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Aggregates of cyanine dyes: photographic problems

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Abstract. The aggregation of cyanine dyes on the surfaces of AgHal microcrystals is examined. It is shown that the photochemical activity of the aggregates in processes involving the spectral sensitisation of photographic materials is determined to a large extent by the occurrence of secondary dark reactions in which photoelectrons recombine with dye holes—the so called type II dye self-desensitisation processes. The inhibition of the self-desensitisation of dyes increases the effectiveness of the spectral sensitisation, i.e. leads to supersensitisation. The principal mechanisms of the supersensitisation of photographic emulsions are discussed. The bibliography includes 149 references.

I. Introduction

The history of more than a century of the development of the spectral sensitisation of silver halides (AgHal) has led to a definite selection of the cyanine dyes used to sensitise AgHal in the visible and infrared ranges of the spectrum. *J*-Aggregating dyes, which make it possible to attain the highest level of additional photosensitivity, are nowadays as a rule generally used for the spectral sensitisation of colour and black and white photographic materials. The phenomenon of the aggregation of cyanine dyes is a striking example of the self-organisation of matter. It was discovered by Jelley[1] and Scheiber,[2] although the first observations apparently date back to an earlier period.[3] They showed that an increase in the concentration of solutions of the dyes displaces the absorption maximum towards shorter wavelengths (*H*-aggregation) or shifts it sharply towards longer wavelengths (*J*-aggregation). The anomalously large (up to 90–100 nm) bathochromic shift of the absorption and sensitisation of certain dyes adsorbed on silver halides, which are characteristic of thiacarbocyanines with substituents in the *meso*-position in the chain, were classified in 1939 by Schwarz as sensitisation of the second kind.[4] Numerous communications and reviews (see, for example, Refs 3–7) have been devoted to the phenomenon of the aggregation of dyes and the influence on the latter by the substrate, by the structure of the dyes, and by a series of emulsion factors and also to problems of the structure and properties of the aggregates themselves.

The *J*-aggregation of dyes on the surface of microcrystals of silver halides is by itself a necessary but not a sufficient condition for their high photographic effectiveness. Many satisfactory *J*-aggregating dyes are relatively ineffective under certain emulsion conditions. Here a characteristic feature is that there is no unambiguous relation between the energy levels of the dyes forming part of the aggregate and the sensitising effect of the *J*-states. This is illustrated in Fig. 1 (see over), which presents the absorption and spectral sensitivity distribution curves for photolayers sensitised by four cyanine dyes forming *J*-aggregates with close absorption maxima of the *J*-bands. The convention adopted in the literature[7] is that the energy levels of the dyes (Dy) are characterised by the polarographic half-wave oxidation and reduction potentials. The potential $E_{1/2}^{Ox}$ represents the energy of the highest occupied electronic level of the dye (ε_{ho}), while $E_{1/2}^{Red}$ reflects the energy of the lowest unoccupied (ε_{lu}) level from which the photoelectron is transferred to AgHal. It is assumed that for effective spectral sensitisers the ε_{lu} level of the dye should be higher than or close to the bottom of the conductivity band of AgHal.[7] On the electrochemical scale, the potential at the bottom of the conductivity band (E_{cb}^{0}) of silver bromide is -1.1 V [relative to the normal hydrogen electrode (rel. n.h.e.)] or -1.34 V [relative to the normal calomel electrode (rel. n.c.e.)].[8] The potential of the top of the valence band (E_{vb}^{0}) = 1.5 V (rel. n.h.e.) or 1.26 V (rel. n.c.e.).[8]

It follows from Fig. 1 (curves *2* and *3*, Fig. 1*b*) that the photographic effectiveness, characterised by the logarithm of the spectral sensitivity (lg S_λ) is significantly different for the two imidacarbocyanines of similar structure. Whereas 2-[3-(5-chloro-1,3-diethyl-2,3-dihydrobenzimidazol-2-ylidene)prop-1-enyl]-5-chloro-1,3-diethylbenzimidazolium iodide **1** ($E_{1/2}^{Ox}$ = 0.55 V and $E_{1/2}^{Red}$ = -1.73 V rel. n.c.e. in methanol) is relatively ineffective, 2-[3-(5,6-dichloro-1,3-diethyl-2,3-dihydrobenzimidazol-2-ylidene)prop-1-enyl]-5,6-dichloro-1,3-diethylbenzimidazolium iodide **2** ($E_{1/2}^{Ox}$ = 0.60 V, $E_{1/2}^{Red}$ = -1.58 V) is highly effective, although the difference between the potentials is comparatively small ($\Delta E_{1/2}^{Ox}$ = 0.05 V, $\Delta E_{1/2}^{Red}$ = 0.15 V). The ε_{lu} levels lie above the bottom of the conductivity band (-1.34 V) for both dyes. The sharply reduced activity of the *J*-aggregate of 2-(1-ethyl-1,2-dihydroquinolin-2-ylidenemethyl)-1-ethylquinolinium iodide **3** (curve *1*, Fig. 1*b*) might seemingly be attributed to the deeper location of the ε_{ho} and ε_{lu} levels ($E_{1/2}^{Ox}$ = 0.99 V, $E_{1/2}^{Red}$ = -1.04 V) relative to the levels of compound **2** and primarily to the higher value of $E_{1/2}^{Ox}$ ($\Delta E_{1/2}^{Ox}$ = 0.39 V). However, 2-[3-(3-ethyl-5-phenyl-2,3-dihydrobenzoxazol-2-ylidene)-2-ethylprop-1-enyl]-3-ethyl-5-

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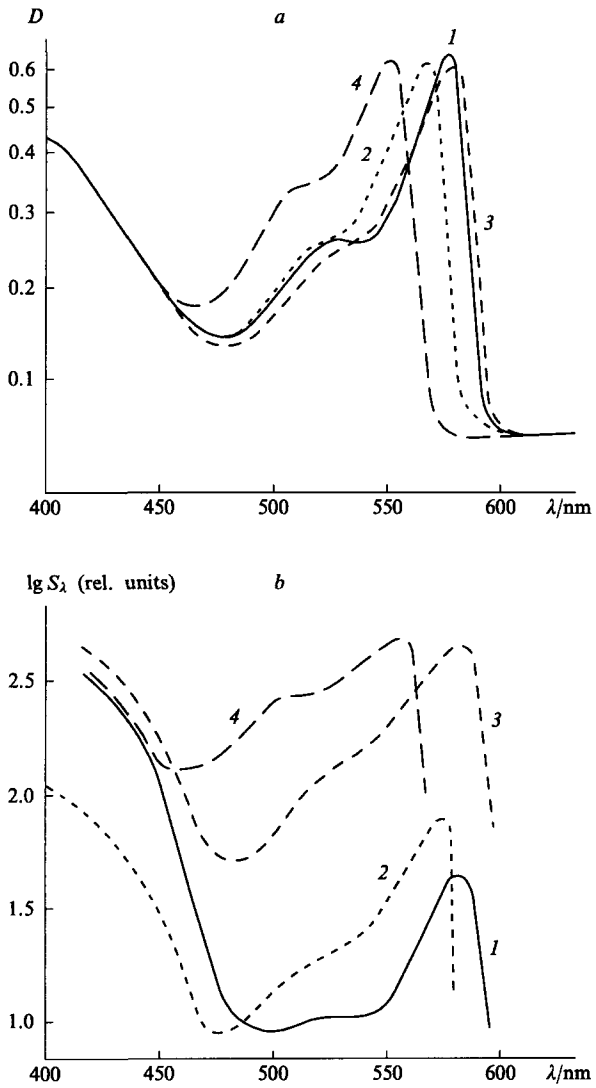
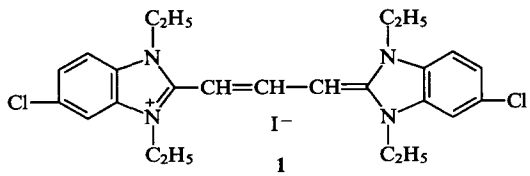
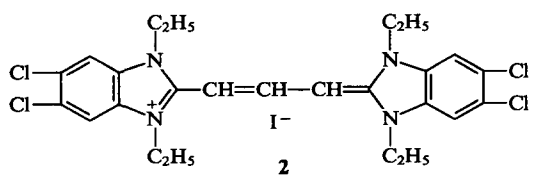
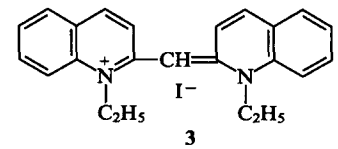


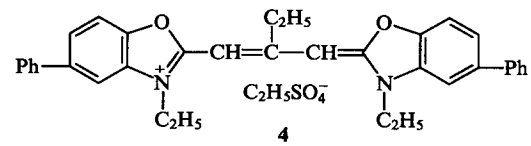
Figure 1. Reflection spectra (*a*) and spectral sensitivity curves (*b*) for the AgBr emulsion [cubic crystals, l = 0.17 μm, (S + Au)-sensitisation] sensitised by dyes **3** (curve *1*), **1** (curve *2*), **2** (curve *3*), and **4** (curve *4*); concentration of dyes — 2 × 10^{-4} mol (mol AgBr)$^{-1}$.

phenylbenzoxazolium ethyl sulfate **4** with $E_{1/2}^{Ox}$ = 0.93 V, which is close to the potential of compound **3**, and with $E_{1/2}^{Red}$ = −1.33 V, which is less negative than for compound **2**, is just as highly effective as compound **2** (curve *4*, Fig. 1*b*). On these grounds, one may conclude that the energetics of the molecules forming part of the *J*-aggregate is not the principal limiting factor.









The absence of a correlation between the photographic activity of cyanine dyes and the positions of their energy levels is apparently due to the following cause. The spectral sensitisation process takes place on the surface of the AgHal microcrystal where the dye is adsorbed. Impurity centres (IC), formed during the chemical sensitisation of the photographic emulsion, are located on the same surface. They play an extremely important role in the separation of the photogenerated charges — photoelectrons and photoholes. The capture of photoelectrons by the impurity centres is in essence the first stage of the formation of the latent photographic image. However, when problems of spectral sensitisation are discussed, as a rule processes in the dye–AgHal binary systems are considered. On the other hand, the real processes include a third important component of the system — the impurity centres which can accept both photoelectrons and holes. The interaction of dyes with impurity centres may be the cause of the secondary reactions which diminish the photographic sensitivity — the so called AgHal desensitisation processes. Methods for the supersensitisation of photographic materials are used to suppress these processes.

The influence of additionally introduced organic compounds — the supersensitisers (S) — on the photographic process in the region where the dye *J*-aggregates absorb is well known (see the relevant reviews [7–13]). The use of supersensitisers has made it possible to increase sharply the photographic activity of a series of *J*-aggregating dyes, frequently without change in the absorption bands of the sensitisers. As will be shown below, because of this the effectiveness of dyes **1**–**4** considered may be made virtually identical. The first publications on supersensitisation date back to 1920 when Bloch and Renwick [14] demonstrated the appreciable supersensitising effect of auramine on layers sensitised by different cyanines. More detailed studies, which led to the formulation of a series of supersensitisation mechanisms, were carried out by West and Carroll, [15] Scheibe and coworkers, [16,17] Bird, Rosenoff, Zuckerman, et al., [18–21] Riester, [22,23] Gilman, [10,24] and other investigators. [10–13] West and Carroll [15] noted that the role of the supersensitiser consists in creating a trap for the exciton formed on photoexcitation of the *J*-aggregate and moving towards the latter at a high rate. The capture of the exciton results in an increase in the probability of its decomposition and of the transfer of a photoelectron to AgHal. According to the ideas of Brunner and coworkers, [16,17] in the supersensitisation step the excitation energy is transferred from the dye to the supersensitiser, the longer lifetime of the excited (triplet) state of which is in fact responsible for the greater probability of the energy transfer to AgHal. Zuckerman and coworkers [18–21] examined the hypothesis that the dye aggregates are broken up with the aid of the supersensitiser molecules, as a result of which the antisensitiser, incorporated in the *J*-aggregate and diminishing the effectiveness of the dye, is localised in small regions of the aggregate and its deactivating effect on the photoexcited state of the entire dye *J*-aggregate (Dy_J^*) is reduced thereby. The separation of the dye from AgHal with the aid of the supersensitiser constitutes the basis of Riester's adsorption model. [22,23] The formation of a layer of supersensitiser (potentiator) molecules between the dye and AgHal promotes, according to Riester, [22,23]

a more effective energy or electron transfer from the photoexcited dye Dy* to AgHal, particularly as a result of the decrease in the contribution by recombination processes.

According to Gilman,[10,24] the supersensitiser, which is a more readily oxidisable compound, captures from the dye a hole formed on photoexcitation of the *J*-aggregate and on photo-transfer of an electron from Dy* to AgHal. There is then a possibility of electron transfer from the supersensitiser to the Dy* molecule (to the ε_{ho} level of the dye liberated on photoexcitation), with formation of the radical-anion $Dy^{-\cdot}$, or to the radical-cation $Dy^{+\cdot}$ (arising after the transfer of an electron to AgHal) with regeneration of the dye. In the first case, the effectiveness of the spectral sensitisation increases by virtue of the higher level of the electron in $Dy^{-\cdot}$ compared with Dy* and in the second it increases as a result of the decrease in the probability of the recombination of electrons with the holes of the dye ($Dy^{+\cdot}$). The above mechanisms have been examined in greater detail in other reviews.[7-13]

It is striking that in the world literature there is no single approach to the supersensitisation processes and the mechanisms discussed are specific to the given case and sometimes contradictory and they are not always justified experimentally. Gilman's hole capture mechanism is most justified for *J*-aggregating dyes, but it is subject to a series of exceptions which will be discussed below. It is essential to note that studies involving the supersensitisation and desensitisation of silver halides by dyes were largely uncoordinated for a long time.

A generalised chemical concept concerning the spectral sensitisation processes has been described in a series of studies by the present author.[8,25,26] According to this concept, the effectiveness of the sensitisation is determined by secondary dark dye desensitisation reactions, whilst the supersensitisation of photographic materials inhibits these processes. The kinetics of the desensitisation processes, which depend on supersensitisers to a greater extent than the energetics of the sensitiser levels, limit the photographic activity of the dye. The main task of the present review is therefore to examine systematically the relation between the processes involving the desensitisation of silver halide emulsions by *J*-aggregates of dyes and the inhibition of these processes by organic compounds of different nature. New approaches to the problem of the effectiveness of spectral sensitisation are also considered.

II. Desensitising effect of *J*-aggregates

Desensitisation is understood as a decrease in the intrinsic (blue) photosensitivity of silver halides under the influence of the adsorbed dye. The desensitisation of AgHal is known to be induced by dyes with a low electron affinity ($E_{1/2}^{Red} < -1.0$ V).[7,27] The desensitisation by such dyes (type II desensitisation) takes place via a mechanism involving the capture of a hole from AgHal.[7,28-36] The dye radical-cations thus produced can serve as centres for recombination with photoelectrons, which are thereby prevented from creating a latent image. This process was first examined by Carroll[37] and Saunders et al.[38] The degree of desensitisation increases as a rule with increase in the dye concentration and is particularly characteristic of dyes adsorbed as polymolecular *J*-aggregates.[7] A hole from the dye moving through the aggregate can reach the electron capture centre and can recombine with a captured electron or even oxidise the silver in the latent image. The type II desensitisation may be represented schematically in the form of the following sequence of reactions:[27]

$$AgHal + h\nu_b \longrightarrow [AgHal]^* \quad (1)$$

$$[AgHal]^* + Dy \longrightarrow [AgHal]^- + Dy^{+\cdot} \quad (2)$$

$$[AgHal]^- + Ag^+ \longrightarrow [AgHal/Ag^0] \quad (3)$$

$$[AgHal]^- + Dy^{+\cdot} \longrightarrow [AgHal] + Dy \quad (4)$$

$$[AgHal/Ag^0] + Dy^{+\cdot} \longrightarrow [AgHal/Ag^+] + Dy. \quad (5)$$

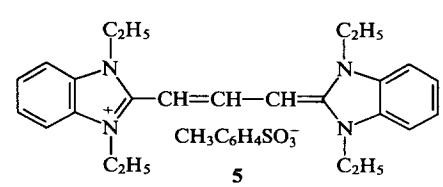
According to the above scheme, the silver halide photoexcited by a 'blue' light quantum ($h\nu_b$) oxidises the dye to the radical-cation $Dy^{+\cdot}$ (the convention that this is referred to as the dye hole may be adopted), which competes with silver ions for the capture of a photoelectron [stages (3) and (4)] or oxidises [stage (5)] the silver of the latent image formed in stage (3).

The desensitisation via the hole mechanism requires that the highest occupied electronic level of the dye ε_{ho} should lie above the top of the valence band (VB) of AgHal. Since the ε_{ho} level may be characterised by the polarographic potential $E_{1/2}^{Ox}$, it would seem that a relationship should be observed between the type II desensitisation and $E_{1/2}^{Ox}$ for dyes. Unfortunately, the dependence of the degree of desensitisation on $E_{1/2}^{Ox}$ for dyes has been investigated to a much lesser extent than its dependence on the reduction potentials $E_{1/2}^{Red}$. This is due to the fact that, for the *J*-aggregating dyes, which desensitise emulsions to the maximum extent (particularly monodisperse emulsions with sulfur sensitisation), the measured potentials $E_{1/2}^{Ox}$ (in solution in the molecular state) do not always characterise adequately the ε_{ho} level of the aggregate.

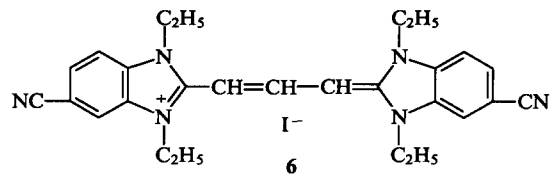
Leubner[39,40] showed that dyes having $E_{1/2}^{Ox} < 0.95$ V actually increase the intrinsic sensitivity of emulsions at low concentrations by accepting holes from AgHal. Only on raising the concentration of the dyes is desensitisation observed.[40] The increase in the sensitivity of fine-grain emulsions under the influence of dyes in the molecular state with $E_{1/2}^{Ox} \leqslant 0.76$ V (rel. n.c.e.) has also been demonstrated in other studies.[41,42] Tani[43] investigated the dependence of the desensitisation on the calculated value of ε_{ho} for a series of dyes. It was found that, with increase in the ε_{ho} level, the degree of desensitisation increases. It is striking that for dyes in which ε_{ho} lies 0.3 eV above the top of the valence band of AgHal not only is desensitisation observed but an EPR signal appears, which the author attributes to the dye radical-cation formed on excitation of AgHal [stage (2)]. These conclusions concerning the position of ε_{ho} relative to the AgHal valence band are not unambiguous because the dyes investigated were adsorbed in different states (in the molecular state *M* and in the aggregated states *H* and *J*), while the calculations of ε_{ho} were performed for molecular forms of the dyes. Another study by Tani was devoted to the exchange of holes between the dye and the valence band of AgHal.[44]

It is essential to note that the hole desensitisation is determined to a large extent by the topography of the centres formed on chemical sensitisation. For example, emulsions with bulk-phase chemical sensitisation[45,46] or emulsions containing Ir^{3+} ions in the bulk of the microcrystals[40] are desensitised by *J*-aggregating dyes to a lesser extent than by the surface sensitivity centres. The influence of oxygen on the type II desensitisation is not quite so unambiguous as for electron-accepting dyes.[7]

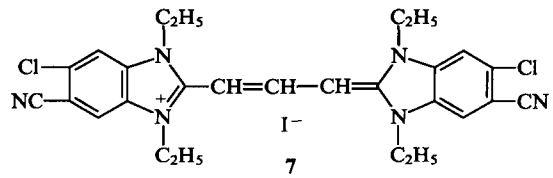
In order to determine the dependence of the type II desensitisation on the structure of the dyes and on their oxidation-reduction potentials (in the first place $E_{1/2}^{Ox}$), a systematic study has been made[47-49] of the influence on photosensitivity by four types of dyes with a low electron affinity ($E_{1/2}^{Red} < -1.0$ V): imidacarbocyanines, thiacarbocyanines, oxacarbocyanines, and quino-2-monomethinecyanines. Dyes **1**–**4** and **5**–**17**, the structures of which are presented below, were investigated.



