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Study of Organic Compound Adsorption on (Ag,Au)S Centers by the Method of Chemical Microscopy

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A new method is proposed for investigating Ag_2S and (Ag,Au)S centers by selective adsorption of some electron-acceptor dyes on centers formed in the process of chemical sensitization of AgHal emulsions. This new technique is called *chemical microscopy* because it permits us to obtain information about microscopic impurity centers.

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Introduction

Earlier a technique for investigating Ag_2S and (Ag,Au)S centers by selective adsorption of a phenothiazine dye, e.g., methylene blue (MB), on such centers was discussed.[1] It was shown that when adsorbed on the products of sulfur and sulfur+gold sensitization, MB caused fog to develop. The fogging action of MB^+ cation was explained by its adsorption on impurity centers of chemical sensitization and by catalysis of electron transfer thereupon from developing agents (Red), as is shown schematically in Fig. 1. According to this scheme the direct transfer of electrons from Red to the Ag_2S center is kinetically hindered because of the high activation energy barrier, E_{act} [Fig. 1(a)]. As a result of MB adsorption onto the Ag_2S center the electron transfer reaction appears to be split into two stages, the first of which is electron transfer from Red to the dye acceptor (Dye A). Because of the lower activation energies of the two stages, E_{act}' and E_{act}'', in comparison with E_{act}, catalysis of the redox reaction is achieved, as expressed in the fogging of the photographic layers [Fig. 1(b)]. It was also shown[1] that some other electron-accepting dyes with positively charged chromophoric systems provided a similar effect.

Accordingly[1] a new phenomenon was disclosed, namely, catalysis of electron transfer from electron donors to AgHal through impurity centers (IC), mediated by electron-acceptor dyes adsorbed on that IC. The basic factors beneficial for catalysis appear to be selective adsorption of dyes on the Ag_2S centers, their electron affinity, and large cross section for electron capture, reflecting both the positive charge of the chromophore π-system and its size. In the classic photographic process catalysis is realized by positively charged Ag_n^+ particles formed on Ag_2S centers during exposure; thus the cationic dye molecule functions analogously as a catalyst. Therefore, on MB adsorption sulfide centers are transformed into development centers and MB action is intensified by a factor of about 10^9. Hence, we called the new technique of Ag_2S and (Ag,Au)S center investigation *chemical microscopy* because it provides information about microscopic impurity centers on the AgHal grain surface.[2]

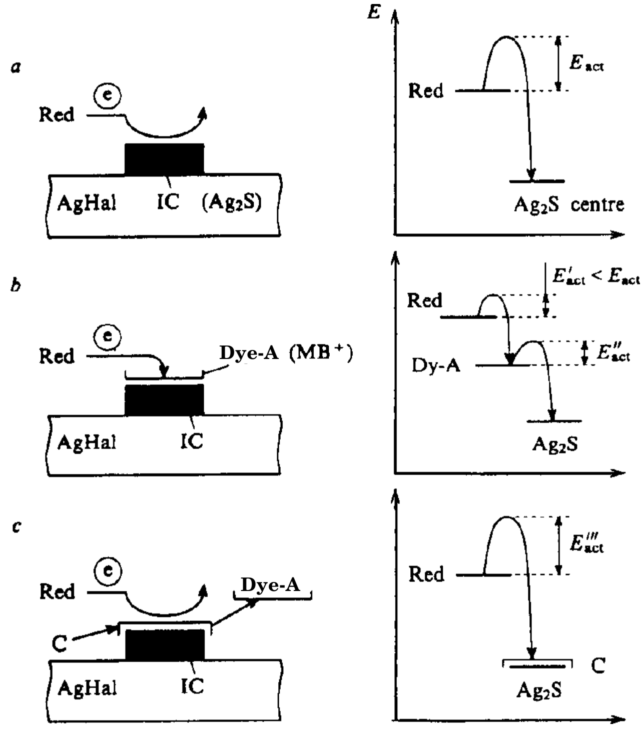

Figure 1. Scheme of catalysis of electron transfer from developing agent (Red) to Ag_2S center by the use of electron-acceptor dye (Dye A, including MB) and inhibition of the transfer by compound (C) adsorbing on the Ag_2S center.

