative mechanisms and the kinetics of the self-desensitisation processes are determined by the positions of the energy levels of the dyes relative to the energy bands of AgHal and also relative to the local surface levels.

It is striking that the infrared dye may play the role of an oxidation catalyst in the secondary processes. In a general sense, the vacant molecular orbitals of π-conjugated systems such as the molecules of polymethine dyes can therefore participate in the catalysis of the oxidation reactions of photographically active species. The role of oxygen and water protons is very important in these processes. To use a picturesque expression, one may say that the infrared photographic material, as it were, 'breathes' after photoexcitation. The silver atoms (the latent image precentres) are burnt up in the oxidative flame blown up by the infrared dye itself.

The supersensitisation processes reduce to a large extent to the inhibition of the secondary self-desensitisation reactions, *i.e.* the inhibition of the oxidation reactions of the products of the primary photochemical reaction. The ways in which oxidative processes are inhibited can be extremely diverse. They are determined both by the properties of the spectral sensitisers and by the type of the emulsion, so that the supersensitisers may be compounds with significantly different properties. There is a possibility of the self-supersensitisation of dyes as a result of the introduction into their molecular structure of self-desensitisation inhibitors. For example, dyes with the polymethine chain 'protected' to the maximum extent are promising. This can be achieved either by introducing hydrophobic substituents into the chain or by the 'truncation' of the outer polymethine chain when part of the chromophore chain is incorporated in heterocyclic rings. The use of various supersensitisers and their mixtures makes it possible,in principle,to eliminate fully the secondary oxidative processes and to approach thereby the limiting relative quantum yield of the spectral sensitisation. The greatest increment in spectral photosensitivity should then be expected for infrared photographic materials with a sensitisation zone longer than 1000 nm. Indeed, the effectiveness of the spectral sensitisation in the IR region with $\lambda \approx 1000$ nm has been increased by a factor of 100 and made to approach the values for the visible region of the spectrum [5, 102] despite the fact that the level of the photoexcited electron in the thiapentacarbocyanine, used as the spectral sensitiser, is located approximately 0.7 eV deeper than the bottom of the AgBr conduction band.

One should note that the problem of the effectiveness of the spectral sensitisation of the direct positive process, based on the oxidation of pregenerated silver centres, is diametrically opposite to the problem of the effectiveness of the negative process already considered. Whereas in negative emulsions one is dealing with the inhibition of secondary oxidation reactions, in direct positive emulsions the supersensitisation is actually associated with the acceleration (promotion) of secondary oxidation reactions. In order to accelerate the oxidation of silver by dye holes, it is necessary either to introduce additional hole-transferring agents or to create conditions for the preferential adsorption of dyes on the centres containing silver particles which catalyse the development. Oxidative hole processes may intensify when the infrared dyes form extended *J*-aggregates. The formation of infrared dye *J*-aggregates on AgHal has been observed.[143, 144] The promotion of electron capture reactions requires catalysis of electron transfer to oxygen and the water protons with the aid of additionally introduced electron-accepting compounds. Questions concerning the supersensitisation of direct positive emulsions have been examined, for example, by Belous *et al.*[145] and Steiger and Reber.[146]

In conclusion, attention must be drawn to the following factor. In previous studies on spectral sensitisation, attention was concentrated on the primary spectral sensitisation step, on the effectiveness of which the effectiveness of the entire spectral

sensitisation process was assumed to depend. On the other hand, the effectiveness of the primary step was considered from physical standpoints, namely from the standpoint of the relation between the electronic levels of the photoexcited dyes and the electron bands of AgHal. Although secondary reactions were also taken into account in this approach, a secondary role was nevertheless attributed to them, *i.e.* their influence depended significantly on the probability of the primary process. On the other hand, in the chemical approach discussed here, the most important role in the establishment of the photographic parameters of the process is assigned to the secondary reactions. The primary spectral sensitisation step is treated as a surface oxidation-reduction reaction of the photoexcited dye with the silver ions,[147] which is virtually equally probable for the majority of the adsorbed dyes. Thus the problem of spectral sensitisation may be transferred from the class of 'purely physical' problems to the class of chemical problems, reducing to the search for effective ways of the inhibition, or, conversely, the promotion of the secondary oxidation reactions. The new chemical approaches have made it possible to expand the region of spectral sensitisation approximately to 1500 nm.[147]

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