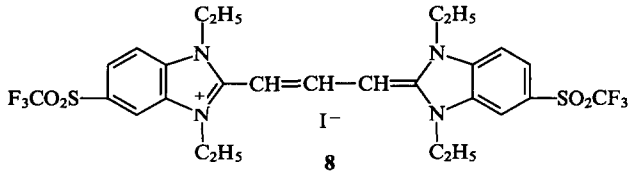
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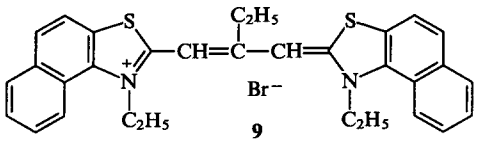
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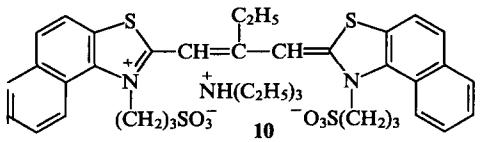
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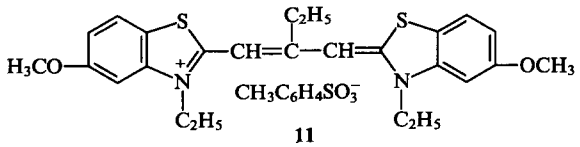
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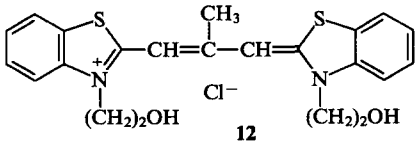
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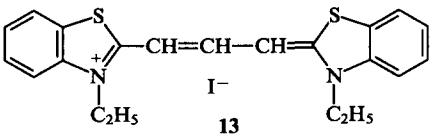
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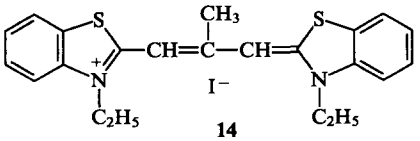
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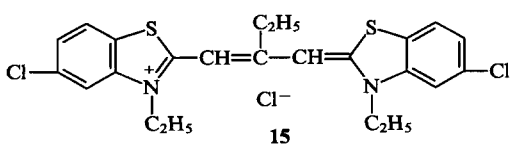
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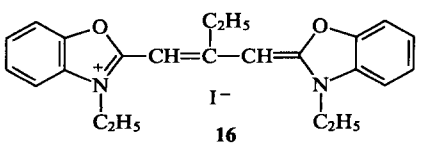
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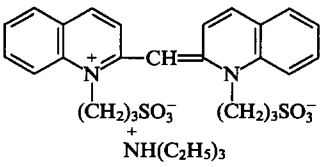
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The photographic effect of the dyes was studied on a monodisperse AgBr emulsion with cubic microcrystals subjected to sulfur–gold (S + Au) sensitisation.

Table 1 presents certain characteristics of the dyes investigated. Depending on their structure, the dyes have been divided into the following groups: imidacarbocyanines **1**, **2**, and **5**–**8**, thiacarbocyanines **9**–**15**, oxacarbocyanines **4** and **16**, and quino-2-monomethinecyanines **3** and **17**. The influence of sensitisers on the intrinsic sensitivity of AgBr emulsions (behind a UFS-1 light filter with a transmittance range of 240–400 nm) has been characterised by the degree of desensitisation (DD).

It follows from the data in Table 1 that all the dyes investigated desensitise the AgBr emulsion. The degree of desensitisation (DD) varies from 1.2 to 3.6. In the series of dyes, a lower degree of desensitisation is induced by dyes in the *M* state (compounds **8** and **13**). The *J*-aggregating dyes **1**, **5**, **6**, and **11** give rise to

Table 1. Desensitising activity of cyanine dyes and some of their characteristics.[49]

Dye	DD	$E_{1/2}^{Ox}$/V	$E_{1/2}^{Red}$/V	$\lambda_{C_2H_5OH}^{max}$/nm	λ_{AgBr}^{max}/nm	State
5	3.0	0.49	−1.83	500	507	*M*
					528	J_1
					555	J_2
1	3.5	0.55	−1.73	507	568	*J*
2	1.6	0.60	−1.58	515	577	*J*
6	3.3	0.67	−1.53	513	581	*J*
7	1.7	0.70	−1.44	523	598	*J*
8	1.5	0.79	−1.37	522	555	*M* (*H*)
9	1.9	0.67	−1.27	578	606	*M*
					662	*J*
10	2.1	0.67	−1.34	581	668	*J* (*H*)
11	3.1	0.68	−1.31	562	590	*M*
					630	*J*
12	1.6	0.76	−1.28	549	523	*J*
					595[a]	
13	1.7	0.76	−1.04	562	592	*M* (*H*) (*J*)
14	2.1	0.77	−1.16	544	518	*J*
					590[a]	
15	2.8	0.94	−1.05	553	643	*J*
16	1.4	0.93	−1.36	492	500	*M*
					524	*J*
4	2.1	0.93	−1.33	504	545	*J*
3	1.3	0.99	−1.04	523	575	*J*
17	1.2	0.99	−1.14	530	575	*J*

Note. The concentration of the dyes was 2×10^{-4} mol mol^{-1} AgHal and the polarographic potentials in CH_3OH are expressed relative to the normal calomel electrode. The absorption maxima of the dye solutions refer to solutions in ethanol and in the AgBr emulsion; if the state of the dye adsorbed on AgBr is insufficiently clear-cut to determine the absorption band maximum, the latter is indicated in brackets. The degree of desensitisation (DD) was calculated on the basis of the criterion $D = 0.85 + D_0$; the colour temperature of the light source was 5000 K; developer — UP-2; development time — 8 min; layer contrast coefficient $\gamma \geqslant 4.0$.

[a] Two transitions.

the maximum desensitisation (DD $\geqslant 3.0$). However, an unambiguous relation between the tendency of the dyes to undergo *J*-aggregation and their desensitising activity has not been discovered. For example, dyes **1** and **2**, which have similar structures and absorptions and form aggregates, differ significantly as regards desensitisation. A similar behaviour has been observed also for dyes **6** and **7**. The quino-2-monomethinecyanines **3** and **17**, which give rise to *J*-aggregates, have a weak desensitising effect. Thus *J*-aggregation itself is not a necessary and sufficient condition for desensitisation.

It is noteworthy that the desensitisation is not associated in a definite manner with the charge on the dyes, since cationic and ionic dyes with the same chromophoric component of the molecule desensitise to approximately the same extent (cf. compounds **11** and **12** and compounds **3** and **17**). There is also no unambiguous relation between the degree of desensitisation and the potentials $E_{1/2}^{Ox}$ of the dyes. For example, dyes **1** and **2** as well as **6** and **7** with similar potentials $E_{1/2}^{Ox}$ differ by a factor of approximately two in terms of their desensitising activity. This is partly associated with the fact that, on aggregation of the dyes, their energetics may change and it is not altogether legitimate to characterise the aggregates by their polarographic potentials. It has been shown by luminescence and photographic methods in relation to quino-2,2′-monomethinecyanine **3**[48] that the energies of the levels of the dye do indeed change on *J*-aggregation. A change in the positions of the energy levels of a series of carbocyanines on *J*-aggregation has also been demonstrated by photoelectrochemical methods.[50,51] However, the main cause is different, namely the probability of desensitisation is determined not only by energy factors but also to a considerable extent by kinetic factors.[8,26]

A kinetic model of the electron transfer reactions in a photographic emulsion has been developed in the present author's studies[8,25–27,52,53] on the basis of the electrochemical potentials of the dyes and other components of the emulsion. Since the processes examined are typical oxidation-reduction reactions, the ideas of Marcus's theory, which describes electron transfer reactions in polar media, are applicable to them.[54–56] According to this theory, there is a linear relation between the change in the free energy of the transition state and the thermodynamic characteristics of the elementary oxidation-reduction step:

$$\Delta G^{\neq} = -RT \ln k \approx a\Delta G^0 + b \approx anF\Delta E^0 + b \ , \qquad (6)$$

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

In this case, the rates of electron transfer reactions between the components of the photographic layer — the Dy*, Dy, [AgHal]*, and AgHal molecules as well as those of other compounds — can be expressed in 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. The kinetics of the hole processes are determined by the rate of exchange of the hole between [AgHal]* and Dy, between Dy* and AgHal, and between $Dy^{+\cdot}$ and other components of the layer. The rate of capture of holes from the valence band of AgHal by the components of the emulsion and in the first place by the dye can be represented by the sum of the reaction rates:

$$\sum_i -\frac{dn_i(p)}{dt} = \sum_i k_i c_i n(p)$$

$$= \sum_i A_i \exp(-\alpha_i \Delta E_i^0/T) c_i n(p) \ , \qquad (7)$$

where $n_i(p)$ is the number of holes, c_i the concentration of the hole-acceptor form of the ith system, and ΔE_i^0 the difference between the normal potential of the ith system and the potential of the top of the valence band (E_{vb}^0). When a hole is captured by the dye, $\Delta E_i^0 = E_{1/2}^{Ox} - E_{vb}^0$. According to the data of Mikheeva et al.,[57] $E_{vb}^0 = 1.5$ V (or 1.26 V rel. n.c.e.) for AgBr. Thus the capture of holes from AgHal by the dye is in principle possible for dyes with $E_{1/2}^{Ox} < 1.26$ V, i.e. for all the dyes presented in Table 1.

However, the capture of holes from AgHal by the dye is only the beginning of the type II desensitisation process, which ultimately represents the recombination of the dye hole with the photoelectrons present in the traps, including the impurity centres (IC_e). Such impurity centres may be chemical sensitisation products (in the first place, the products of the sulfur or sulfur-gold sensitisation).[7] According to the kinetic model, the rate of recombination can be defined by an equation of type (7) in which ΔE_i^0 is the difference between the electrochemical potentials of the electron in the trap and the dye hole ($\Delta E_D^0 = E^0(IC_e) - E_{1/2}^{Ox}(Dy)$]. Consequently the desensitisation rate constant can be formulated as follows:[53]

$$k_D = A_D \exp(-\alpha_D \Delta E_D^0/T) \ . \qquad (8)$$

Since ΔE_D^0 is a function of $E_{1/2}^{Ox}$ (Dy), one would have to expect the existence of a relation between the degree of desensitisation, determined by k_D, and $E_{1/2}^{Ox}$(Dy). However, as mentioned above, such a relation does not exist. The question arises of the cause of such behaviour of the dyes.

According to Eqn. (8), the rate of desensitisation is determined not only by the exponential term but also by the pre-exponential term A_D. One may assume that in type II desensitisation processes the pre-exponential term plays an appreciable role. As a rule, for simple electron transfer processes, the rate of the oxidation-reduction reactions in nonorganised (stochastic) systems, particularly in solutions, depends significantly on the exponential term, i.e. on the activation energy, or, according to the Marcus theory, on ΔE^0. It is noteworthy that such a dependence on ΔE^0 has indeed been observed for type I desensitisation reactions proceeding via a mechanism involving electron capture by electron-accepting dyes in the ground state.[7,27,46,57–61] This is manifested by the steady increase in the degree of desensitisation with increase in the electron affinity of the dyes. However, in the case of organised systems, such as the *J*-aggregates of dyes on the surface of AgHal, the characteristic features of the rates of oxidation-reduction processes are different. Here the frequency factor A_D assumes a special importance. Type II desensitisation processes should depend significantly on the position in space of the *J*-aggregate (in which the hole is located) relative to the impurity centre (in which a photoelectron is captured), i.e. on the distance r between Dy and IC_e.[53,62] This is illustrated schematically in Fig. 2 (see over). On photoexcitation of AgHal, an electron (e) – hole (p) pair is formed. The electron is captured by the electron-acceptor centre IC_e, while the hole is captured either by the hole-acceptor centre IC_p or by the dye aggregate.

If the self-organisation of the dye molecules in the form of a *J*-aggregate is difficult, it begins on the surface defects of AgHal, which diminish the activation energy for the initiation of the aggregates.[63] Surface defects have in addition centres for the localisation of the impurity centres, including the photosensitivity centres formed during sulfur sensitisation.[7,64,65] As a result of the contact between the *J*-aggregate and the electron-acceptor impurity centre $IC_e(r \to 0)$, the frequency factor A_D and the rate of recombination increase, which is manifested by the appreciable desensitisation of the dye. The probability of contact between the *J*-aggregates and IC_e is high, since according to estimates[64] the number of Ag_2S centres is several thousand per μm^2, i.e. approximately per single AgHal microcrystal. On the other hand, the number of dye molecules on such a microcrystal reaches $10^5 - 10^6$, so that there are between several tens and several hundreds of dye molecules per Ag_2S centre.

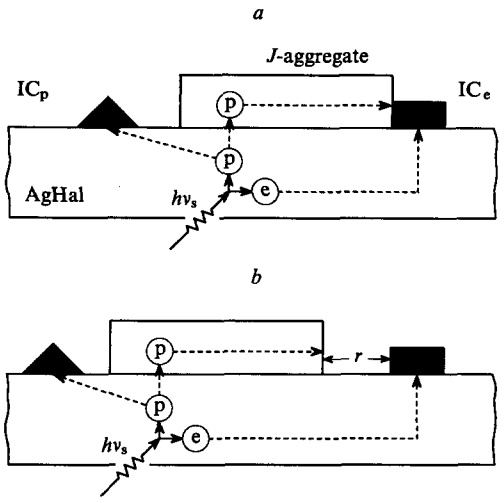


Figure 2. Schematic representation of the type (II) desensitisation processes via the hole mechanism: (*a*) *J*-aggregate in contact with the electron acceptor impurity centre (IC_e); (*b*) *J*-aggregate separated from the IC_e by a distance r; IC_p—hole acceptor impurity centre; $h\nu_s$—light quantum absorbed by AgHal; e = photoelectron; p = photohole.

On the other hand, if *J*-aggregation is achieved readily aggregates may be formed not only on AgHal defects but also at other sites, the probability of contact between the aggregate of IC_e falls, r increases (Fig. 2*b*), and hence the frequency factor A_D and the rate of recombination diminish.

If a hole is transferred from $Dy^{+\cdot}$ to IC_e via a tunnel mechanism, then the probability W of the transfer of the particle under the potential barrier per unit time is expressed by Gamow's classical formula, the simple version of which is

$$W = \nu \exp(-2r/a) , \qquad (9)$$

where ν is the frequency factor, r the distance corresponding to the width of the barrier, $a = \gamma h/[2m(U_{max}-E)]^{1/2}$ is the parameter characterising the attenuation of the wave function of the particle under the barrier, $\gamma \approx 1$ is a numerical coefficient which depends on the form of the barrier, m is the mass of the particle, U_{max} is the height of the barrier, and E is the energy of the particle. It follows from Eqn. (9) that the probability of the tunnel transition diminishes exponentially with the distance r. Thus $A_D = f[\exp(-2r/a)]$ and the type II desensitisation rate constant should therefore depend very greatly on r. This approach may serve as one of the explanations of the complex dependence of the hole desensitisation on the structure of the dyes.

The oxidising capacity of holes derived from all the dyes presented in Table 1 is apparently sufficient to accept electrons located on the impurity centres. According to the data of Berriman and Gilman,[59] the electrochemical potential corresponding to the oxidation of the silver film on the AgHal surface is 0.4 V (rel. Ag/AgCl electrode). Thus, even if account is taken of the possibility of a change in $E^{Ox}_{1/2}$ on aggregation of the dyes, all the sensitisers investigated are capable of oxidising the silver particles formed on the impurity centres. The observed difference between the desensitising properties [of the dyes] can be attributed to their different capacities for *J*-aggregation or the consequent different distances r between the *J*-aggregate and the IC_e.

Apart from the distance r, the frequency factor A_D can be determined by the velocity of the hole within the *J*-aggregate or by the mobility of the dye hole μ. The latter quantity must be related to the structure of the *J*-aggregate and in the first place to the interplanar distance between the dye molecules, their packing angle, and the molecular structure. For a low hole velocity in the aggregate, the probability of the decomposition of the latent image centre is naturally lower than for a high hole velocity. Therefore in a general form we have $A_D = f(r, \mu)$.[53]

III. Selective desensitisation and self-desensitisation of *J*-aggregates

The desensitisation processes should occur also on photoexcitation of dyes. In this case, one is dealing with selective desensitisation in the region of spectral sensitisation, the presence of which has been discussed.[35,66,67] Unfortunately the selective desensitisation of the spectral sensitiser itself, or, in terms of the nomenclature used by James[7] and Shapiro,[25] the self-desensitisation of the dye, cannot be measured directly, since it is impossible to achieve a controlled exposure of the photographic material at the same wavelength without the spectral sensitiser. At the present time, the degree of selective desensitisation is estimated by an indirect method from the influence of compounds introduced additionally on the intrinsic and spectral sensitivities of photographic emulsions. This method has been used to investigate selective type I desensitisation; electron-accepting compounds with a variable electron affinity were introduced into spectrally sensitised layers. It has been shown[57] that selective desensitisation can greatly exceed the intrinsic desensitisation.

One may postulate that experiments on the selective desensitisation of photographic emulsions via additionally introduced *J*-aggregating dyes, in which there is a possibility of the translation of a hole from the main spectral sensitiser, may serve as a definite test for type II self-desensitisation processes. Such a method has been used by the present author and his coworkers.[68]

Compositions comprising highly effective and weakly desensitising dyes combined with dyes which are weakly effective and induce an appreciable desensitisation via the hole mechanism were investigated. The highly effective dyes were compounds **4** and **14**, while the desensitising dyes were compounds **1** and **6** (Table 1). The dyes were introduced at equal concentrations and in a series of experiments the order of their introduction into the composition was varied. Fig. 3 presents spectral sensitivity and absorption curves for layers sensitised by dyes **4** and **1** individually and also by the **1** + **4** composition. According to the absorption spectrum (Fig. 3*a*), the use of a sensitiser composition has little effect on the positions of the absorption bands of the individual dyes (of curves *1*, *2*, and *3*). However, the introduction of the desensitising dye **1** leads to an appreciable suppression of the effectiveness of the spectral sensitisation at the sensitisation maximum of compound **4** (cf. curves *1* and *3*, Fig. 3*b*). The degree of desensitisation in the region of the AgHal absorption also increases under these conditions.

Fig. 4 illustrates the results for the **14** + **1** composition. Two absorption bands with λ_{max} = 518 and 590 nm are characteristic of 9-methylthiacarbocyanine **14**. Different assignments of these bands exist. They have been attributed either to the *H*- or *J*-aggregates respectively or to two spectral transitions in a single *J*-aggregate with a 'parquet' type of structure. According to Reich,[69] the splitting of excited dye levels into two components (S_1^1 and S_1^2) is observed for such molecular packing, where the structure cell contains two dye molecules at an angle close to 90°. Two spectral transitions, $S_0 \rightarrow S_1^1$ and $S_0 \rightarrow S_1^2$, of equal intensity then take place. The addition of dye **1** does not alter the positions of the absorption bands of dye **14** (cf. curves *1* and *3*, Fig. 4*a*), but it suppresses sharply the effectiveness of the sensitisation in bands with λ_{max} = 518 and 590 nm and approximately to the same extent for both bands (cf. curves *1* and *3*, Fig. 4*b*). It is noteworthy that similar results have been obtained for the reverse order of introduction of the dyes into the composition, i.e. **14** + **1** and **4** + **1**. The replacement of the desensitising dye **1** by compound **6** did not alter fundamentally the results—its introduction together with dye **14** diminished the photographic activity of the *J*-aggregates of dye **14**. Thus selective type II desensitisation does indeed take place.