This work demonstrates possibilities for using the new technique of chemical microscopy for systematic study

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of chemical sensitization by impurity centers in the AgHal grains of various habitus, as well as interactions of these impurity centers with different organic compounds.

Experimental

Investigations were carried out on cubic AgBr emulsions with (100) crystal faces (l = 0.20 µm, coefficient of variation $C_v = 10.4\%$) and octahedral crystals (l = 0.19 µm, $C_v = 10.8\%$) with sulfur and sulfur+gold sensitization. Sulfur sensitization was carried out at 48°C with $Na_2S_2O_3$ (8×10^{-4} mol/mol AgBr). Sulfur+gold sensitization was also carried out at 48°C with $Na_2S_2O_3$ and $HAuCl_4$ (8×10^{-4} and 2.3×10^{-5} mol/mol AgBr, respectively).[3] Aqueous solutions of MB (1.25×10^{-4} *M*) in an amount equivalent to 5×10^{-5} mol/mol AgBr were added in the melted emulsions at definite points of chemical ripening. Investigations of interactions of impurity centers with a number of organic compounds—stabilizers, antifoggants, fogging electron-acceptor dyes—were carried out with a cubic emulsion with sulfur+gold sensitization. Stabilizers and antifoggants were added to the melted emulsion before MB over a wide range of concentration (2×10^{-4} to 1.6×10^{-2} mol/mol AgBr); then MB was added in the amount of 5×10^{-5} mol/mol AgBr.

As stabilizing and antifogging agents the following classes of compounds were studied: derivatives of benzotriazole, nitroderivatives of indazole, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (Sta-salt) and its analogs, mercapto derivatives of some heterocyclic compounds, monomethinecyanine, dyes, etc. As electron-acceptor dyes besides MB symmetrical and unsymmetrical pyrylo-, thiapyrylo-, and selenapyrylocyanines, phenosafranine, Janus green, and pynacryptol green were studied. Energy levels of dyes were estimated on the basis of polarographic half-wave reduction potentials ($E^{red}_{1/2,dye}$), which were measured in acetonitrile, relative to SCE.

Cyanine dyes of structures III and V, and mesoionic thiazole derivatives of general formula IV were synthesized at the Institute of Organic Chemistry, National Academy of Sciences of the Ukraine, and identified by chemical analysis and NMR.[4–7] The other compounds were commercially available and used as received.

For molecular geometry, approximate calculations by molecular mechanics were used, taking into consideration conjugation, using PCMOD3.2 and the similar MMP2 program.[8] Calculations of π-electron density distribution in cyanine dyes molecules were carried out by Pariser-Pople-Parr approximation with 25 excited configurations and using a molecular mechanics optimized geometry. Atom and bond parameters were taken from Ref. 9. Our computational technique is described in more detail in Refs. 1 through 7.

Study of the Chemical Sensitization Processes

Using the method of MB adsorption, the kinetics of S and (S+Au) sensitization of cubic and octahedral crystals were investigated. This method provides information about the rate of accumulation of Ag_2S centers and in fact confirms observations of Moisar[10] and Klein[11] about the kinetics of Ag_2S formation during S sensitization. According to Moisar and Klein, Ag_2S center formation rate and yield on (111) planes are both significantly greater than on the (100) planes. Large numbers of Ag_2S centers formed on the highly defective (111) planes result in competition among centers for photoelectrons, resulting in a sensitivity-level decrease during extended S ripening of the octahedrons.