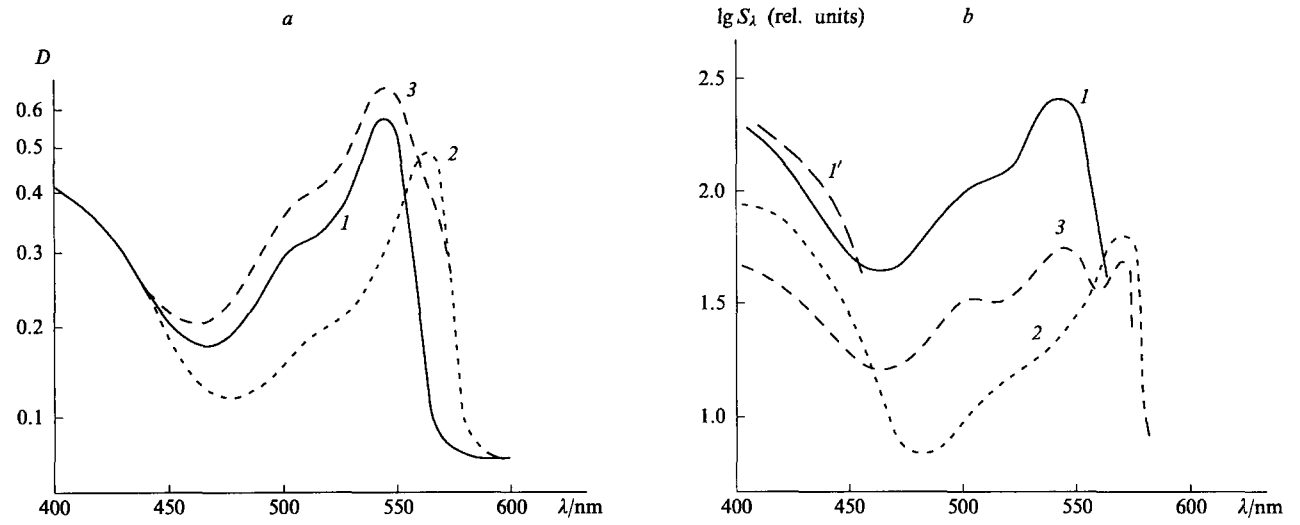


Figure 3. Reflection spectra (*a*) and spectral sensitivity curves (*b*) for AgBr emulsion layers sensitised by dyes **4** (curve *1*) and **1** (curve *2*) and by the **1** + **4** dye composition (curve *3*); (*1'*) layer without dye. AgBr emulsion—cubic crystals, $\bar{l} = 0.17$ μm, (S + Au)-sensitisation; concentration of dyes—2×10^{-4} mol (mol AgBr)$^{-1}$.

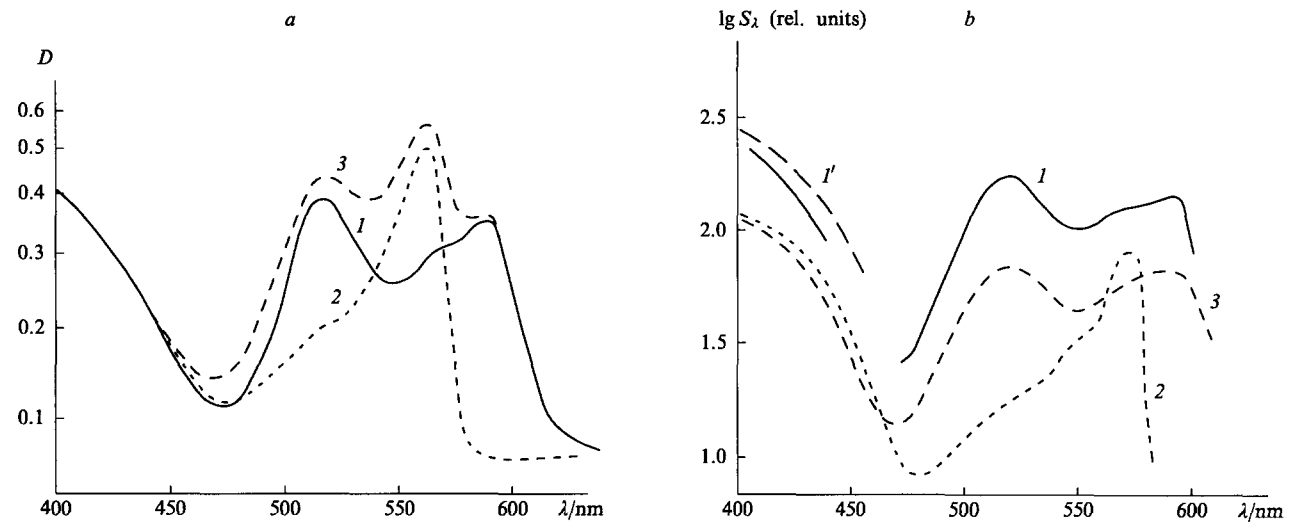


Figure 4. Reflection spectra (*a*) and spectral sensitivity curves (*b*) for AgBr emulsion layers sensitised by dyes **14** (curve *1*) and **1** (curve *2*) and by the **1** + **14** dye composition (curve *3*); (*1'*) layer without dye. Concentration of dyes—2×10^{-4} mol (mol AgBr)$^{-1}$.

The desensitising effect of dyes **1** and **6**, i.e. the decrease in the intrinsic sensitivity of AgHal, is apparently due to the capture of a hole from AgHal, its translation in the *J*-aggregate to the photoelectron capture centre (IC_e), and the recombination of the dye hole with the captured electron (Fig. 2*a*). The large desensitisation effects produced by these dyes (Table 1) may be due to two causes. Firstly, we have the energy-based cause. According to the data in Table 1, $E^{Ox}_{1/2}(\mathbf{1}) = 0.55$ V and $E^{Ox}_{1/2}(\mathbf{6}) = 0.67$ V, i.e. is appreciably lower than the potential corresponding to the upper limit of the AgBr valence band [estimated as 1.26 V on the same electrochemical potential scale (rel. n.c.e.)].[57] Thus the capture of a hole from AgBr by the dye is extremely likely (even when account is taken of the possible change in the energy levels on *J*-aggregation[48,50]). Secondly there is the kinetic cause. The probability of desensitisation may increase owing to contact between the *J*-aggregates of dyes **1** and **6** and the impurity centres—electron acceptors.[49] In the case of the effective dyes **4** and **14**, the lower desensitising effect is to some extent due to energy dependent causes [$E^{Ox}_{1/2}(\mathbf{4}) = 0.93$ V, $E^{Ox}_{1/2}(\mathbf{14}) = 0.77$ V (Table 1)], but it is determined to a large extent by kinetic causes—due to the lower probability of contact between the *J*-aggregates and the impurity centres.

We shall consider the effect of dye compositions. The decrease in the effectiveness of the spectral sensitisation by dyes **4** and **14** following the additional introduction of the desensitiser **1** or **6**, observed by Shapiro et al.,[68] may be a consequence of the decrease in the probability of processes involving the recombination of dye photoelectrons and holes. The use of the second dye is equivalent to a decrease in the distance *r* between the *J*-aggregate and the IC_e, which is illustrated schematically in Figs. 5*a* and 5*b* (see over). According to this scheme, the hole of the first dye (for example, compound **4**) is translocated to the second dye (compound **1**), as a result of which there is a sharp increase in the pre-exponential term A_D in Eqn. (8) and hence in the rate of desensitisation. The translocation of the holes of dyes **4** and **14** to dyes **1** and **6** is possible, since $E^{Ox}_{1/2}(\mathbf{4}, \mathbf{14}) > E^{Ox}_{1/2}(\mathbf{1}, \mathbf{6})$.

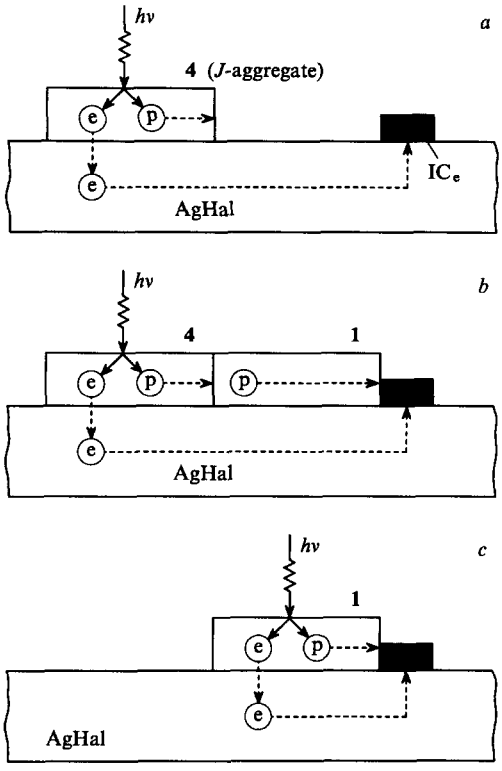


Figure 5. Schematic representation of the selective type (II) desensitisation (*a*, *b*) and self-desensitisation (*c*) of dyes.

According to Fig. 4*b*, the additional introduction of compound **1** has the same influence on the effectiveness of sensitisation in both absorption bands of dye **14** (cf. curves *1* and *3*, Fig. 4*b*), so that one can assume that they indeed belong to the same *J*-aggregate and, according to Reich,[69] both spectral transitions take place from the same ground level S_0. As a result of this, the holes generated under the conditions of both bands have the same energy. In essence, it is the same hole and its transfer through the *J*-aggregate of the second dye is equally probable regardless of the band used for its excitation.

It is essential to bear in mind that the translocation of a hole from one aggregate to another should not always be manifested as desensitisation. One can imagine a situation where, on photoexcitation of a desensitising dye in contact with the impurity centre, on the one hand, and with the *J*-aggregate of another dye, on the other, the hole of the first *J*-aggregate may be captured by the second. For this, it is necessary that Gilman's condition[10] $E_{1/2}^{Ox}(Dy'') < E_{1/2}^{Ox}(Dy')$ should hold. On the other hand, on photoexcitation of the second dye, the *J*-aggregate of the first as it were insulates the hole from IC_e. Thus there is a possibility of the mutual supersensitisation of the dyes. This case is apparently characteristic of the so called cation-anionic dyes containing in their structure two dyes one of which (cationic) has alkyl groups attached to the nitrogen atom of the heterocycle, while the other (anionic) has acid groups. As a rule individual sensitisers have different values of $E_{1/2}^{Ox}(Dy)$. Furthermore, the composition comprising such dyes frequently incorporates the desensitising quinomonomethinecyanine **3** as the orthochromatic sensitiser and one of the effective thiacarbocyanines as the panchromatic sensitiser. The cation-anionic dyes are known[70,71] to be highly effective and photochemically more active than a mixture of individual sensitisers. The explanation of this may be as follows. Since the charge on the individual cyanines is compensated by the counterion, on aggregation the *J*-aggregates of two different dyes need not necessarily be in contact. On the other hand, in the case of cation-anionic dyes contact between oppositely charged *J*-aggregates of the two dyes is more probable and hence there is also a greater probability of the supersensitising transfer of a hole from one aggregate to the other.

It is noteworthy that the processes involving the translocation of a hole from one dye to another should be manifested particularly clearly in direct positive materials. In such materials, the holes oxidise the silver fogging centres generated beforehand and the translation of holes between different dyes should lead not to the desensitisation of the photographic layers but actually to their supersensitisation. Indeed the supersensitisation of the photobleaching of the fogging centres by cyanine dye compositions has been observed.[72] The possibility of the translocation of holes from one dye to another with a lower value of $E_{1/2}^{Ox}$, leading to an increase in the effectiveness of the direct positive process, has been discussed.[73]

Thus the reality of selective type II desensitisation processes has been demonstrated.[68] This can be regarded as an argument in support of the existence of type II dye self-desensitisation processes via a hole mechanism. The probability of this process as well as the type II desensitisation process is determined by the distance *r* between the *J*-aggregate and the IC_e impurity centre of the electron-acceptor type. The self-sensitisation on photoexcitation of the dye (the spectral sensitiser) is particularly probable on contact between the *J*-aggregate and the IC_e (Fig. 5*c*).

It is essential to note that the type II desensitisation process consists of a greater number of stages than the self-desensitisation of the dyes. This condition is illustrated conventionally in Fig. 2 *a*. On photoexcitation of AgHal, some of the holes may be captured by the dye on the surface of the microcrystal with formation of dye holes, whilst others are captured by impurity centres—hole acceptors (IC_p). On the other hand, the type II self-desensitisation process is simpler, since a dye hole inevitably arises on spectral sensitisation, i.e. on transfer of electrons from the photoexcited dye to AgHal (Fig. 5*c*). Thus the number of dye holes may be larger. The probability of self-desensitisation can therefore be also greater than the probability of desensitisation and hence its influence on the spectral sensitivity may exceed that of desensitisation on the intrinsic photosensitivity of the emulsion. This apparently leads to the very pronounced difference between the effectiveness of the spectral sensitisation by dyes **1**—**4** illustrated in Fig. 1 despite the similar maxima and intensities of the absorption bands of the *J*-aggregates. Table 2 presents certain photographic characteristics of the layers sensitised by individual *J*-aggregating dyes.[68] The relative quantum yield of the spectral sensitisation was determined by means of the equation[74]

$$\varphi_r = \frac{A_{410}\, S_\lambda\, 410}{A_\lambda\, S_{410}\lambda}, \qquad (10)$$

where A_{410} and A_λ are the absorption coefficients of the emulsion layer at 410 nm and at the wavelength λ corresponding to the absorption maximum of the dye, while S_{410} and S_λ ($cm^2\,erg^{-1}$) are the photosensitivities of the layer at the corresponding wavelengths. The coefficient φ_r is the ratio of the number of quanta in the regions corresponding to absorption by AgHal (410 nm) and the dye (λ, nm) leading to the same photographic effect—in the given instance to the blackening density $D = 0.5$ over the fogging level.

According to the data in Table 2, dye **1**, which exhibits a desensitising effect, tends to decrease the intrinsic sensitivity of the emulsion (S_{410}). In contrast to dye **1**, dye **3** has little effect on S_{410}, which may be due to the difference between the potentials $E_{1/2}^{Ox}$ (Table 1). The highly effective dyes **2**, **4**, and **14** have virtually no desensitising effect [cf. the degrees of desensitisation (DD) in Table 2]. The quantum yields φ_r for the dyes are comparatively high—0.70 to 0.85, i.e. in order to induce the same effect as that of the 'blue' quantum 1.2—1.4 quanta absorbed by the dye are required. In the case of self-desensitising dyes **1** and **3**, the quantum yields φ_r are significantly smaller (0.40—0.08), i.e. 2.5—12 quanta are now required per 'blue' quantum.

Table 2. Photographic characteristics of layers based on the AgBr emulsion sensitised by individual *J*-aggregating dyes.[68]

Dye	λ_{max}^{sens}/nm	S_{410}^{a}/cm² erg⁻¹	S_{λ}/cm² erg⁻¹	DD	φ_r[a]
Without dye	–	1.2	–	–	–
1	568	0.5	0.4	2.4	0.40
2	577	1.1	1.6	1.1	0.85
3	575	1.1	0.2	1.1	0.08
4	545	1.1	1.6	1.1	0.85
14	518	1.1	0.9	1.1	0.70
	590		0.7		0.70

[a] Calculated on the basis of the criterion $D = 0.5 + D_0$.

Thus the effectiveness of the light quanta absorbed by the sensitiser is much smaller than that of the photons absorbed by the AgHal lattice, the latter being suppressed by desensitisation in the case of dye **1**.

The well known experimentally observed decrease in spectral sensitisation with increase in the concentration of *J*-aggregating dyes above the optimum value can also be accounted for within the framework of ideas concerning the self-desensitisation of dyes. By virtue of the increase in the coating of the surface of the AgHal microcrystals by the *J*-aggregates, the distance *r* between them and the IC_e should decrease and hence the rate of recombination process should increase.

On the basis of the foregoing, one may conclude that the self-desensitisation processes can in essence determine the effectiveness of the spectral sensitisation itself. As a result of the examination of the role of the self-desensitisation processes in the spectral sensitivity of silver halide photographic materials, it has been concluded [25] that the spectral sensitisation of negative silver halide emulsions is determined not by the primary photoreaction but by the kinetics of secondary reactions, i.e. self-desensitisation reactions. The theory of the spectral sensitisation of such materials must therefore be in the first place a theory of the self-desensitisation of dyes. It is noteworthy that this postulate is valid only if desensitisation (and self-desensitisation) via the hole mechanism is included in the concept of desensitisation. Subsequent studies [8, 26, 47–49, 57, 68] only increased the author's certainty about the validity of this postulate.

IV. Supersensitisation of *J*-aggregating dyes as inhibition of their self-desensitisation

Within the framework of the mechanism of the spectral sensitisation of *J*-aggregating dyes under discussion, it is possible to consider at least three methods for increasing the effectiveness of the sensitisation, i.e. three supersensitisation methods. They all reduce to the inhibition of the self-desensitisation via the hole mechanism and hence to the inhibition of recombination processes. One of the supersensitisation methods mentioned in the introduction consists, according to Gilman's 'reductive' mechanism, [10, 24] in the capture (reduction) of the dye holes by the more readily oxidised organic compound. Thus the supersensitisation conditions already mentioned may be expressed in the form [10]

$$E_{1/2}^{Ox}(S) < E_{1/2}^{Ox}(Dy) .$$

A hole of the *J*-aggregate is then translocated to the supersensitiser (S), loses its mobility, and no longer participates in the recombination processes. Since Gilman's supersensitisation mechanism has already become in essence classical and has been discussed in detail in a number of reviews, [7–13] it will not be considered separately in the present article.

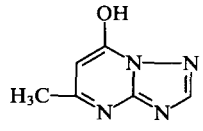
The second supersensitisation method reduces to the insulation of the *J*-aggregates of the impurity centres, which prevents the recombination of the dye holes with the electrons captured by these centres. This 'insulation' mechanism of supersensitisation will be examined in detail below.

The generally acknowledged factors influencing the aggregation of dyes are their structure, the halide composition of the photographic emulsion, the type of faces of the AgHal microcrystals, the concentration of silver ions, the acidity of the medium, and the nature of various substances introduced into the emulsion.[7] Since the self-association of dyes is a process which takes place over a period of time, it is logical to postulate that some of the factors enumerated influence the kinetics of the formation of the ordered structures of the aggregates. On the other hand, the aggregation kinetics can undoubtedly determine the structure of the aggregate — primarily the packing angle of the dye molecules in the aggregate and their number and hence the topography on the surface of AgHal and in particular the distance *r* from the IC_e. The third supersensitisation method consists in the regulation of the *J*-aggregation of the dyes with the aid of organic substances, introduced additionally into the emulsion, which are either adsorbed or not adsorbed on AgHal.

1. The 'insulation' mechanism of supersensitisation

Towards the end of the 1970's, a considerable number of experimental data accumulated according to which the supersensitisation of photographic layers with *J*-aggregating dyes was induced by organic compounds oxidised with greater difficulty than the dyes. Since the principal condition for supersensitisation via Gilman's 'reductive' mechanism was infringed in such cases, it followed naturally that one could deal only with some other supersensitisation mechanisms.

The supersensitising effect of a familiar stabiliser — 4-hydroxy-6-methyl-1,3,3*a*,7-tetraazaindene **18** (the sta-salt) — has been described in greatest detail. It is manifested on emulsions with sulfur sensitisation.[3, 9, 75–79]



18

The increase in the additional sensitivity induced by certain *J*-aggregating dibenzothiacarbocyanines and unaccompanied by a change in the nature of the absorption centres has been explained [78, 79] by the facilitation of the transfer of the energy absorbed by the dye to the AgHal lattice. The effect of various 2- and 5-alkyl derivatives of compound **18** has been investigated.[80] An increase in the intrinsic sensitivity and the preferential growth of the spectral sensitivity of the emulsion were noted. The influence of the compounds on the additional sensitivity is regarded by the authors as the sum of two effects: (1) the influence on the intrinsic sensitivity of the microcrystals because of the deactivation of a number of sensitivity centres following the chemisorption of compound **18** and its derivatives on the impurity centres as a result of which the latter cease to serve as the sites for the capture of electrons;[81] (2) the influence on the state of aggregation of the dye adsorbed on AgHal.