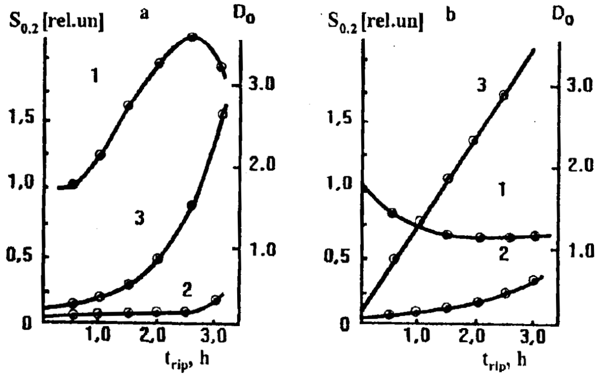


Figure 2. Dependence of sensitivity, $S_{0.2}$, (1) and fog, D_o, without (2) and in the presence of MB (3) on S-ripening duration of AgBr emulsion with cubic (a) and octahedral (b) grains.

Addition of MB at various points during the chemical sensitization significantly increases the fog of photographic layers as a result of MB adsorption on Ag_2S and (Ag,Au)S centers, as illustrated in Fig. 2.

TheAg_2S center formation process consists of two stages, nucleation and growth, as was shown by Cash.[12] Observation of the curves with MB permits us to recognize peculiarities of those stages for crystals with different habit. The Ag_2S center formation rate, reflected in the rate of growth of fog produced by MB adsorption, could be characterized by rate constant k_i, which takes various values during chemical ripening. Rate constant values for the crystals with different habitus during S and (S+Au) ripening are given in Table I.

The cubic grains stages differed significantly in rates: The rate of the first stage ($k_1 = 0.21$ h^{-1}) is about four times less than the rate of the second stage ($k_2 = 0.83$ h^{-1}). The first slow stage (induction period) appears to cause nucleation of Ag_2S centers. At k_2 the sensitivity achieved its maximal value so that stage is connected with Ag_2S center growth. The significant value of $k_2/k_1 = 3.95$ testifies to the differentiation of two basic stages of Ag_2S impurity center formation. Further acceleration of Ag_2S formation ($k_3 = 3.43$ h^{-1}) leads to a sensitivity decrease [Curve 1, Fig. 2(a)], probably connected both with excess enlargement of impurity centers, resulting in fog growth, and with competition by increasingly greater numbers of centers for photoelectrons capture.

TABLE I. Values of Fogging Rate Constants in the Presence of MB for AgBr Crystals of Various Habits in the Processes of S and (S+Au) Sensitization (T = 48°C)

Habitus	k_1, (h^{-1})	k_2, (h^{-1})	k_3, (h^{-1})	k_2/k_1
		S Sensitization		
{100}	0.21	0.83	3.43	3.95
{111}	1.10	1.10	1.10	1.00
		S+Au Sensitization		
{100}	0.70	1.73	1.73	2.47
{111}	0.50	1.10	0.20	2.20

For octahedral crystals a sharp rise of the fog level with MB is immediately observed [Curve 3, Fig. 2(b)] characterized by the rate constant $k_1 = 1.10$ h^{-1}. Nucleation and growth appeared to occur simultaneously and very efficiently ($k_2/k_1 = 1.00$). Therefore, all formed nucleation centers quickly grow to sensitivity centers and compete with each other.

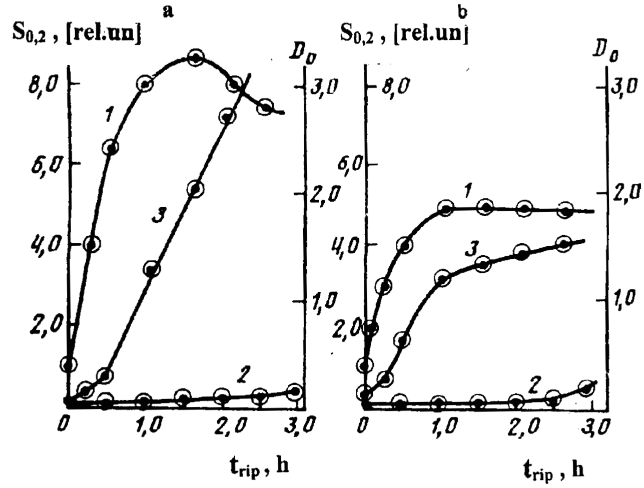


Figure 3. Dependence of sensitivity, $S_{0.2}$, (1) and fog, D_o, without (2) and in the presence of MB (3) on (S+Au) ripening duration of AgBr emulsion with cubic (a) and octahedral (b) grains.

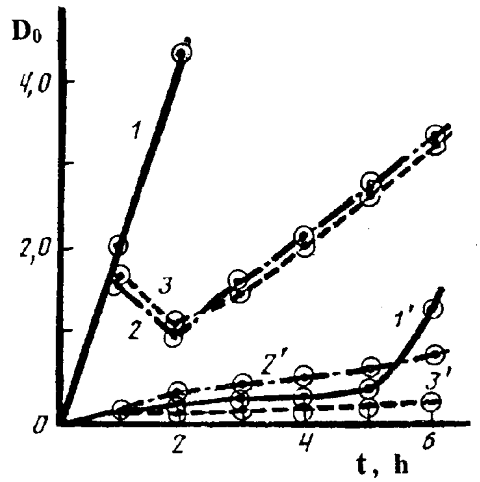


Figure 4. Change of the fog level, D_o, for unstabilized (1,1^1), stabilized by TAI (2,2^1) and TMMC (3,3^1) AgBr emulsion with cubic grains with duration of emulsion storage at $T = 48°C$ without MB ($1^1 - 3^1$) and with MB (1-3); TAI concentration: 5×10^{-3}, TMMC concentration: 5×10^{-4} mol/mol AgBr.

On (S+Au) sensitization of cubic crystals [see Fig. 3(a)], the induction period of nucleation is retained though shortened. The process itself is carried out with a significantly larger rate constant, $k_1 = 0.70$ h^{-1}. Also nucleation growth performs faster ($k_2 = 1.73$ instead of 0.83 h^{-1}), which appears to explain why the (S+Au) sensitization process is more efficient. But differentiation by rates of the two processes is retained because $k_2/k_1 = 2.47$.

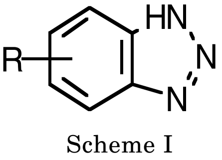
For octahedral grains in the case of (S+Au) sensitization a clearly defined nucleation period is observed [Curve 3, Fig. 3(b)] that occurs at a lower rate, $k_1 = 0.50$ h^{-1}, compared with the S sensitization ($k_1 = 1.10$ h^{-1}) process. Then, with (S+Au) ripening, differentiation of the two processes takes place ($k_2/k_1 = 2.20$) at the cost of retardation of the nucleation stage. It appears to be a main reason for sensitivity increase with octahedral grains [see Curve 1, Fig. 3(b)]. Nucleation growth is accompanied with reaction acceleration to the constant value of $k_2 = 1.10$ h^{-1}, which, however, after achievement of the sensitivity maximum, sharply decreases to $k_3 = 0.20$ h^{-1}. It is probably connected with inactivation of large Ag_2S centers at the cost of their transformation to the mixed gold and silver sulfides of decreasing catalytic activity.[13] Cash showed[14] that with fast sulfide formation the presence of gold caused a decrease in the rate of photographic digestion.

On the basis of data obtained using the MB technique, it is possible to conclude that: (1) gold ion function lies in acceleration of the nucleation process and growth of sulfide clusters for (100) grains, and in retardation of Ag_2S nucleation and inactivation of the large sulfide centers growth for (111) grains; and (2) the difference between nucleation and sulfide particle growth rates is a necessary condition for optimal chemical sensitization process.