The photographic effect of compound **18** and other tetra- and penta-azaindenes has been investigated in a series of studies by Tani and coworkers.[82–86] It was shown[82] that compound **18** is primarily a chemical sensitiser of monodisperse emulsions with sulfur sensitisation. Various sulfur-containing anti-fogging substances exhibit an influence similar to that of compound **18**.[83] The mechanism of the action of the stabiliser **18** on the intrinsic sensitivity of AgHal is treated as an increase in the depth of the electron traps formed on sulfur sensitisation and a decrease in the number of fine traps on the surface of microcrystals acted upon by the adsorbed tetraazaindene.[85] It is not difficult to see in this interpretation a definite similarity with the concept proposed previously.[80, 81] The preferential influence of compound **18** and other supersensitisers on the spectral sensitivity of emulsions with

sulfur sensitisation has been explained[84] by a decrease in the desensitising effect of dyes both due to the increase in the fraction of electrons captured by the sulfide-silver centres at greater depth and due to the decrease in the mobility of the dye holes in the aggregates. In addition, the increase in the rate of electron transfer on fragmentation of the *J*-aggregates by the supersensitiser,[87] similar to that described by West and Carroll,[15] has been considered.

The influence of compound **18** on various *J*-aggregating dyes has been considered in a series of studies by the present author.[8,26,47–49,68] In the first place, the influence of the sta-salt was considered in relation to the repeatedly investigated quino-2,2′-monomethinecyanine **3**. For a monodisperse AgBr emulsion (cubic crystals, $\bar{l} = 0.17$ μm) with sulfur-gold sensitisation it has been shown that a transformation of the *J*-band ($\lambda^{J}_{max} = 575$ nm) is observed under the influence of the sta-salt, namely its hypsochromic shift at low concentrations of compound **18** amounting to $(1-2) \times 10^{-3}$ mol (mol AgBr)$^{-1}$, the appearance of two absorption bands ($\lambda^{J_1}_{max} = 570$ nm, $\lambda^{J_2}_{max} = 581$ nm) with increase in the concentration of compound **18** to $(2-5) \times 10^{-3}$ mol (mol AgBr)$^{-1}$, and finally the appearance of one long-wavelength J_2 band at a concentration equal to or greater than $(8-10) \times 10^{-3}$ mol (mol AgBr)$^{-1}$ (Fig. 6). According to Fig. 6*b*, the content of compound **18** does not induce the growth of the photographic activity of the J_1-aggregates (cf. curves *1* and *2*, Fig. 6*b*) but it does supersensitise the J_2-aggregates. It is noteworthy that the nature of the aggregation and the effectiveness of the supersensitisation depend to a large extent on the order in which the supersensitiser and the dye are introduced. When compound **18** is introduced before the dye, the maximum supersensitisation effect and subsequent formation of the J_1- and J_2- aggregates are observed; when compound **18** is introduced after the dye, the effectiveness of the supersensitisation is reduced sharply and is accompanied by a slight transformation of the *J*-band.[47] The influence of the order in which compound **18** is introduced on the aggregation has been noted also in another study.[76]

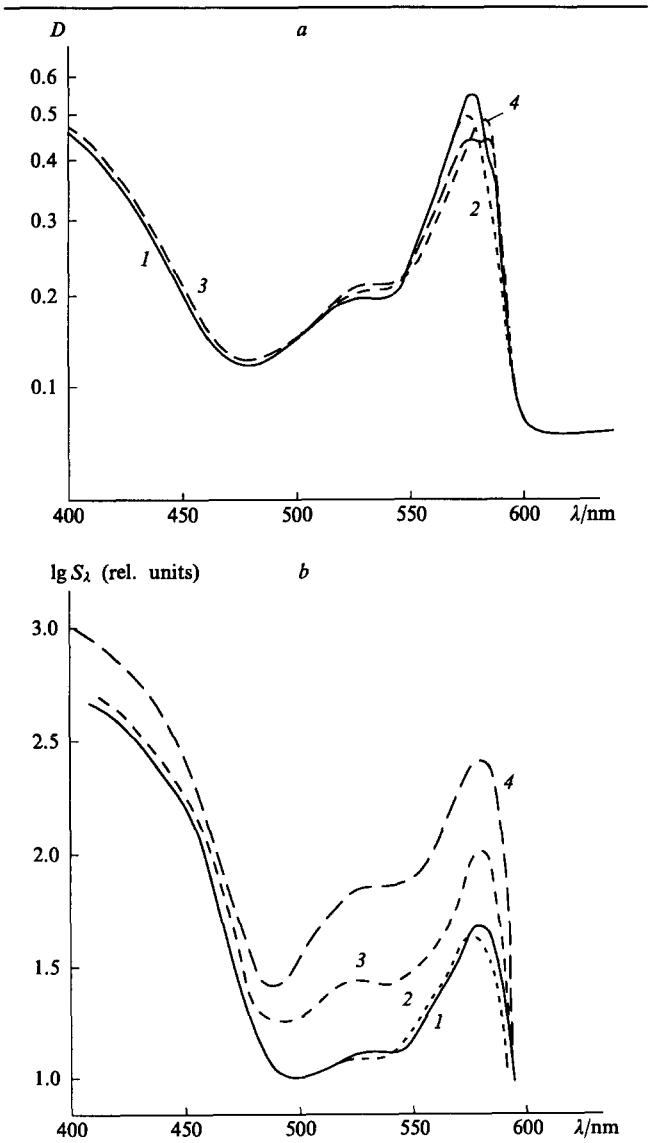
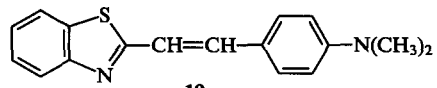


Figure 6. Reflection spectra (*a*) and spectral sensitivity curves (*b*) for AgBr emulsion layers sensitised by dye **3** [2×10^{-4} mol (mol AgBr)$^{-1}$] without a supersensitiser (curve *1*) and with the supersensitiser **18** at different concentrations [10^{-3} mol (mol AgBr)$^{-1}$]: (*2*) 1.0; (*3*) 4.0; (*4*) 8.0; emulsion with (S + Au)-sensitisation.

It has been shown[47] that the introduction of the supersensitiser 2-(*p*-dimethylaminostyryl)benzothiazole **19**, which is traditional for dye **3** and which operates via Gilman's 'reductive' mechanism, into spectrally sensitised layers containing various amounts of compound **18** does not alter the nature of the absorption spectra.



19

It is striking that the supersensitising effect of compound **19** on layers with J_1-aggregates is significantly smaller than the effect on the *J*-aggregates of dye **3** without compound **18** (cf. curves *5* and *6*, Fig. 7), while on layers with J_2-aggregates an additional supersensitisation effect was observed (cf. curves *3* and *7* and curves *4* and *8* in Fig. 7).

Table 3 presents the calculated relative quantum yields of the spectral sensitisation of the photographic layers investigated.[47] It follows from the data in Table 3 that, at low concentrations of compound **18**, whereupon J_1-aggregates are formed preferentially, there is virtually no supersensitising effect of compound **19**. On the other hand, at higher concentrations of compound **18**, in the region where J_2-aggregates are formed, a superadditive effect of compounds **18** and **19** is observed. In this case, $\Delta \lg S_\lambda^{18+19} \approx \Delta \lg S_\lambda^{18} + \Delta \lg S_\lambda^{19}$, and $\varphi_r^{18+19} > \varphi_r^{18} + \varphi_r^{19}$. These data led to the conclusion[47] that the superadditive effect may serve as definite evidence for the different mechanisms of the supersensitisation of the layers by compounds **18** and **19**.

Table 3. The influence of the supersensitisers **18** and **19** on the relative quantum yield of the spectral sensitisation of the photolayers sensitised by quino-2-monomethinecyanine **3** [2×10^{-4} mol (mol AgBr)$^{-1}$].[47]

Supersensitiser	$10^3 c$/mol (mol AgBr)$^{-1}$ [a]	φ_r [b]			Nature of *J*-aggregation [c]
		λ_{570}	λ_{575}	λ_{581}	
–	–	0.02	0.02	0.02	*J*
18	2.0	0.03	0.02	0.03	J_1
18	5.0	0.09	0.11	0.16	$J_1 + J_2$
18	20.0	0.19	0.21	0.19	J_2
19	0.02	0.23	0.22	0.20	*J*
18 + 19	2.0 + 0.02	0.04	0.04	0.04	J_1
18 + 19	5.0 + 0.02	0.36	0.44	0.53	$J_1 + J_2$
18 + 19	20.0 + 0.02	0.49	0.69	0.55	J_2

[a] *c* = supersensitiser concentration.
[b] Calculated on the basis of the criterion $D = 0.2 + D_0$.
[c] AgBr emulsion with (S + Au)-sensitisation.

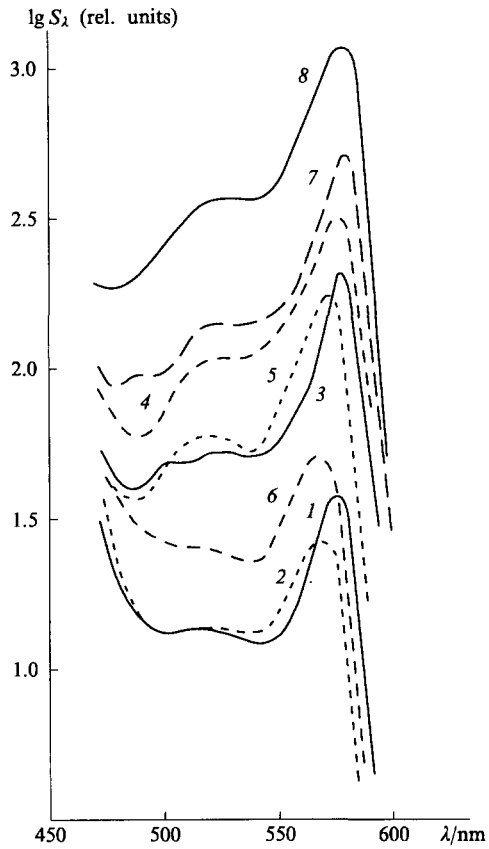


Figure 7. Spectral sensitivity distribution curves for AgBr emulsion layers sensitised by dye **3** [2 × 10^{-4} mol (mol AgBr)$^{-1}$] without a supersensitiser (curve *1*) and with the supersensitiser **18** at different concentrations [10^{-3} mol (mol AgBr)$^{-1}$]: (*2*) 2.0; (*3*) 5.0; (*4*) 20.0; emulsions sensitised by dye **19** at a concentration of 2 × 10^{-5} mol (mol AgBr)$^{-1}$ (curve *5*); emulsion sensitised by the **18** + **19** composition at different concentrations [mol (mol AgBr)$^{-1}$]: (*6*) 2 × 10^{-3} and 2 × 10^{-5}; (*7*) 5 × 10^{-3} and 2 × 10^{-5}; (*8*) 20 × 10^{-3} and 2 × 10^{-5}; emulsion with (S + Au)-sensitisation.

It is striking that the photographic effect of compound **18** on the same AgBr emulsion but without chemical sensitisation is completely different despite the similar influence of compound **18** on the transformation of the *J*-bands of aggregates of dye **3**. At low concentrations of compound **18** [$\leqslant$ 2 × 10^{-3} mol (mol AgBr)$^{-1}$], a slight increase in the photographic sensitivity of the layer is observed in the region of absorption by the J_1-aggregates, but, as the content of compound **18** rises and J_2-aggregates are formed, a decrease in the effectiveness of the dye is observed. This is illustrated in Fig. 8, from which it also follows that aminostyrylbenzothiazole **19** supersensitises the *J*-aggregates of dye **3** regardless of its chemical sensitisation (cf. curves *1* and *5*, Fig. 8*b*). Thus the photographic effect of compound **18** is due to at least three causes: (a) the adsorption of compound **18** on the AgBr surface before the adsorption of the dye, (b) the presence of the products of the sulfur-gold sensitisation, and (c) the type of the *J*-aggregate.

The effect of the sensitiser **18** has been investigated[49] for a series of *J*-aggregating dyes of different structure: imidacarbocyanines **1**, **2**, **6**, and **7**, thiacarbocyanines **9**, **11**, **12**, **14**, and **15**, and oxacarbocyanine **4**. It is striking that the greatest photographic effect of compound **18** is observed on photographic emulsions sensitised by aggregating dyes, which gives rise to appreciable desensitisation (compounds **1**, **6**, **9**, and **15**). For dyes similar to quinomonomethinecyanine **3**, after the introduction of compound **18** a hypsochromic shift of the absorption *J*-bands is observed initially, then their bathochromic shift, and finally, at concentrations [**18**] $\geqslant$ 10^{-2} mol (mol AgHal)$^{-1}$ (except for compound **15**) there is again a hypsochromic shift of the *J*-band. On formation of long-wavelength J_2-aggregates under the influence of compound **18**, there is an appreciable decrease in the degree of desensitisation and there is a sharp jump in the additional photosensitivity. For example, for dye **6**, the supersensitisation coefficient is K_s = 20. Under these conditions, K_s significantly exceeds the change in the degree of desensitisation. For the highly effective and less desensitising dyes **2**, **7**, **12**, **14**, and **4**, for which only a slight hypsochromic shift of the *J*-band under the influence of the stabiliser **18** is observed, the decrease in the degree of desensitisation leads to an increase in the additional sensitivity of similar magnitude. The significantly greater value of K_s relative to the change in the degree of desensitisation for dyes **1**, **6**, **9**, and **15** has

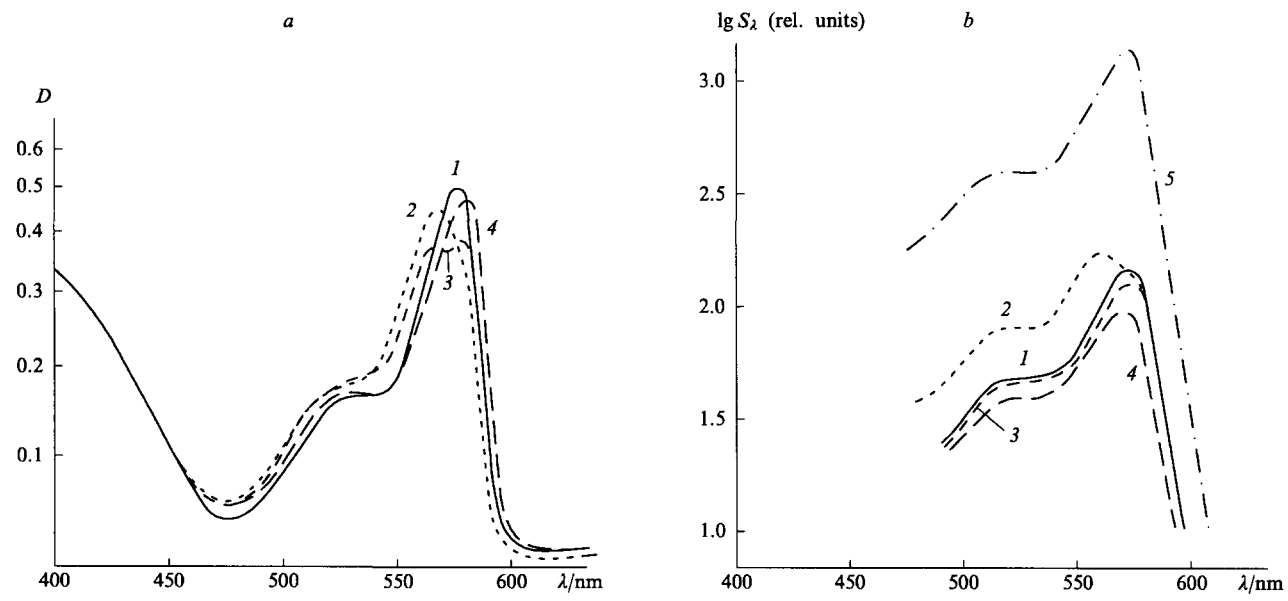


Figure 8. Reflection spectra (*a*) and spectral sensitivity curves (*b*) for AgBr emulsion layers sensitised by dye **3** [2 × 10^{-4} mol (mol AgBr)$^{-1}$] without a supersensitiser (curve *1*) and with the supersensitiser **18** at different concentrations [10^{-3} mol (mol AgBr)$^{-1}$]; (*2*) 1.0; (*3*) 5.0; (*4*) 20.0; with the supersensitiser **19** at a concentration of 2 × 10^{-5} mol (mol AgBr)$^{-1}$ (curve *5*); emulsion without chemical sensitisation.

been considered[49] as additional evidence for the difference between the processes involving the desensitisation of AgHal by dyes and the self-desensitisation of the dyes. If this is so, then the inhibition of the self-desensitisation by compound **18** should affect the spectral sensitivity of the emulsion to a greater extent than its intrinsic sensitivity.

The effect of the stabiliser **18**, manifested on AgHal emulsions with chemical sensitisation, has been explained by the formation of an 'insulating' layer between the *J*-aggregates and the impurity centres (IC_e) — the products of the sulfur-gold sensitisation. This layer, comprising molecules of the supersensitiser (S), should prevent the recombination of the dye holes with the electrons captured by the IC_e, which is illustrated schematically in Fig. 9*a*. The formation of the layer between the products of the sulfur sensitisation and the dye should be promoted by the known preferential adsorption of compound **18** on Ag_2S compared with AgHal.[88] The formation of such a layer between the dye *J*-aggregates and the silver sulfide clusters has been demonstrated by the luminescence method.[89,90] It has been established[91–93] that the sulfur sensitisation of silver halide emulsions is accompanied by the appearance of a low-temperature luminescence in the near infrared. The sulfide-silver clusters of the type $(Ag_2S)_n$ or $(Ag_2S)_n.Ag_m$ generated during chemical sensitisation, are responsible for the above luminescence, the position of the luminescence band in the spectrum depending on the value of *n*.[93,94] Belous and Tolstobrov[95] observed that the absorption of light by the dye *J*-aggregate adsorbed on silver sulfide in the dye–Ag_2S cluster system diminishes the intensity of the luminescence of the Ag_2S cluster in the IR region of the spectrum.

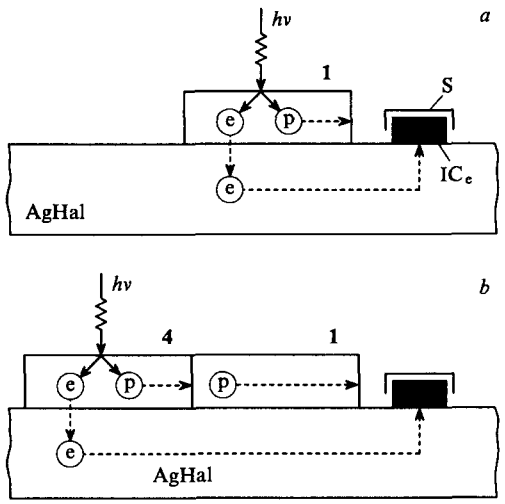
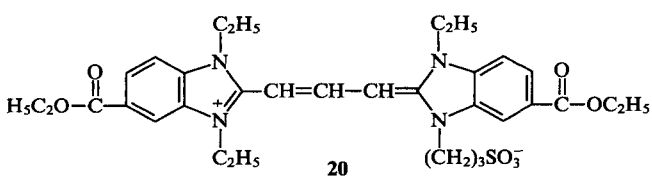


Figure 9. Schematic representation of the 'insulation' supersensitisation mechanism involving the inhibition of the type (II) self-desensitisation (*a*) and the selective desensitisation by compositions comprising *J*-aggregating dyes (*b*).

Fig. 10 presents the dependence of the luminescence intensity *I* of the silver sulfide clusters on the exciting light wavelengths λ_e.[90] The Ag_2S clusters were spectrally sensitised by dye **3** and 3-{2-[3-(5-ethoxycarbonyl-1,3-diethyl-2,3-dihydrobenzimidazol-2-ylidene)prop-1-enyl]-5-ethoxycarbonyl-1-ethylbenzimidazol-3-yl}propanesulfonate **20**.