In Refs. 1 and 15 it is shown that MB could be desorbed from Ag_2S centers by introduction of a number of cyanine dyes and stabilizers, for example, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI). This is explained by the greater tendency for that compound to be adsorbed on Ag_2S centers. In the present work, those processes were investigated more carefully. The stabilizing action of 3,3'-diethylbenzothiacyanine tosylate (TMMC) and TAI was investigated on AgBr emulsion with cubic grains.[3] Results are given in Fig. 4. The stabilizing action of TAI and TMMC is clearly demonstrated by data with MB. At introduction of MB during (S+Au) ripening, fast fog level growth was observed (Curve 1, Fig. 4). Introduction of TAI and TMMC after 1 h of chemical sensitization initially brings about a fog level decrease connected with agent adsorption on (Ag,Au)S centers and their isolation from MB. That introduction of TAI and TMMC sharply retards the process of (Ag,Au)S center formation, and their overgrowth with time to the fog centers that cause fog from MB decreases (compare Curves 1, 2, and 3, Fig. 4). Therefore, both compounds are stabilizers by the mechanism of adsorption on (Ag,Au)S centers. According to the curves 2 and 3 of Fig. 4, the stabilizing effects of TAI and TMMC are practically equal but TMMC concentration is one order of magnitude less than TAI concentration. It is likely connected with better adsorption of the dye on the impurity centers of chemical sensitization.

Interaction of Stabilizing and Antifoggant Agents with (Ag,Au)S Centers

The method based on adsorption of MB on the impurity (Ag,Au)S centers has provided a new view of both the problem of the mechanism action of stabilizers and of the search for new stabilizers and antifoggants. Because MB introduction in the chemically sensitized emulsion brings about fog level growth, and because the fogging effect is connected with MB adsorption on the impurity centers, introduction of the agents having specific adsorption on Ag_2S and (Ag,Au)S centers can cause desorption of MB from that center and, as a consequence, the fog level decreases. But introduction of agents whose effect is connected only with adsorption on AgHal does not influence the MB fog level. In the present work, from the point of view of their adsorption on (Ag,Au)S centers benzotriazole (BTA) and its derivatives with the general formula of Scheme I were investigated:

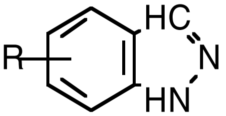


Scheme I

where R = H (C – 1); 5-NO_2 (C-2); 5-COOH (C-3);5-CH_3 (C-4); 5-Br (C-5); 5-CH_3, 6-Cl (C-6); 5-C(O)OPh (C-7); 4,5,6,7-Cl (C-8); 5-OH, 4,6,7-Cl (C-9).

Results of the investigation are given in Table II. Compound activity was estimated as the fog decrease (ΔD) equal to the difference between fog values with MB (D_{MB}) and of emulsion where the test compound and then MB were added (D_{com+MB}). According to the results for benzotriazole and its derivatives, it was concluded that benzotriazole and its 5-NO_2 and 5-COOH derivatives are not adsorbed on the (Ag,Au)S centers. These compounds, well-known antifoggants, are likely working as organic acids, whose anions form difficultly soluble salts with silver ions on the AgHal surface. Indeed, solubility products of silver salts of those compounds are small: 3.9×10^{-14} for benzotriazole; 1.58×10^{-12} for 5-nitrobenzotriazole at 25°C.[16] At the same time 5-CH_3, 5-Br, and 5-CH_3,6-Cl derivatives of BTA as well as 4,5,6,7-tetra-Cl and 4,6,7-tri-Cl, 5-OH-BTA already have some ability to be adsorbed on the impurity centers. The 5-C(O)OPh-BTA takes a special place; it is adsorbed on the (Ag,Au)S centers and appears to be a stabilizer by the mechanism of adsorption on that centers.

It was shown that nitroderivatives of indazole with the general formula of Scheme II:



Scheme II

where R = 3-NO_2(C-10); 4-NO_2 (C-11), 5-NO_2 (C-12); 6-NO_2 (C-13), independent of nitro-group position, do not decrease MB fog and hence are incapable of being adsorbed on the (Ag,Au)S centers.

Studies of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) and some of its derivatives show that TAI to a finite degree could be adsorbed on the (Ag,Au)S centers. For example, in a concentration of 2×10^{-2} mol/mol AgBr, TAI decreases MB fog from $D_{MB} = 2.20$ to $D_{comp+MB} = 1.27$, which confirms discussions in the literature[16] about the mechanism of TAI stabilization by adsorption on the Ag_2S centers. Investigated TAI analogs (2-heptyl-4-hydroxy-6-methyl-TAI, 2-methylthio-4-hydroxy-6-methyl-TAI, 4-hydroxy-6-phenyl-TAI, 4-hydroxy-6-methyl-1,2,3,3a, 7-pentaazaindene) are significantly inferior to TAI both in the action on the MB fog and in stabilizing effect.[17] Only 2-heptyl-4-hydroxy-5-bromine-6-methyl-TAI approaches TAI in efficiency.

Studies of 1-phenyl-5-mercaptotetrazole (C-14), 2-mercaptobenzoxazole (C-15), mercaptobenzimidazole (C-16), and 2-mercapto-4-amino-thiadiazole (C-17) have shown that those compounds efficiently decrease MB fog. Some results are given in the Table III. Hence, the antifoggant effect of mercaptoderivatives of heterocyclic compounds also could be connected with adsorption on (Ag,Au)S centers. Adsorption of C-14 on Ag_2S particles is known. According to the data of Wood[18] heat of adsorption of C-14 on Ag_2S is twice as large as on AgBr. But this does not rule out the action of compounds of that class around all AgHal grain surfaces because they form difficultly soluble salts with Ag^+. Thus, solubility products of silver salts of C-14 – C-17 are very small[14] and equal to 6.3×10^{-17}, 1×10^{-18}, 2.5×10^{-16}, and 1×10^{-15}, respectively. Therefore their action could be two-fold, they could be stabilizers of AgHal emulsions both by adsorption on (Ag,Au)S centers and by binding Ag^+ ions on the AgHal surface.

TABLE II. Photographic Effect of Benzotriazole Derivatives

No.	Compound	Concentration of compound (mol/mol AgBr)	D_o	D_{MB}	$D_{comp+MD}$	DD
1	C-1	1×10^{-3}	0.22	2.20	2.00	0.20
		3×10^{-3}	0.22	2.20	1.80	0.40
2	C-2	1×10^{-3}	0.22	2.20	2.07	0.13
		3×10^{-3}	0.22	2.20	1.80	0.40
3	C-3	1×10^{-3}	0.22	2.20	2.20	0.00
		3×10^{-3}	0.22	2.20	2.20	0.00
4	C-4	1×10^{-3}	0.29	3.10	2.30	0.80
		3×10^{-3}	0.29	3.10	2.10	1.00
5	C-5	1×10^{-3}	0.22	2.20	1.50	0.70
		3×10^{-3}	0.22	2.20	1.00	1.20
6	C-6	1×10^{-3}	0.22	2.20	1.45	0.75
		3×10^{-3}	0.22	2.20	1.05	1.15
7	C-7	1.6×10^{-3}	0.28	2.20	0.67	1.53
		3.2×10^{-3}	0.28	2.20	0.36	1.94
8	C-8	1.6×10^{-3}	0.28	2.20	0.95	1.25
		3.2×10^{-3}	0.28	2.20	1.00	1.20
9	C-9	1×10^{-3}	0.29	3.10	2.30	0.80
		3×10^{-3}	0.29	3.10	2.20	0.90