20

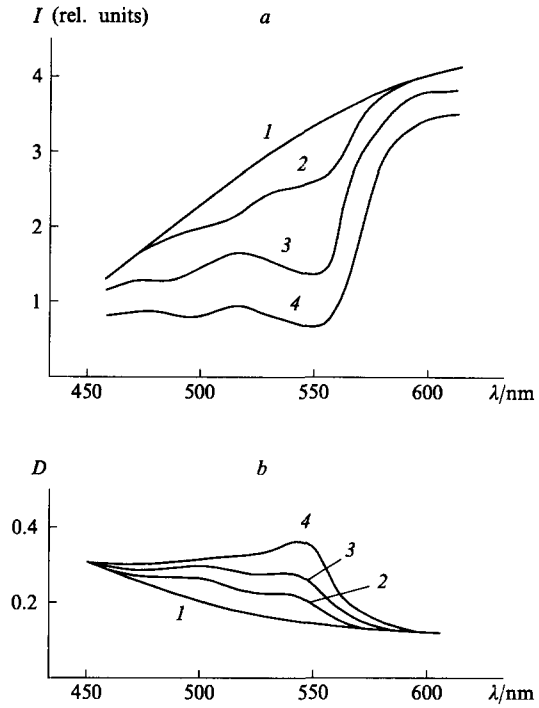


Figure 10. Dependence of the intensity of IR luminescence on the incident light wavelength (*a*) and the spectral distribution of the absorbances (*b*) of gelatine layers containing Ag_2S clusters and compound **18**. Dye concentration (10^{-4} M): (*1*) 0; (*2*) 0.1; (*3*) 0.25; (*4*) 0.5.

According to Fig. 10, as the *J*-aggregates of the dyes are formed, a decrease in *I* is observed. The decrease was explained by the Fano antiresonance effect[96] due to the interference of the excited state of the dye and Ag_2S, which may lead to the observation of a sharp decrease in the absorption coefficient within narrow spectral regions. A similar decrease in the luminescence intensity of the Ag_2S clusters (with λ_{max} = 800 nm), formed on sulfur sensitisation of monodisperse AgBr emulsions with cubic microcrystals, occurred on excitation by light corresponding to the absorption band of the *J*-aggregates of different dyes.[89,90] Fig. 11*a* illustrates the decrease in the intensity of the IR luminescence of Ag_2S clusters at the wavelength of the band due to the *J*-aggregate of dye **20**. A similar pattern has been observed also for other *J*-aggregating dyes.[90]

A necessary condition for the manifestation of the antiresonance, apart from the energy correspondence between the excited levels of the dye and the Ag_2S clusters, is also direct contact of the sensitiser with the impurity centre. The luminescence method therefore makes it possible to establish unambiguously the occurrence of the direct interaction of the dyes with the chemical sensitisation products. An increase in the distance between the cluster and the dye should entail a sharp decrease in the antiresonance and hence an increase in the intensity of the sensitised luminescence of the Ag_2S cluster. Experiments[89,90] have shown that the introduction of compound **18** weakens the decrease in *I* caused by the antiresonance (Fig. 11*b*) and, at concentrations exceeding 0.1 g per litre of the emulsion, a typical case of sensitised luminescence can be recorded. A similar pattern has been observed when the Ag_2S and dye aggregates were separated by AgBr shells grown on the AgBr microcrystal after sulfur sensitisation and before the introduction of the dye (Fig. 11*c*). Thus comparison of the data presented permits the conclusion that compound **18** does indeed ensure the spatial insulation of the dye from the Ag_2S clusters and the explanation of the photographic effect of this compound may be the inhibition by the above 'insulating' layer of the secondary reactions involving the oxidation of the photographically active centres by the dye

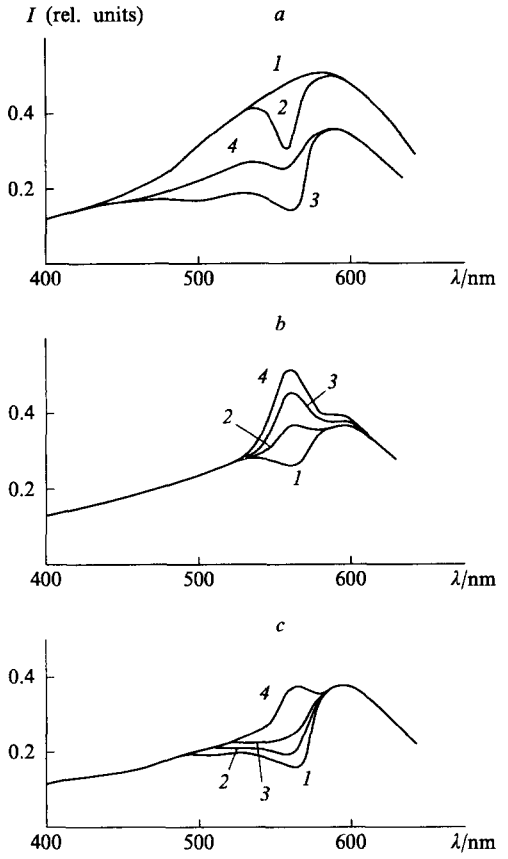


Figure 11. Dependence of the luminescence intensity of the sulfur-sensitised AgBr emulsion with λ_{max} = 800 nm on the wavelength of the light incident on layers sensitised by dye **20** [10^{-4} mol (mol AgBr)$^{-1}$]: (*a*) without a dye (curve *1*); with the dye at concentrations of 0.1 (curve *2*), 0.6 (curve *3*), and 1.0 mol (mol AgBr)$^{-1}$ (curve *4*): (*b*) with the dye and the supersensitiser **18** at concentrations of 0 (curve *1*), 0.1 (curve *2*), 0.3 (curve *3*), and 0.8 g litre^{-1} (curve *4*); (*c*) with the dye at a concentration of 6 × 10^{-5} mol (mol AgBr)$^{-1}$; thickness of the AgBr shell on the microcrystals (Å): (*1*) 0; (*2*) 10; (*3*) 15; (*4*) 30. The $I = f(\lambda)$ relations have been normalised for λ = 400 nm.

holes (Fig. 9*a*). Evidence for the insulation of the dye from the impurity centres is provided by the experiments, mentioned above, designed to elucidate the influence of the order of the introduction of compound **18** into the emulsion on the photographic and spectral characteristics of the photolayers. When compound **18** is introduced before the dye, the adsorption of the supersensitiser on the Ag_2S centres and hence their insulation from the dye *J*-aggregates are more likely. When the dye is introduced first, the *J*-aggregates apparently come into contact with the Ag_2S centres and the subsequent addition of compound **18** now has little influence on the state of the dye and its photographic effect.

The question arises of the cause of the different photographic effects of compound **18** on the dye J_1- and J_2-aggregates and in particular on the *J*-aggregates of quinomonomethinecyanine **3**. When the light quanta absorbed by the *J*-aggregates of dye **3** are of similar magnitude ($\Delta h\nu$ = 0.04 eV), this difference may be a consequence of the different oxidising capacities of the holes, which are determined both by the positions of the highest occupied electronic levels of the aggregates ε_{ho} (the energy factor) and by the length of the associated dye species and their proximity to the impurity centres (the frequency factor). An attempt to determine the position of the energy levels of the *J*-aggregates of dye **3** has been undertaken [48] using photographic and luminescence methods for the purpose. The difference between the oxidising capacities of the J_1- and J_2-aggregates has been demonstrated in a study of the photochemical oxidation of the latent image centres generated by the preliminary exposure to light of the AgBr emulsion with sulfur-gold sensitisation. *N,N'*-Dimethyl-4,4'-bipyridylium dichloride (methylviologen) was used as the photoelectron acceptor. The J_1- and J_2-aggregates were formed by the procedures described above with the aid of the stabiliser **18**. Fig. 12 presents the corresponding spectrograms. The photochemical oxidation of the latent image is most effective in layers which do not contain or contain only small amounts of compound **18**, i.e. in the presence of J_1-aggregates (Figs 12*b* and 12*c*). Photobleaching is then most pronounced in the region of the absorption maximum of the J_1-aggregates at 570 nm. On raising the concentration of compound **18**, i.e. with increase in the amount of J_2-aggregates, the effectiveness of the photobleaching falls (Figs 12*d*, 12*e*, and 12*f*). It is striking that in the region of the absorption by the J_2-aggregate (λ = 581 nm) the extent of photobleaching diminishes sharply and then is not observed at all. Furthermore, a negative image is produced (Figs 12*d* and 12*e*). The formation of the J_2-aggregate is accompanied by a decrease in the extent of photobleaching by the light corresponding to the intrinsic absorption band of AgBr (λ < 400 nm, cf. Figs 12*a* and 12*c* and Figs 12*d*, 12*e*, and 12*f*). At concentrations of compound **18** greater than 10^{-2} mol mol^{-1} AgBr, at which new J_2'-aggregates are formed (λ = 578 nm), the effectiveness of the bleaching again increases (Figs 12*g* and 12*h*). Thus the oxidising capacity of the holes of the J_1-aggregate is greater than that of the holes of the J_2-aggregate; the J_2'-aggregate apparently occupies an intermediate position.

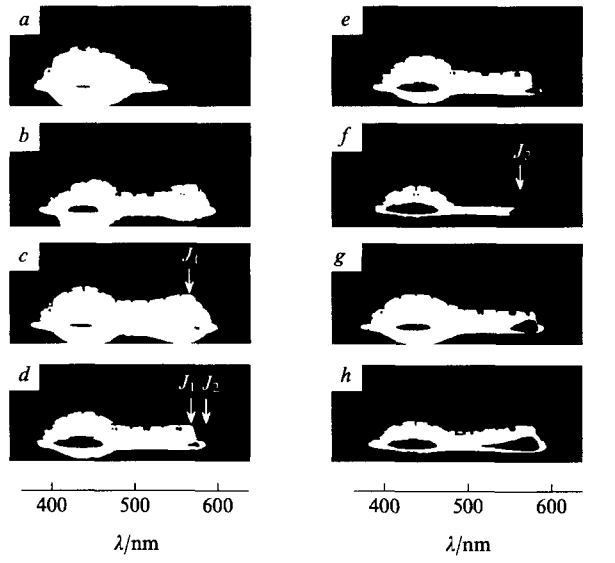


Figure 12. Photobleaching sensitisation spectra for AgBr emulsion layers without a dye (*a*), spectrally sensitised by dye **3** [2 × 10^{-4} mol (mol AgBr)$^{-1}$] without a supersensitiser (*b*), and with the supersensitiser **18** introduced before the dye at different concentrations [10^{-3} mol (mol AgBr)$^{-1}$]: (*c*) 2; (*d*) 4; (*e*) 5; (*f*) 9; (*g*) 10; (*h*) 20; emulsion with (S + Au)-sensitisation exposed beforehand to light until the attainment of a fogging level D_0 = 2.0; methylviologen concentration 7.5 × 10^{-4} mol (mol AgBr)$^{-1}$.

The question arises why the stabiliser **18** layer does not protect the latent image centres from the holes of the J_1- and J_2'-aggregates but prevents their oxidation by the holes of the J_2-aggregates. One of the explanations may be that the position of the ε_{ho} level of the J_1-aggregate is adequate for the injection of the hole directly into the silver halide, as a result of which the insulation of the J_1-aggregates from the impurity centres cannot significantly inhibit the recombination of the electrons captured by the traps in AgBr with the holes which have also been injected into AgBr. Experiments, using Gilman's method, [10] on the supersensitisation of these aggregates by the additionally introduced

carbocyanine dyes with different polarographic potentials $E_{1/2}^{Ox}$ varied in the range 0.54–0.98 V (in methanol, rel. n.c.e.) were carried out in order to characterise the disposition of the ε_{ho} levels of the J_1- and J_2-aggregates of dye **3** relative to one another and relative to the AgBr valence band. It was shown[48] that, in the case of the J_1-aggregates of dye **3**, the supersensitising dyes do not affect the spectral sensitivity over the entire range of $E_{1/2}^{Ox}$. For layers containing J_2-aggregates, a distinct supersensitisation effect is observed (Fig. 13). This is consistent with data[47] indicating the different supersensitising effects of the traditional supersensitiser 2-(*p*-dimethylaminostyryl)-benzothiazole **19** on the J_1- and J_2-aggregates of compound **3** (Table 3). For layers with J_2-aggregates over a certain range of $E_{1/2}^{Ox}(S)$, a nearly linear dependence of the logarithm of the supersensitisation coefficients lg K_s on $E_{1/2}^{Ox}(S)$ is observed (Fig. 13). For a potential $E_{1/2}^{Ox}(S) \geqslant 0.82$ V, there is no supersensitisation effect and this value was therefore chosen as a characteristic of the position of the ε_{ho} level of the J_2-aggregate. The conclusion that the ε_{ho} level of the J_1-aggregate is deeper (by 0.10–0.15 eV) than the ε_{ho} level of the J_2-aggregate was reached on the basis of experiments on the quenching of the fluorescence of the aggregates by the same supersensitising dyes.[48] The ε_{vb} level of the J_1-aggregates was estimated in terms of the potential $E_{1/2}^{Ox}(J_1) \approx 0.9-0.95$ V. If one assumes, in conformity with the data of Mikheeva et al.,[57] that the potential of the top of the valence band of AgBr is $E_{vb} = 1.26$ V (rel. n.c.e.), then, in conformity with the data of Shapiro et al.,[48] the time required for the injection of a hole from the J_1-aggregate into the valence band of AgBr is $\tau = 10^{-7}$ s. For the J_2-aggregate, this time is much longer ($\sim 10^{-4}$ s). Thus the injection of a hole from the J_1-aggregate of dye **3** into AgBr is entirely probable.

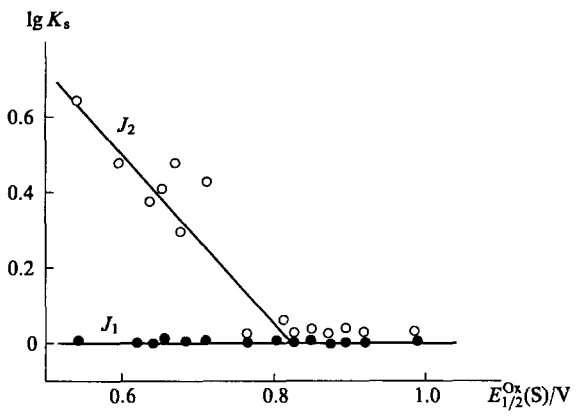


Figure 13. Dependence of the logarithm of the supersensitisation coefficient (lg K_s) for AgBr emulsion layers spectrally sensitised by dye **3** [2×10^{-4} mol (mol AgBr)$^{-1}$] in the J_1- and J_2-states on the potential $E_{1/2}^{Ox}$ of the supersensitiser dyes [4×10^{-6} mol (mol AgBr)$^{-1}$].

In view of the foregoing, it is important to revise the conditions for the supersensitisation via Gilman's 'reductive' mechanism. When rapid injection of holes from the *J*-aggregate into AgHal is possible, supersensitisers satisfying Gilman's condition $E_{1/2}^{Ox}(S) < E_{1/2}^{Ox}(Dy)$ may have insufficient time to capture a dye hole owing to kinetic limitations. The conditions for supersensitisation via the 'reductive' mechanism have been expressed[48] in the form 0.8 V $> E_{1/2}^{Ox}(S) < E_{1/2}^{Ox}(Dy)$.

Thus a dual influence on the spectral sensitisation processes is characteristic of the hydroxy-derivative of tetraazaindene **18**. This compound promotes the formation of *J*-aggregates of certain types. It has been noted[63] that the formation of the dye *J*-aggregates begins on defects and primarily on AgHal surface steps. The rate of formation of aggregates is then higher and their size is smaller (absorption at shorter wavelengths) on the more defective (111) surface than on the (100) surface. The influence of surface defects on the formation of *J*-aggregates has been fully accounted for from the standpoint of the initiation of a regular structure such as the *J*-aggregate.[7] Apparently the stage involving the initiation of aggregates, requiring a definite activation energy, determines to a large extent the aggregation process itself. Surface defects diminish its energy.

One should recall that surface defects are the sites at which impurity centres are located, including photosensitivity centres formed in the sulfur sensitisation process.[7] One may assume that the introduction of compound **18** at low concentrations leads to the insulation of a comparatively small number of 'deep' defects by the molecules of compound **18** adsorbed on them and that *J*-aggregates are formed on a large number of 'fine' surface defects, which leads to the formation of the smaller J_1-aggregates. We may note that without compound **18** *J*-aggregates are formed on both 'deep' and 'fine' defects, which is the reason for the appearance of a single band with $\lambda_{max} = 575$ nm, arising as a consequence of the superposition of the absorption bands due to at least two *J*-aggregates.

On further increase in the concentration of compound **18**, the tetraazaindene molecules are adsorbed also on finer defects as a result of which the number of these defects diminishes, which promotes the formation of the larger J_2-aggregates. Finally, for a still higher content of compound **18**, the defectiveness of the surface diminishes so much that new J_2'-aggregates are formed on a larger number of surface sites—defects of another type. Thus the stabiliser **18** is a regulator of the defectiveness of the AgHal surface and hence a regulator of the aggregation of the dye.

As a consequence of the causes discussed above, the stabiliser **18** influences the energy levels of the *J*-aggregates. The observed changes in the energy levels of the *J*-aggregates of the same dye either depend on the different numbers of molecules combined in the aggregate or may be determined by the angle of inclination of the molecules in the aggregate.[7] As a rule, an increase in the number of molecules and a decrease in the angle of inclination lead to a bathochromic shift of the absorption owing to the increased length of the delocalised π-system. If the main cause of the difference between the properties of the *J*-aggregates is the number of molecules in the aggregate, then this can be regarded as evidence for a small number of structural elements entering into the polymer, since only in this case should one expect a significant difference between the energetics of the aggregates on increase in their size. This agrees, in particular, with the conclusions reached in studies[97,98] in which *J*-aggregates comprising four dye molecules were considered. *J*-Aggregates consisting of tens or several tens of molecules have been considered in the literature.[7,99]

Fig. 14 presents a photomicrograph of luminescing *J*-aggregates of oxacarbocyanine on a real cubic 1 μm AgBr crystal.[100] It follows from the figure that, at the dye concentrations employed in practice, the *J*-aggregates are preferentially extended in one direction and their size is small.

The lower photographic effectiveness of the J_1-aggregates in the negative process compared with the J_2-aggregates[47] is determined by the deeper disposition of both the highest occupied level ε_{ho} and the lowest unoccupied level ε_{lu} (since the J_1- and J_2-aggregates absorb approximately the same energy). A consequence of the deepening of the ε_{ho} level is the injection of holes into the valence band of AgHal and an increase in the probability of secondary recombination processes, including, as shown by Shapiro and his coworkers,[48] the oxidation of the latent image centres. Owing to the high rate of injection of holes into AgHal, under these conditions the supersensitisers operating in accordance with Gilman's mechanism are apparently unable to capture a dye hole. According to luminescence data,[48,101] the ε_{lu} levels of the *J*-aggregates of dye **3** are located under the conduction band of AgBr. A decrease in the ε_{lu} level in the J_1-aggregate therefore reduces also the probability of the photochemical reduction of AgHal via electron transfer either to the conduction band or to the surface capture levels. Despite the absence of the direct injection of holes from the J_2-aggregate into

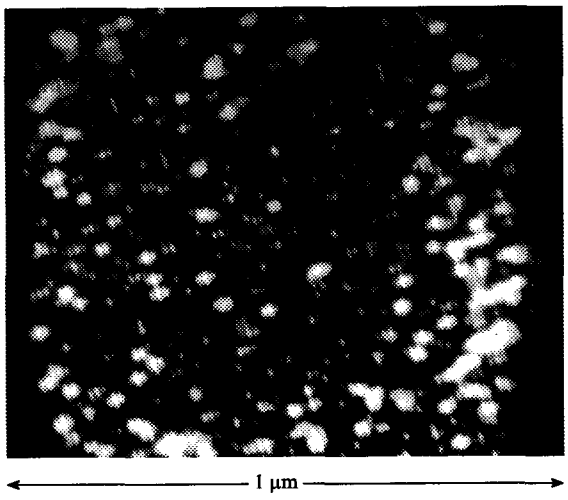
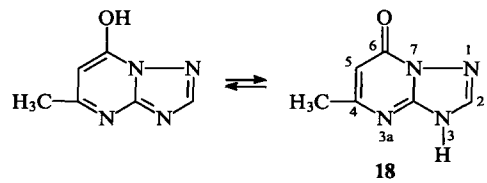


Figure 14. Photomicrograph of luminescing *J*-aggregates of oxacarbocyanine on a 1 μm cubic AgBr microcrystal.

the valence band of AgBr and the higher location of ε_{lu}, the photographic effectiveness of these aggregates is also low in the absence of compound **18**.[47] This indicates the occurrence of secondary reactions involving the recombination of photoelectrons and holes without the participation of the valence band of AgBr. As already noted, the recombination reactions or dye self-desensitisation processes proceeding via a hole mechanism[8,25,26] are apparently determined to a large extent by the presence of direct contact between the *J*-aggregates and the impurity of sulfide-silver centres (Fig. 5*c*). This contact may be a consequence of the localisation of the impurity centres on the surface defects, i.e. the sites where *J*-aggregation begins. Another possible cause is increased adsorption of the dyes on the Ag_2S centres themselves.

Owing to the specific adsorption on Ag_2S, the stabiliser **18** insulates the J_2-aggregates from the impurity centres and hence inhibits the self-desensitisation reactions of the dyes in accordance with the scheme in Fig. 9*a*. Additional evidence in support of the 'insulation' mechanism has been obtained in experiments on the inhibition by compound **18** of the type II selective desensitisation caused by the use of compositions comprising two *J*-aggregating dyes,[68] which was considered in Section III (see Figs. 3 and 4). If the selective desensitisation is associated, in conformity with Fig. 5*b*, with the translation of a hole of the highly effective dye **4** through the *J*-aggregate of dye **1** in contact with the IC_e and hence with the increase in the probability of the recombination processes at the IC_e, then the insulation of the impurity centres in the *J*-aggregates should sharply diminish the selective desensitisation. Indeed it has been shown[68] that the introduction of the sta-salt before the introduction of the **1** + **4** and **1** + **14** dye compositions suppressed the selective desensitisation to a large extent at wavelengths corresponding to the absorption bands of dyes **4** and **14** (Fig. 15). It follows from a comparison of Figs. 4 and 15 that, in the presence of compound **18**, a sharp increase in sensitivity is observed at the wavelengths corresponding to both absorption bands of dye **14** (λ_{max} = 518 and 590 nm) despite the presence of dye **1** in the photographic layer (cf. curves *3* in Figs. 4*b* and 15*b*). This constitutes another piece of evidence indicating that these bands belong to the same dye *J*-aggregate. A similar picture has been observed for the **6** + **14** dye composition. It is striking that the supersensitisation effect at the wavelengths corresponding to the bands of dyes **14** and **4**, estimated in terms of K_s, is close to the selective desensitisations (SD_λ),[68] on the basis of which one may conclude that the supersensitisation is definitely associated with the inhibition of the selective desensitisation and in the general case with the self-desensitisation of the dye. Thus the translation of a hole of one dye through the *J*-aggregate of another becomes ineffective probably owing to the insulation of the *J*-aggregates from the impurity centres, which is illustrated schematically in Fig. 9*b*.

The question arises what determines the specific adsorption of compound **18** on the sulfide-silver centres which imparts unique properties to this stabiliser and supersensitiser. In order to discover the structural element in the molecule of compound **18** promoting the 'insulating' effect, model experiments were performed with heterocyclic compounds having structural elements in common with the sta-salt.[102] The structural formulae of some of them are presented below.



18

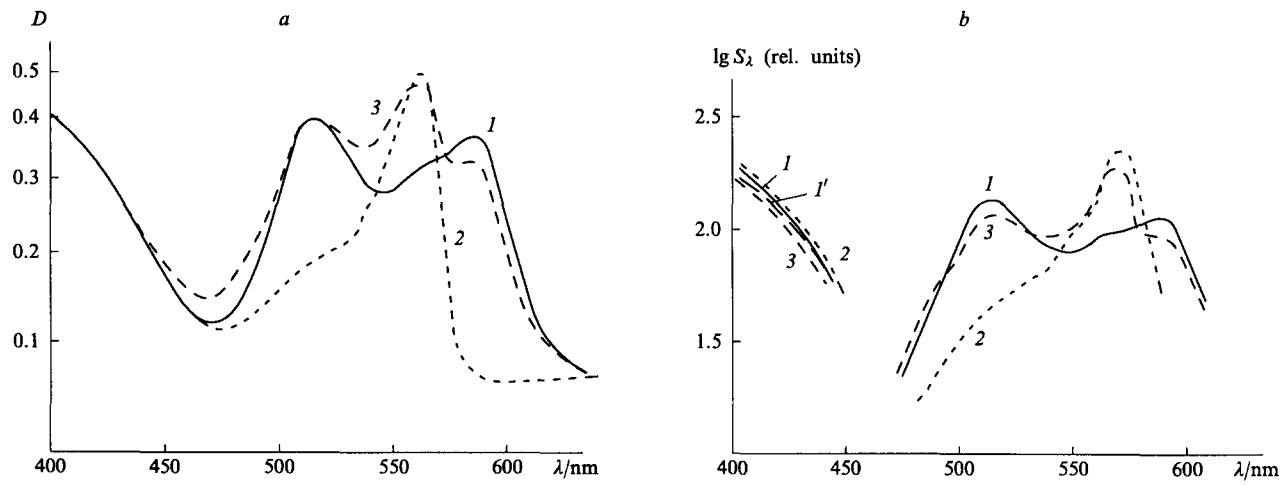
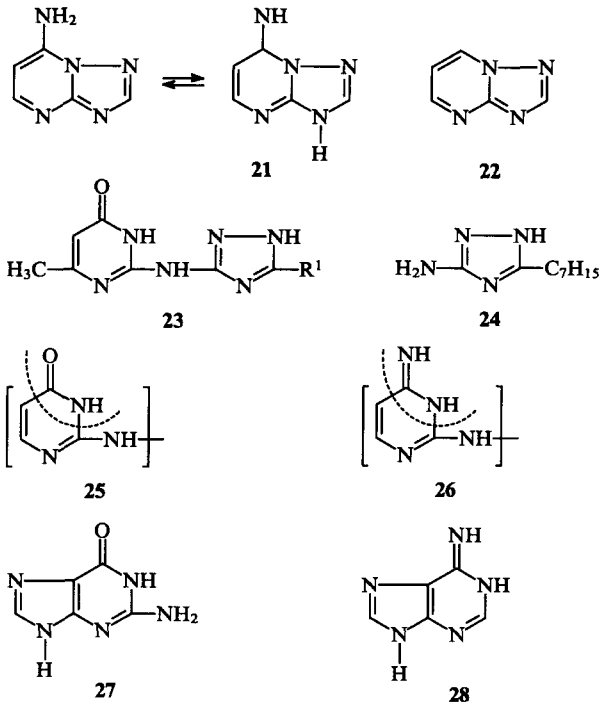


Figure 15. Reflection spectra (*a*) and spectral sensitivity distribution curves (*b*) for AgBr emulsion layers containing the supersensitiser **18** and sensitised by dyes **14** (curve *1*) and **1** (curve *2*) and the **1** + **14** dye composition (curve *3*); (*1'*) layer without dye. Concentration of compound **18**—8 × 10^{-3} mol (mol AgBr)$^{-1}$; concentration of dyes—2 × 10^{-4} mol (mol AgBr)$^{-1}$.



The structural formula with a carbonyl oxygen atom is best justified for compound **18**.[103,104] The study was carried out on fine-grain monodisperse AgBr emulsion [cubic crystals, $\bar{l}$ = 0.17 μm, (S + Au)-sensitisation spectrally sensitised by dye **1**; dye concentration 2 × 10^{-4} mol (mol AgBr)$^{-1}$]. According to the results presented above, the *J*-aggregates of this dye are appreciably supersensitised by compound **18**. The concentration of the substances introduced into the emulsion before the dye was varied over a wide range [from 10^{-4} to 10^{-2} mol (mol AgBr)$^{-1}$].

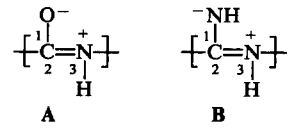
It has been shown that the replacement of the CH_3 group in the 6-position in compound **18** by hydrogen and also the introduction of alkyl groups (up to n-C_7H_{15}) in the 2- and 5-positions do not affect fundamentally the supersensitisation effect. The replacement of the hydroxy-group in the 4-position in compound **18** by an amino-group (compound **21**) also did not change significantly the results, which is illustrated by the supersensitisation coefficients presented in Table 4. On the other hand, compound **22** (without a hydroxy-group) was photographically inactive. Experiments with compound **23** (R^1 = H, CH_3, n-C_7H_{15}, C_6H_5) in which the triazole ring is not condensed with the rest of the molecule, demonstrated their photographic activity, although these compounds were in fact inferior to compound **18** as regards the supersensitising effect. 5-Amino-1,2,4-triazole **24**, which is a fragment of compound **23** (R^1 = C_7H_{15}), by itself had little effect in the concentration range investigated.

Table 4. Photographic effect of compounds **18**, **21**–**24**, **27**, and **28** on layers sensitised by imidacarbocyanine **1**.[102]

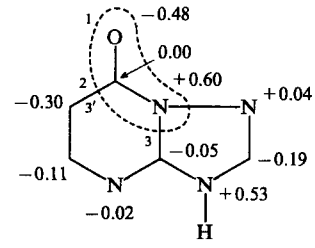
Compound	10^4c/mol (mol AgBr)$^{-1}$	K_s	D_0	λ_{max}^{sens}/nm
Control	–	1.0	0.10	568
18	60	8.0	0.20	571
21	60	7.0	0.26	571
22	60	0.8	0.16	568
23 (R^1 = n-C_7H_{15})	60	3.5	0.11	569
24	60	1.4	0.12	567
27	30	4.8	0.30	569
28	30	6.0	0.20	569

On the basis of the experiments presented, it proved possible to locate extremely approximately the photographically active group within the limits of fragments **25** and **26**. The results obtained with purine bases (guanine **27** and adenine **28**), the structure of which contains the fragments **25** and **26** mentioned above, served as indirect confirmation of this finding. According to the data presented in Table 4, these compounds also have a supersensitising effect on layers with dye **1**.

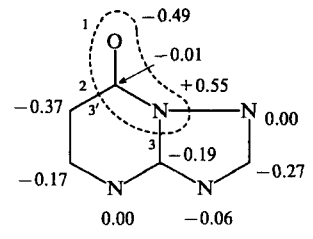
It has been postulated, with a certain amount of caution,[62] that the photographic activity of compounds containing the fragments **25** and **26** is associated with the presence of amide (**A**) or amidinium (**B**) 1,3-dipolar structures.



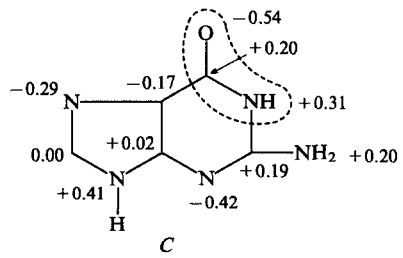
Molecular diagrams of the distribution of π-electron density in the molecule of compound **18** (*A*) and in its anion (*B*), calculated by the molecular orbital method in terms of the Hückel approximation (MOH), are presented below.[62] The parameters taken from Streitwieser[105] were adopted for the Coulombic and exchange integrals. The calculations for the anion of compound **18** were carried out because the anion has in fact been considered in the literature[104] as the photographically active form of compound **18**.



A



B



C

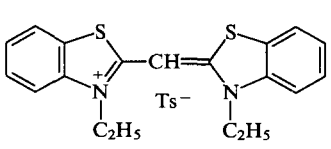
According to molecular diagrams, structures *A* and *B* both contain distinct 1,3-dipoles with a marked localisation of the charges on the oxygen and nitrogen. A characteristic feature of the structures examined is also the presence of a large negative charge on the C(3′) atom of the pyrimidine ring, i.e. a second 1,3-dipole incorporating N(3) and C(3′). A similar pattern in the distribution of π-electron density in guanine has been presented by Pullman and Pullman.[106] The diagram of the π-charges (*C*), calculated by the MOH method, also contains a 1,3-dipole.

The presence of 1,3-dipolar structures is apparently an essential but not a sufficient condition for the photographic activity of the compound. The inclusion of such groups (one or several) in the cyclic system probably promotes the manifestation of supersensitising properties associated with the specific adsorption on the Ag_2S centres.

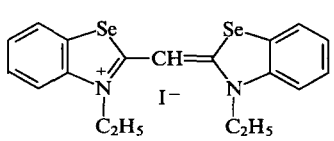
The stabiliser **18** is not the only compound oxidised with difficulty which exerts a supersensitising effect on the dye *J*-aggregates. For example, the application for supersensitisation of compounds, which are clearly oxidised with greater difficulty than the dyes which they supersensitise, has been described in a series of patents mentioned in Mudrovčič's review.[9] It was shown in the early studies by Scheibe and coworkers[17,107] that, together with the readily oxidisable bases of styryl dyes, thiamonomethinecyanine, the polarographic oxidation potential of which ($E_{1/2}^{Ox}$ = 1.20 V) exceeds significantly the potential of quinomonomethinecyanine **3** ($E_{1/2}^{Ox}$ = 0.99 V in CH_3OH rel. Ag/AgCl electrode), has a supersensitising effect on quinomonomethinecyanine **3** *J*-aggregates.[108] We confirmed that certain monomethinecyanines supersensitise the *J*-aggregates of dye **3**; under these conditions, a bathochromic shift of the absorption band maximum of the *J*-aggregate is observed, as for compound **18**.[109] It has been suggested that in this case the 'insulation' supersensitisation mechanism operates.[62,109] It is essential to note that the application of monomethinecyanines as well as quaternary salts of heterocyclic bases as substances increasing the spectral sensitivity of AgHal emulsions sensitised by cyanine dyes has been claimed in a series of patents in the 1970s–1980s (see, for example, Refs 110–113).

The photographic effect of such compounds has been studied in detail.[114] The experiments were performed on a monodisperse AgBr emulsion with cubic microcrystals ($\bar{l}$ = 0.17 μm) with sulfur-gold sensitisation. The principal studies were carried out on two *J*-aggregating dyes — quinomonomethinecyanine **3** and imidacarbocyanine **1**. The choice of these two particular dyes was determined by the following factors. Firstly, following adsorption on AgBr microcrystals, both dyes form *J*-aggregates with similar absorption maxima — λ_{max}(**3**) = 575 nm and λ_{max}(**1**) = 568 nm. Secondly, they have significantly different potentials $E_{1/2}^{Ox}$ ($\Delta E_{1/2}^{Ox}$ = 0.44 V), which should affect the type (II) hole self-desensitisation processes.

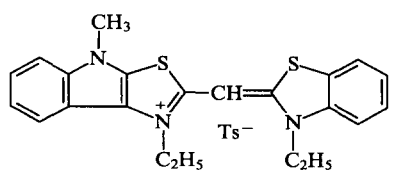
Numerous monomethinecyanines, merocyanines, and styryl dyes have been investigated as supersensitisers. However, the most detailed study has been made of the photographic effect of the four supersensitiser dyes (Dy-S) **29**–**32**. The polarographic potentials of these supersensitiser dyes are presented in Table 5.



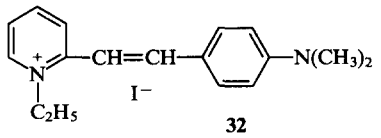
29



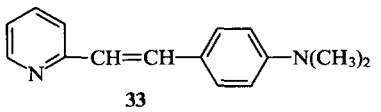
30



31



32



33

Table 5. Characteristics of the dyes investigated[144] (potentials in acetonitrile rel. n.c.e.).

Compound	$E_{1/2}^{Ox}$/V	$-E_{1/2}^{Red}$/V
3	0.94	1.15
1	0.50	1.77
29	1.21	1.52
30	1.21	1.53
31	0.75	1.84
32	0.73	1.24
33	0.60	1.50
19	0.60	1.62

It follows from Table 5 that the supersensitiser dyes **29** and **30** are oxidised with greater difficulty than dye **3** and in addition all the supersensitisers **29**–**32** investigated are oxidised less effectively than dye **1**. The supersensitiser dyes were introduced into the emulsion over a wide range of concentrations [(0.5–8) × 10^{-4} mol (mol AgBr)$^{-1}$] before the *J*-aggregating dyes. Their effect was compared with that of compound **18** and also with the effect of readily oxidisable bases of the styryl dyes **19** and **33** (Table 5) acting on the layers containing dye **3** via Gilman's 'reductive' mechanism.[10]

The main result of the investigation[114] was that the supersensitiser dyes, also oxidised with greater difficulty than dyes **3** and **1**, gave rise to the supersensitisation effect in photographic layers with *J*-aggregates of both spectral sensitisers. It is striking that a definite analogy was observed between the spectral and photographic effects of these supersensitiser dyes and compound **18**. When thiamonomethinecyanine **29** is introduced into the emulsion, the same transformation of the spectra as that occurring after the addition of compound **18** is observed, namely at comparatively low concentrations of compound **29** the maximum of the main absorption band initially undergoes a hypsochromic shift, then, as the concentration is increased, two absorption bands due to two *J*-aggregates (J_1 and J_2) are observed simultaneously, and finally, after further rise in concentration, the longer-wavelength band of the J_2-aggregate is established. The appearance of J_2-aggregates is accompanied by an increase in the effectiveness of the spectral sensitisation by dye **3**. A similar pattern in the changes in the spectra of dye **3** has been observed on treatment with supersensitisers **30**–**32**.

The supersensitising effect is also characteristic of other short-wavelength dyes **30**–**32** investigated (Fig. 16), the maximum effect being obtained for compounds **31** and **32** (by a factor of 5–6). The observed effect of the monomethinecyanines **29** and **30** (in conformity with the potentials $E_{1/2}^{Ox}$), which are difficult to oxidise, cannot be accounted for within the framework of Gilman's 'reductive' mechanism. On the other hand, the capture of a hole from dye **3** is possible for the supersensitiser dyes **31** and **32** in conformity with the potentials $E_{1/2}^{Ox}$ listed in Table 5. However, one should note that, in contrast to the typical supersensitiser **19** (according to Gilman), these dyes induce a significant transformation of the *J*-bands already noted above.

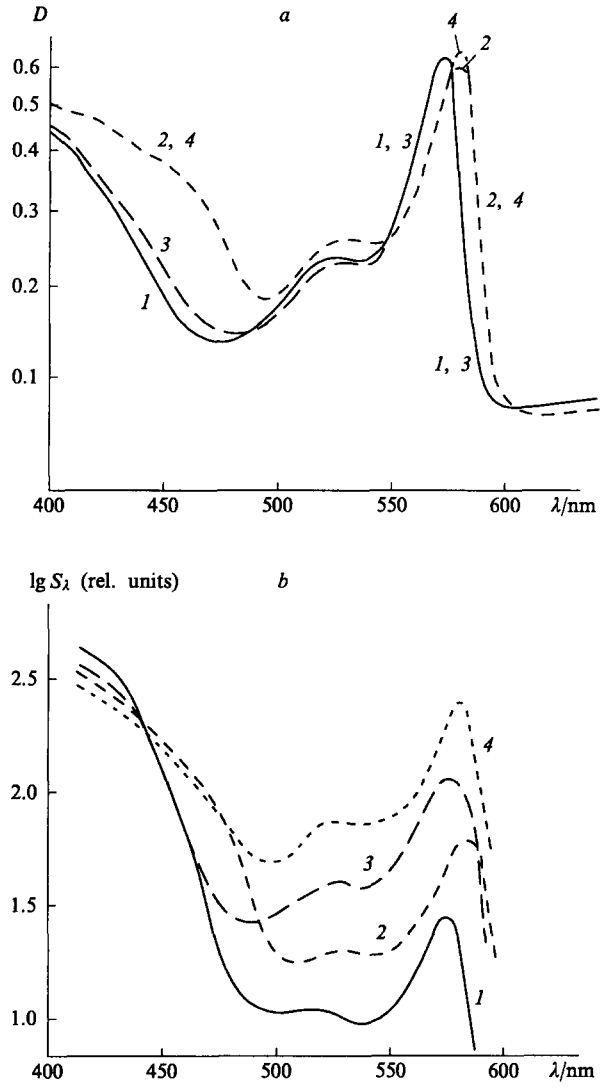


Figure 16. Reflection spectra (*a*) and spectral sensitivity curves (*b*) for AgBr emulsion layers spectrally sensitised by dye **3** [2 × 10^{-4} mol (mol AgBr)$^{-1}$] without a sensitiser (curve *1*) and in the presence of other dyes: (*2*) dye **30** at a concentration of 4 × 10^{-4} mol (mol AgBr)$^{-1}$; (*3*) dye **19** at a concentration of 0.5 × 10^{-4} mol (mol AgBr)$^{-1}$; (*4*) the **30** + **19** composition at concentrations of 4 × 10^{-4} and 0.5 × 10^{-4} mol (mol AgBr)$^{-1}$.

The results of experiments in which compositions of difficult to oxidise supersensitiser dyes with styryl bases **19** and **33** ($E_{1/2}^{Ox}$ = 0.60 V) were used to provide evidence for another mechanism of the influence of compounds **29** and **30** (a non-Gilman mechanism). As with compositions comprising compounds **18** and **19** in earlier studies[47] (Fig. 7 and Table 3), a supersensitisation effect greatly exceeding the effect of the individual substances was observed for the supersensitiser compositions under these conditions. One of the examples of such superadditive effect of compounds **30** and **19** is presented in Fig. 16 (cf. curves *1*–*4*, Fig. 16*b*). It is striking that, in contrast to selenamonomethinecyanine **30**, the styryl base **19** does not alter the position of the *J*-band of the dye (cf. curves *1*, *2*, and *3*, Figs 16*a* and 16*b*). A similar effect has been observed also for the styryl dye **32** and the corresponding base **33**.

The study of the photographic effect of compositions comprising the stabiliser **18** and the supersensitiser dyes **29** and **30** which are difficult to oxidise demonstrated the absence of an additive supersensitisation effect by the compositions, which can be regarded as evidence that the components of the compositions exert an influence of the same type.

The supersensitisation by compounds which are difficult to oxidise is manifested even more clearly on layers with imidacarbocyanine **1**. In this case, all the supersensitisers **29**–**33** were oxidised with greater difficulty than the *J*-aggregating dye **1** (cf. $E_{1/2}^{Ox}$ in Table 5). When compounds **29**–**32** as well as compound **18**[49] are introduced into the emulsion, a characteristic transformation of the *J*-band, analogous to that occurring under the influence of compound **18**, and an increase in the effectiveness of the spectral sensitisation (by a factor up to 5) are observed. Fig. 17 presents examples of the supersensitising effect of the monomethinecyanines **29** and **30**. The introduction of these dyes before the *J*-aggregating dye **1** leads to a bathochromic shift of the absorption bands and to an increase in the spectral sensitivity of the layers (cf. curves *1*–*3*, Figs 17*a* and 17*b*).

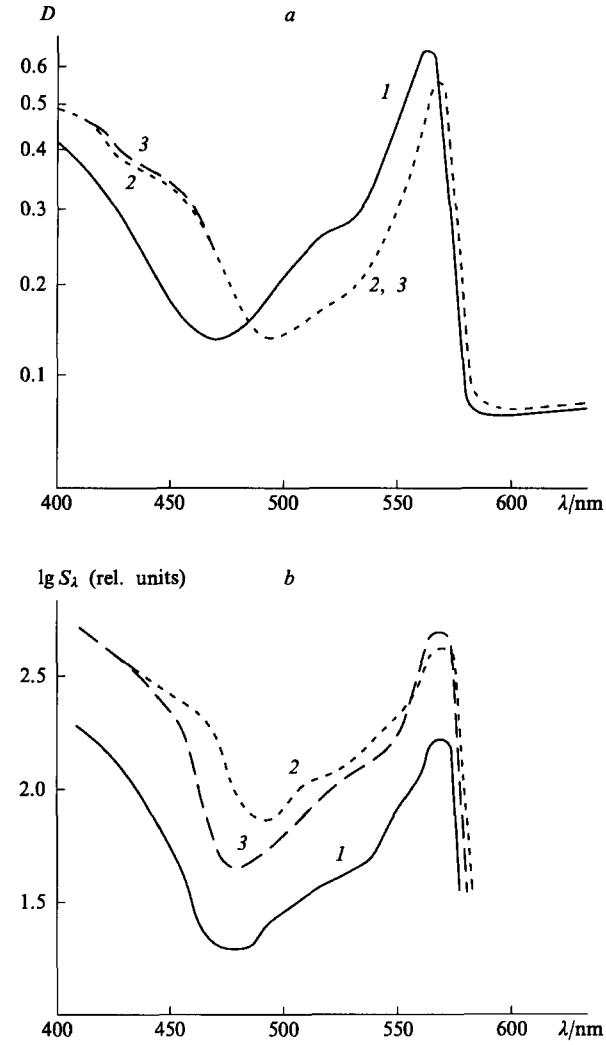


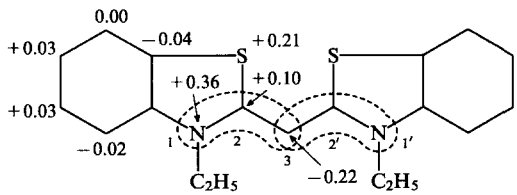
Figure 17. Reflection spectra (*a*) and spectral sensitivity curves (*b*) for AgBr emulsion layers spectrally sensitised by dye **1** [2 × 10^{-4} mol (mol AgBr)$^{-1}$] without a sensitiser (curve *1*) and in the presence of selenamonomethinecyanine **30** (curve *2*) and thiamonomethinecyanine **29** (curve *3*); concentration of the supersensitiser — 4 × 10^{-4} mol (mol AgBr)$^{-1}$.

Since dye **1** is itself a readily oxidised compound ($E_{1/2}^{Ox}$ = 0.50 V), it is hardly subjected to a supersensitising influence by the typical supersensitiser **19** ($E_{1/2}^{Ox}$ = 0.60 V) described in the literature;[10] on the other hand, all the dyes investigated belonging to the classes of monomethinecyanines, merocyanines, and styryl dyes, which are known to be oxidised with greater difficulty than dye **1**, lead to an appreciable increase in the effectiveness of the sensitisation at the wavelength corresponding to the *J*-band of

imidacarbocyanine. It is quite natural that there is also no additive increase in the sensitivity for compositions of the supersensitiser dyes **29** and **30** with the styryl base **19**.

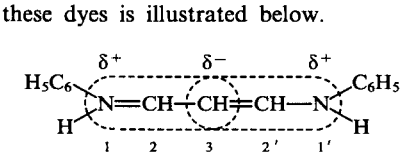
The change in the spectra and in the photographic effect of the difficult to oxidise dyes investigated, similar to the influence of compound **18**, permits the conclusion that the nature of their photographic effect is the same, namely that it entails a single 'insulation' supersensitisation mechanism. This is probably due to the preferential adsorption of dyes belonging to the classes of thia(selena)monomethinecyanines, styryl dyes, and merocyanines on the Ag_2S centres. The selective adsorption of dyes and of the sta-salt on the Ag_2S lattice may be associated with the significant difference between the parameters of this lattice and those of the AgHal lattice and also with the specific properties of the Ag_2S centres having a high concentration of mobile silver ions according to Van Doorselaer's hypothesis.[115] The superionic properties of Ag_2S were examined by Kartuzhalskii et al.[116]

It had been postulated earlier in relation to the sta-salt and its analogues[102] that the selective adsorption of the supersensitiser on the Ag_2S centre may be due to the presence of 1,3-dipolar structures. It is striking that distinct 1,3-dipolar fragments are present in the molecules of cyanines and in the first place monomethinecyanines. According to the molecular diagram for the distribution of π-electron density in thiamonomethinecyanine **29**,[62] calculated by the PPP method, there are several 1,3-dipoles in the supersensitiser dye, including the nitrogen and sulfur atoms of the heterocyclic nuclei and the methine carbon atom.

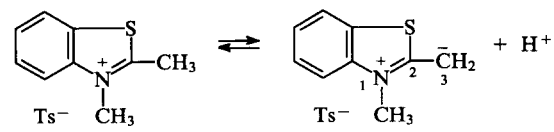


It is striking that the distance between the sulfur atom and the methine carbon atom (~2.6 Å) is close to the distance between the Ag^+ and S^{2-} ions in the Ag_2S clusters (2.58 Å on the AgBr surface).[117] It is significantly smaller than the distance between the Ag^+ and Br^- ions in the AgBr lattice (~2.9 Å). Thus the selective adsorption of organic compounds containing 1,3-dipoles may be due to the correspondence of the distance between the charge centres in the 1,3-dipoles and the distance between the Ag^+ and S^{2-} ions in the Ag_2S clusters.

Experiments with the simplest streptocarbocyanines, also containing 1,3-dipoles in their structure, showed that their introduction into an emulsion sensitised by dye **1** leads to a fourfold increase in additional sensitivity. The increase in sensitivity is accompanied by a bathochromic shift of the *J*-band. The alternation of the π-electron density in the most effective of these dyes is illustrated below.



The supersensitising effect of a quaternary benzothiazole salt (2-methylbenzothiazolium toluene-*p*-sulfonate **34**) has been noted,[114] although it is significantly lower than that of the supersensitiser dyes **29**—**32**. It is well known that the quaternary salts of thiazoles, exhibit, like compound **18**, antifogging and stabilising effects on photographic emulsions.[118] The supersensitisation by the quaternary salt of 2-methylbenzothiazole may be a consequence of the acid properties of the salt, in which a 1,3-dipole may arise after dissociation in accordance with the scheme below.



34

It was noted at the beginning of this review that the first publication by Bloch and Renwick on supersensitisation described the appreciable photographic effect of auramine on layers sensitised in the panchromatic region of the spectrum.[14] We confirmed the sensitising effect of auramine G on layers with the *J*-aggregating dye **1**. Like compound **18**, auramine induces a bathochromic shift of the band of the aggregate. According to the molecular π-electron distribution diagram, calculated by the MHO method, the molecule of auramine G contains 1,3-dipolar fragments and supersensitisation by this dye can therefore also be considered within the framework of the 'insulation' mechanism.

The special role of surface defects in the 'insulation' supersensitisation mechanism necessitated the development, as the next task, of a method which would make it possible to infer the interaction of spectral sensitisers and supersensitisers with the impurity centres formed on chemical sensitisation. The fogging effect of a phenothiazine dye—Methylene Blue (MB)—has been described.[119–121] Eggert and Reitstötter[119] as well as Steigman[120] attribute the fogging to the catalysis of electron transfer from the developer to AgHal involving the adsorbed MB^+ cation. Dähne[121] explains the fogging as a result of the formation of MB^+ dimers following their adsorption on AgHal. It has been noted[119,120] that other sulfur-containing dyes as well as the sulfur-free dye Janus Green also exhibit a fogging capacity.

Preliminary experiments carried out on a monodisperse AgBr emulsion containing cubic microcrystals with sulfur-gold sensitisation showed that the introduction of MB in an amount of $(1-5) \times 10^{-5}$ mol (mol AgBr)$^{-1}$ induces an intense increase in the fog density D_0, from 0.12 to 2.0—4.0, when unexposed emulsions are treated in UP-2 developer (development time 8 min). Naturally, an appreciable desensitisation is also observed under these conditions. It is striking that there was virtually no fogging at the same MB^+ concentrations on the same emulsion not subjected to the (S + Au)-sensitisation. However, in the course of chemical sensitisation, the fogging due to the MB steadily increased[122] with increase in sensitivity, the latter being attributed to the formation of electron-accepting Ag_2S sensitivity centres.[59]

Thus fogging is undoubtedly associated with the presence of Ag_2S centres, formed on sulfur and sulfur-gold sensitisation. One can therefore assume that the fogging effect of MB^+ is caused by its adsorption not on silver halides, as claimed by Eggert and Reitstötter,[119] but on impurity Ag_2S centres (IC_e). The adsorption of MB^+ can be associated with the presence of 1,3-dipoles in the structure of the phenothiazine dye. As a result of the specific adsorption of the electron-accepting MB^+ on the IC_e, there is a possibility of catalysis of the electron transfer from the developer to the Ag_2S centre and further to AgHal. This is illustrated schematically in Fig. 18 (see over), according to which direct electron transfer from the developer (Red) to the Ag_2S centre is kinetically hindered owing to the high energy barrier corresponding to the activation energy E_{act} (Fig. 18*a*). As a result of the specific adsorption of MB^+ on the Ag_2S centre, the electron transfer reaction is divided into two stages, the first of which is electron transfer from Red to MB^+. Owing to the lower activation energies for the two stages (E'_{act} and E''_{act}) compared with E_{act}, catalysis of the oxidation-reduction reaction, expressed by the fogging of the photolayers, is observed (Fig. 18*b*). According to the data of Eggert and Reitstötter,[119] the dye Janus Green also exhibits a fogging capacity. It has likewise been demonstrated that electron-accepting pyrylo- and thiapyrylo-monomethinecyanines are effective fogging agents.

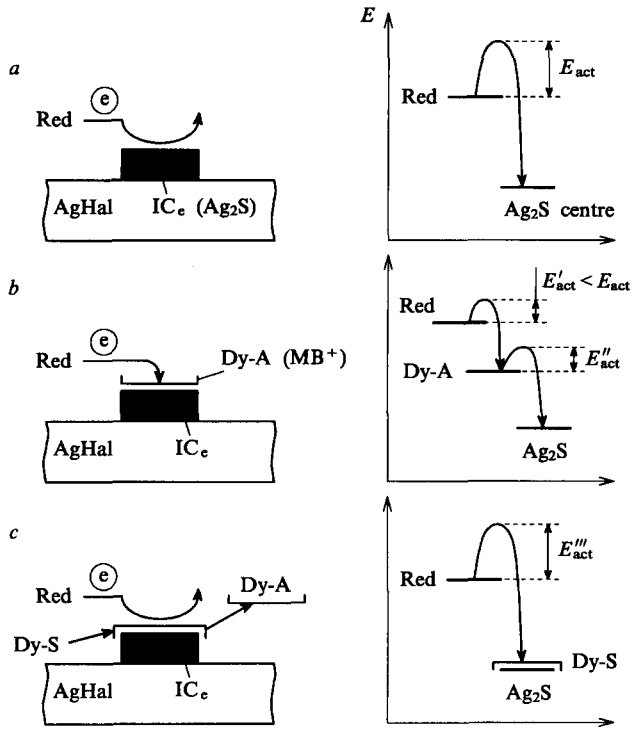


Figure 18. Schematic representation of the catalysis of electron transfer from the developer (Red) to the Ag_2S centre (IC_e) with the aid of an electron acceptor dye (Dy-A) and of the inhibition of the transport process by the supersensitiser dye (Dy-S).

By use of the specific adsorption of MB^+ and other electron-accepting dyes on the Ag_2S centres, manifested by the fogging of the AgBr and AgBr(I) photographic emulsions, experiments designed to investigate the influence of a series of supersensitisers, operating, in conformity with our ideas, via the 'insulation' mechanism, on the fog within the photolayers, have been carried out.[62,122] For the selective adsorption of the supersensitisers on the Ag_2S centres, one should expect the desorption of the fogging dyes from these centres and hence a decrease in fogging. Experimental methods involved the initial introduction of supersensitisers into the AgBr emulsion in amounts inducing the supersensitisation of the *J*-aggregating dyes, with subsequent addition of MB or another fogging dye at concentrations leading to a fog level $D_0 = 2.0-3.0$ within the layers. Supersensitiser dyes **29** and **30** have been studied in greatest detail.

Indeed the introduction of thia- and selena-monomethinecyanines **29** and **30** suppresses sharply the fogging in the photolayers due to MB. It is striking that it is not associated with the desorption of MB from AgBr because the desensitisation of the emulsion not only does not diminish under these conditions but sometimes actually increases. The influence of the stabiliser **18** on fogging is weaker than that of monomethinecyanines. Like monomethinecyanines, auramine G also suppresses the fogging induced by MB, i.e. its effect is similar to that of cyanines.

The explanation of the antifogging effect of supersensitisers can also be associated with the displacement of MB^+ from the impurity centres, with the increase in the activation energy for the redox reaction E''_{act}, and with the inhibition of the catalysis. This is illustrated schematically in Fig. 18*c*. Thus, on the basis of the experimental data obtained one may conclude that the supersensitisers are adsorbed selectively on the Ag_2S centres and hence that the 'insulation' supersensitisation mechanism really operates.

It is essential to note that, in the course of the development of methods designed to demonstrate the existence of the 'insulation' supersensitisation mechanism, the present author[122] observed in essence a new phenomenon—catalysis by dyes and reactions involving electron transfer from reductants to Ag_2S impurity centres. Whereas in the classical photographic negative process, the catalysis is effected by the Ag_n^+ silver species, formed on the Ag_2S centres following exposure, in the present instance the catalyst is the electron-accepting dye molecule having a specific affinity for the impurity centre. The possibility of the inhibition of the catalysis (negative catalysis) with the aid of substances competing with the acceptors for specific adsorption sites is no less important.

It must be emphasised that monomethinecyanines and other dyes can function not only as supersensitisers but also as stabilisers as well as antifogging agents in photographic emulsions as a consequence of their specific adsorption on the Ag_2S centres. The results obtained lead to the expectation that the stabilising capacity of cyanine dyes is higher than that of the traditional stabiliser **18**. According to modern ideas,[104] the stabilisation of emulsions is associated with the interaction of compound **18** with the Ag_2S centres. Thus the method developed may be useful for a rational selection of not only supersensitisers but also of stabilisers and antifogging agents.

The results obtained indicate the existence of at least two mechanisms of the supersensitisation of the *J*-aggregating dyes: the 'insulation' and Gilman's 'reductive' mechanisms. The difference between these two mechanisms is shown particularly clearly in the experiments, already examined, with compositions comprising readily oxidisable bases of the styryl dyes (compounds **19** and **33**) together with the supersensitisers **18**, **29**, and **30** which are difficult to oxidise. The observed superadditive supersensitisation effect (Figs 7 and 16, Table 3) can be explained by the hypothesis that supersensitisers of two types act on two consecutive stages in the inhibition of the hole-type self-desensitisation reactions. In this case, there is either initial hole capture from the dye by the readily oxidisable supersensitiser **19** (in accordance with Gilman's mechanism) and subsequent insulation of the remaining holes from the photographically active centres by compound **18**, which is difficult to oxidise, or the supersensitisers act in the opposite sequence. When the supersensitisers act consecutively, the probability of the entire recombination process is in fact determined by the product of the probabilities of the processes involving each of the individual substances, as a result of which the supersensitisation coefficient may approach the product of the coefficients for the individual supersensitisers, i.e. may be superadditive.[8,52]

The requirements which must be met by supersensitisers working in accordance with the above mechanisms are different: $0.8\ V > E_{1/2}^{Ox}(S) < E_{1/2}^{Ox}(Dy)$ for supersensitisers of the first kind working in accordance with the 'reductive' mechanism; $E_{1/2}^{Ox}(S) > E_{1/2}^{Ox}(Dy)$ for supersensitisers of the second kind working in accordance with the 'insulation' mechanism.[8,48] There is also a possibility of a variant where the supersensitiser dyes exhibiting a specific affinity for the Ag_2S centres and at the same time meeting the requirements of the 'reductive' mechanism may operate simultaneously via the two mechanisms. This case is in principle applicable to the supersensitiser dyes **31** and **32**, which were examined above and which are oxidised more readily than the quinomonomethinecyanine **3** supersensitised by them.

It is essential to note that the 'insulation' mechanism of the supersensitisation of the *J*-aggregating dyes differs significantly from Riester's mechanism.[23,24] Whereas the insulation of dye molecules from the AgHal surface and from one another is considered in Riester's model, the essence of the 'insulation' mechanism consists in the insulation of the sensitiser from the impurity centres alone. Furthermore, the introduction of Riester's potentiators leads to the decomposition of the dye *J*-aggregates and hence to the suppression of the spectral sensitivity.

The model involving the 'insulation' of the dye *J*-aggregates from the photographically active centres is apparently realised in emulsions with deep electron capture centres—in emulsions of the 'core–shell' type and in emulsions with Ir^{3+}.[45,123–127] As a consequence of the capture of photoelectrons, electron-hole

recombination processes are hindered in the bulk of the AgHal microcrystals, which makes it possible to diminish significantly type (II) self-desensitisation and hence to increase the effectiveness of the sensitiser.

2. Regulation of the *J*-aggregation of dyes

The self-association of dyes into *J*-aggregates should apparently have a series of analogies with crystallisation processes and should therefore involve at least two stages — the nucleation stage and the stage involving the growth of the ordered structure. Cyanine dyes aggregate on the real, and hence defective surface of AgHal microcrystals. The nucleation stage should therefore be determined by, apart from the structure of the dye molecule, the number and type of surface defects as well as the degree of supersaturation of the dye solution. On the other hand the *J*-aggregate growth stage is determined mainly by the degree of supersaturation of the sensitiser solution. The defectiveness of the surface of microcrystals is linked directly to the type of faces of the microcrystals and to the type of chemical sensitisation during which new defects (impurity centres) are formed. An analysis of the factors influencing the *J*-aggregation may be found in a number of reviews.[3,7,66]

The organic or inorganic substances introduced into a photographic emulsion during the growth of microcrystals and chemical and spectral sensitisation are capable of influencing the *J*-aggregation either in the aggregate nucleation stage, by altering the defectiveness of the surface, or in the aggregate growth stage. The influence of the stabiliser **18**, some of its analogues, and cyanines on the *J*-aggregation as regulators of the defectiveness of the surface was examined in Section I. In the present section, we shall consider the effect of a number of other organic compounds on the *J*-aggregate growth stage.

It has already been noted that the influence of a series of photographically relatively inactive compounds (for example, ketones, nitriles, quinoline derivatives, etc.) on the *J*-aggregation of dyes has been described in the literature.[9] The photographic effect of phenol added to the emulsion together with dyes has been investigated.[128] Its strong influence on the position of the absorption *J*-bands and on the effectiveness of the spectral sensitisation was observed. At a phenol concentration of 0.5–1.0 mol (mol AgHal)$^{-1}$, a bathochromic shift of the *J*-band up to 20 nm occurs. This is illustrated in Fig. 19 for the cation-anionic dye **35** and the anionic dye **36** adsorbed on a monodisperse AgBr(I) emulsion (cubic crystals, $\bar{l} = 0.25$ μm).

According to Fig. 19, phenol induces a bathochromic shift of the bands of orthochromatic and panchromatic sensitisers incorporated in compound **35** (cf. curves *1* and *2*) and of the *J*-band of the panchromatic dye **36** (cf. curves *3* and *4*). The changes in the *J*-bands are accompanied by an increase in the effectiveness of the spectral sensitisation. The influence of phenol was observed also for a series of other cationic, anionic, and cation-anionic dyes.

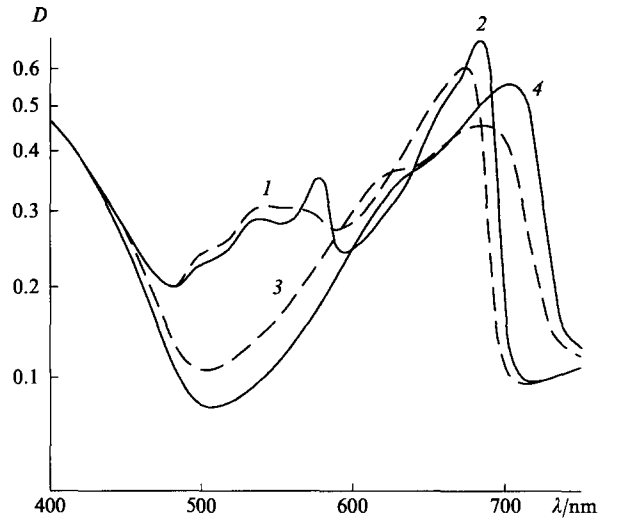
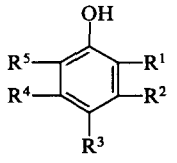


Figure 19. Reflection spectra of AgBr emulsion layers spectrally sensitised by dyes **35** (curves *1* and *2*) and **36** (curves *3* and *4*) individually (curves *1* and *3*) and in the presence of phenol (curves *2* and *4*). Concentration of dyes — 2 × 10^{-4} mol (mol AgBr)$^{-1}$; concentration of phenol — 0.5 mol (mol AgBr)$^{-1}$.

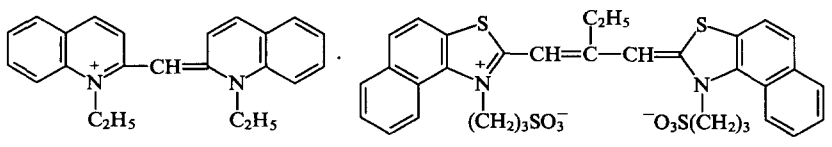


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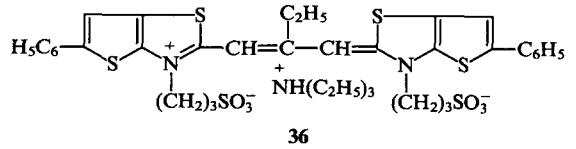
R^1–R^5 = H, Alk;

The influence of phenols having the general formula **37** has been investigated.[128] It was shown that cresol (R^3 = CH_3; R^1, R^2, R^4, R^5 = H) acts similarly to phenol. The introduction of longer alkyl groups in the *para*-position suppresses the *J*-aggregation. Dimethylphenols (1,2,4-, 1,3,4-, 1,3,5-, and 1,4,5-xylenols) have an effective influence on the *J*-aggregation at significantly lower concentrations [0.1–0.25 mol (mol AgHal)$^{-1}$] than phenol.

The bathochromic shift of the *J*-bands is usually attributed either to a decrease in the packing angle of the dyes or to an increase in the number of sensitiser molecules in the aggregate.[3,7] Both parameters should depend on the rate of aggregation. For fast aggregation, the random formation of many aggregates of different sizes should occur on the AgHal surface defects. It has



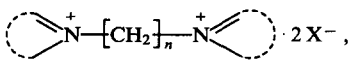
35



36

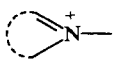
been shown[120] that the influence of the phenol persisted also when it was introduced into the emulsion after the formation of the *J*-aggregates. It was postulated that the 'recrystallisation' of the *J*-aggregates or, in the usual photographic terminology, the 'first ripening of the *J*-aggregates' takes place under the influence of phenols.[62,120] Phenols play the role of the medium (solvent) promoting the recrystallisation. One of the results of this may be the formation of more ordered structures of the *J*-aggregates (having bands which have undergone a bathochromic shift) remote from the impurity centres ($r > 0$, Fig. 2). The second result is the increase in the photographic activity of the *J*-aggregates. It is noteworthy that this may not in fact be a general rule because, for a sufficiently long ordered *J*-aggregate, contact between the latter and the IC_e can arise again with the consequent self-desensitisation of the dye. In this case the insulation of the *J*-aggregates from the IC_e with the aid of supersensitisers should be the main method for increasing the photographic activity of the long-wavelength *J*-aggregates.

Bisquaternary salts of heterocyclic bases having the general formula **38**,



38

exert an appreciable influence on the *J*-aggregation. Here



represents the quaternary salt of the nitrogen-containing base ($n > 2$).

Bisquaternary salts of a hydrogen-containing heterocycle have been used for a comparatively long time.[129–132] The influence of bisquaternary salts of benzimidazole has been studied in detail by Lifshits and coworkers,[133–135] while that of α-picoline has been investigated by the present author and Schelkina.[62,136] The introduction of bisquaternary salts into a photographic emulsion at concentrations comparable to that of the *J*-aggregating dye intensifies the tendency of the dye towards *J*-aggregation, gives rise to a bathochromic shift of the absorption band maximum, and increases the effectiveness of the spectral sensitisation. The effect of the bis-salts is manifested not only on AgHal but also on other semiconductors, in particular on WO_3.[50,51,137,138]

The influence of bisquaternary salts has been treated[62,136] from the standpoint of the facilitation of the *J*-aggregation of the dyes. This phenomenon has been designated as aggregation catalysis. Additional experiments using MB as a test for specific adsorption of the Ag_2S centres demonstrated that the bisquaternary salts do not exhibit an affinity for these centres and hence do not operate via the 'insulation' mechanism. Owing to the correspondence between the paired positive charges localised on the nitrogen atoms and the paired negative charges of the halide ions on the AgHal centre, a potential surface relief of a kind which facilitates the formation of *J*-aggregates not only on the defects but also on other surface sites and which favours the growth of the ordered structures of the aggregates is probably created in the adsorption of the bis-salts on the AgHal microcrystals. A consequence of this may be the absence of contact between the *J*-aggregate and the impurity centre IC_e, which is in its turn manifested by an increase in the photographic effectiveness of the dye. The formation of the ordered structures of the *J*-aggregates may influence the effectiveness of the spectral sensitisation as a consequence of the decrease in the probability of the dissipation of the excitation energy among different *J*-aggregates differing from one another by their sets of energy levels.

It has already been mentioned that the tendency of dyes towards *J*-aggregation is determined to a large extent by the molecular structure. The familiar fact that the replacement of alkyl groups at nitrogen atoms by sulfoalkyl groups, while the chromophoric part of the molecule of the cyanine dye remains unaltered, intensifies the tendency towards *J*-aggregation merits special attention.[7,137] The presence of dipolar betaine structures in anionic dyes can probably facilitate both the nucleation stage on the dipolar surface of the AgHal microcrystals (Ag^+ and Hal^- ions) and the growth of the aggregates themselves. According to Meyer's hypothesis,[140] the molecules of betaine dyes form more stable *J*-aggregates than the cations of the alkylates of carbocyanines.

The creation on the surface of AgHal microcrystals, before the introduction of the spectral sensitiser, of a multiplicity of new defects stimulating the growth of *J*-aggregates at sites not bound to the impurity centres should promote *J*-aggregation. Such numerous defects arise, for example, in the synthesis of AgHal microcrystals with a variable halide composition, particularly in the synthesis of AgBr(I) emulsions. *J*-Aggregation therefore is as a rule facilitated with increase, up to a certain limit, in the content of iodide ions in AgBr(I) emulsions. It has been shown[141] that the addition of iodide ions to a AgBr emulsion with cubic microcrystals leads to the formation on the vertices and edges of the microcrystals of silver iodide, on which *J*-aggregation is facilitated. The influence of thiocyanate and cyanide ions, forming sparingly soluble compounds with Ag^+ ions,[142] can be explained in the same way. There is apparently a possibility also of other methods of regulating the defectiveness of the surface of AgHal microcrystals.[136] In addition, mention should be made of the control of the *J*-aggregation by reducing the rate of introduction of the dye into the solution. This is achieved by introducing into the emulsion dyes sparingly soluble in water in the form of aqueous sols or, for example, by the readsorption of dyes from the surface of an inert substrate (SiO_2 etc.) on AgHal.[7,143] The three principal supersensitisation procedures, examined above, are summarised in Fig. 20.

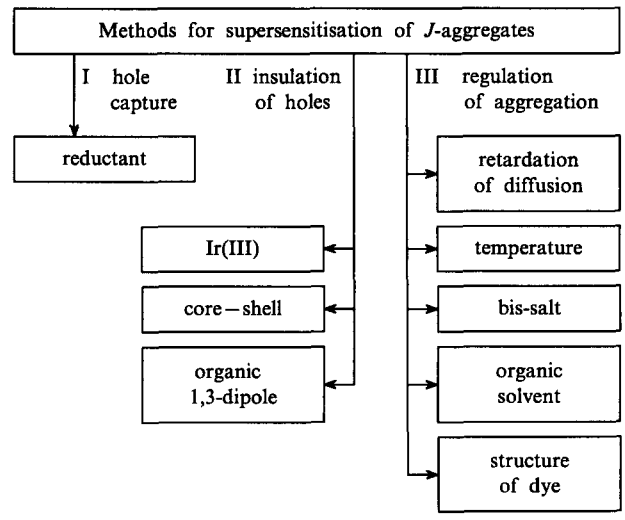


Figure 20. Principal methods for the supersensitisation of *J*-aggregating dyes.

V. Conclusion

The characteristics of the spectral sensitisation of silver halide photographic materials by *J*-aggregating dyes are determined primarily by the unusual structure of the aggregates, which consist of organised structures with delocalised π-electrons. This is reflected both in the spectra (λ_{max}, line widths, absorption coefficient, and the lifetime of the excited state) and in the photographic behaviour of cyanines. The system of delocalised π-electrons of the *J*-aggregate creates conditions for the transfer of

the photogenerated charge carriers (electrons and holes) over distances larger than the molecular size. The delocalisation of holes within the limits of the *J*-aggregates constitutes the basis of the desensitisation and the type (II) self-desensitisation examined above. The hole desensitisation is a typical example of the catalysis of recombination processes in which the *J*-aggregate plays the role of an intermediate species promoting the reaction.

The processes involving the transfer of holes and photoelectrons between aggregates of various dyes not only play a major role in the spectral sensitisation of photographic materials but are also of considerable interest for the future developments in molecular microelectronics.[144–148] Artificially organised systems on the basis of *J*-aggregates serve as electronic elements of molecular dimensions (switches, triodes, memory cells, etc.). Thus one is dealing with the organisation of photoinitiated electronic processes in the microsystems of the *J*-aggregates.

The uniqueness of the *J*-aggregates of cyanine dyes as spectral sensitisers, which has been responsible for their general application in the black and white and colour photographic materials is apparently determined by the effective primary separation of the photogenerated charges between the molecules in the system of the *J*-aggregate. Here one can trace a definite analogy between the spectral sensitisation process created artifically by man and the natural spectral sensitisation processes in photosynthesis, which in the course of many millions of years of evolution have been brought to perfection. The primary step of the spectral sensitisation in the photosynthesising reaction centre involves the separation of charges in the dimeric molecules of bacteriochlorophyll.[149] The effectiveness of the primary charge separation creates favourable conditions for the subsequent multistage processes involving the separation of the charges from one another. The primary charge separation in the *J*-aggregates promotes in exactly the same way the subsequent effective separation of electrons and holes in the dark stages with participation of silver halides. Nature has devoted much effort to the creation of a perfect mechanism of the 'dark' separation of charges in photosynthesis. This has been achieved exclusively by an exact spatial organisation of a transport system for electrons and holes in which electron and hole acceptors are located at rigorously defined distances from the reaction centre.[149] According to the results obtained, the disposition of the *J*-aggregates relative to electron and hole acceptors on the AgHal surface also determines to a significant extent the effectiveness of the charge separation in the photographic process and the spectral sensitivity associated with this. Consequently the topography of the *J*-aggregates on the real surface of AgHal microcrystals is extremely important and the specific regulation of the *J*-aggregation therefore in fact constitutes, in our view, the essential feature of the future developments in the spectral sensitisation of new photographic materials.

It is essential to note that the difficulties which many investigators encountered in their attempts to find a relation between the effectiveness of the spectral sensitisation of specific photographic emulsions and the structure of the *J*-aggregating dyes, which were mentioned in the Introduction, arose in the first place from the one-sided nature of the approach to the problem of spectral sensitisation. This was either a consequence of a one-sided study of the structure and energetics of the energy levels of the dyes incorporated in the *J*-aggregate without reference to the emulsion system (in the first place its impurity levels) or, conversely, a result of overestimating the role of the substrate without taking into account the structural characteristics of the dye. The hopes of the investigators are therefore frequently associated either with the search for a kind of 'golden' dye or with the preparation of a 'special' photographic emulsion showing a tendency towards supereffective spectral sensitisation. Naturally, because of its limitations, neither approach is able to solve this problem. Only the study of processes in a single system incorporating the dye, the AgHal surface, its defects, and, in the first place, the products of the sulfur sensitisation can help to find an answer to the question why a particular cyanine dye in one or other emulsion is either highly effective or, conversely, is photochemically inactive. This review represents an attempt at an integrated consideration of the problem of the effectiveness of the spectral sensitisation of *J*-aggregating dyes.

Attention should be drawn also to one, largely ideological, limitation of the approach adopted to the problem of the effectiveness of spectral sensitisation. Hitherto processes involving the supersensitisation of photographic layers with *J*-aggregating dyes have been considered from the standpoint of the prohibitive principle of the 'fight against holes'. Both the 'reductive' and 'insulation' supersensitisation mechanisms correspond to precisely this principle. However, practice has shown that another principle is more promising — the 'collaboration' principle, in the present instance the principle of collaboration with holes. This means that a desirable organisation of the spectral sensitisation process is one in which it would be useful to employ the energy of the holes, namely their oxidising capacity, which leads to the liberation of the chemical energy stored in the photographic system. One is dealing with the oxidation of certain organic substances — supersensitisers of a new type — as a result of which the oxidised molecule, depleted in bonding electrons, would react with decomposition of the initial cyclic skeleton. Ultimately another molecule would arise with a new cyclic skeleton, possessing reducing properties in relation to AgHal. This means that the chemical reactions of the oxidised form of the supersensitiser would result in the injection into the AgHal microcrystal of one (or more) electron capable of intensifying the latent photographic image. Consequently one is dealing with a latent image intensification process in which the relative quantum yield of the spectral sensitisation can be formally greater than unity. In fact, one would inject not one but several electrons into AgHal per quantum adsorbed by the *J*-aggregate — one electron from the photoexcited dye and the others from the products $Dy^{+\cdot}$ of the oxidation by the hole. The ability of the *J*-aggregate to effect the translation of the hole should in principle increase the probability of such a process. The process probability should increase to an even greater extent following the specific adsorption of a supersensitiser of the type considered on the impurity centre functioning as the electron acceptor. In this case, on capture of a hole by the supersensitiser and after the chemical reaction of the

$$Dy + h\nu \longrightarrow Dy^{*}; \quad (12)$$

$$Dy^{*} + AgHal \longrightarrow Dy^{+\cdot} + [AgHal]^{-}; \quad (13)$$

$$[AgHal]^{-} + Ag^{+} \longrightarrow [AgHal/Ag^{0}]; \quad (14)$$

$$Dy^{+\cdot} + BH \longrightarrow Dy + BH^{+\cdot}; \quad (15)$$

$$BH^{+\cdot} + R^{-} \longrightarrow B^{\cdot} + HR; \quad (16)$$

$$B^{\cdot} + [AgHal/Ag^{0}] \longrightarrow B^{+\cdot} + [AgHal/Ag^{0}]^{-}; \quad (17)$$

$$[AgHal/Ag^{0}]^{-} + Ag^{+} \longrightarrow [AgHal/Ag_{2}^{0}]; \quad (18)$$

$$B^{+\cdot} + \text{medium} \longrightarrow \text{products}; \quad (19)$$

oxidised supersensitiser molecule, a second electron would enter directly the IC_e. A hypothetical mechanism of the 2-electron process could be represented, for example, in the following form: where BH is the supersensitiser and R^- the base. According to this scheme, the supersensitiser BH is oxidised by a dye hole to the radical-cation $BH^{+\cdot}$, which interacts with the base R^- as a consequence of its acid properties, affording the radical $B^{\cdot}$. The latter can serve as a reductant in relation to the silver halide, i.e. it can inject a second electron into AgHal and intensify thereby the latent photographic image centre.

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