TABLE III. Photographic Action of Mercaptoderivatives of Heterocyclic Compounds

No.	Compound	Concentration of compound (mol/mol AgBr)	D_o	D_{MB}	$D_{comp+MD}$	ΔD
1	C-14	1×10^{-3}	0.16	3.00	1.95	1.05
		3×10^{-3}	0.16	3.00	0.72	2.28
2	C-15	1×10^{-3}	0.16	3.00	0.75	2.25
		3×10^{-3}	0.16	3.00	0.12	2.88
3	C-16	1×10^{-3}	0.16	3.00	0.82	2.18
		3×10^{-3}	0.16	3.00	0.15	2.85
4	C-17	1×10^{-3}	0.22	2.00	0.85	1.15
		3×10^{-3}	0.22	2.00	0.37	1.63

For stabilization of high-speed photographic materials, including X-ray films for fast processing, compositions of stabilizing compounds are used that include compounds such as salts of *p*-alkyl phenylthiosulfinic acid, triphenyl-4-nitrophenylphos-phonium salts, salts of 1.4-dihydroxyphenyl-2,5-disulfonic acid, and 1,3-dihydroxyphenyl-4-sulfonic acid. Studies of sodium *p*-*iso*-butylphenylthiosulfinate (C-18), triphenyl-4-nitrophenylphosphonium chloride (C-9) and dipotassium salt of 2,5-disulfohydroquinone (C-20) by the MB adsorption–desorption method have shown that these substances have weak adsorption on (Ag,Au)S centers. In the range of the investigated concentrations (for C-18 and C-20 – $1 \times 10^{-3} - 1 \times 10^{-2}$ mol/mol AgBr; for C-19, $1 \times 10^{-4} - 1 \times 10^{-3}$ mol/mol AgBr), the value of ΔD did not exceed 0.10–0.15. Therefore, their action does not connect with adsorption on impurity centers of chemical sensitization and their functions are different. Probably, in accordance with Refs. 19 for sodium *p*-(*iso*-butyl) phenylthiosulfinate this function lies in oxidation of silver centers formed during photographic material preparation and storage according to the following reaction:

$$i\text{-}C_4H_9\text{-}C_6H_4\text{-}SO_2SNa + 2Ag^0 = \\ = i\text{-}C_4H_9\text{-}C_6H_4\text{-}SO_2Na + Ag_2S. \qquad (1)$$

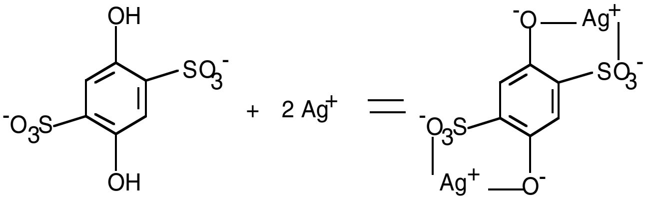
Thus that substance, by oxidizing silver centers, hinders their overgrowth to larger fog centers. Probably such a function is also fulfills by triphenyl-4-nitrophenylphos-phonium chloride, which is an electron acceptor.

A phosphonium salt not having specific adsorption on (Ag,Au)S centers can function as desensitizer (*D*) by serving as an electron carrier between O_2 and H^+, probably by the known scheme[16,20]:

$$Ag^0 + D \rightarrow Ag^+ + D^- \xrightarrow{+O_2} D + O_2^- \xrightarrow{+H^+} HO_2 \xrightarrow{+Ag^0} Ag^+ + HO_2^- \xrightarrow{+H^+} H_2O_2. \qquad (2)$$

As a result silver particles are oxidized by oxygen in a reaction involving protons from the environment. In this process, electron-accepting compound A plays the role of catalyst of oxidation.

Photographic action of the disulfoderivative of hydroquinone (C-20) may result from its adsorption on AgHal and complexation of Ag^+ ions by the formation of chelates involving SO_3^- and OH- groups in ortho-positions of phenyl ring according to the following reaction:



(3)

Hence, that compound is likely to be related to the class of antifoggants increasing the negative charge of AgHal grain surfaces.

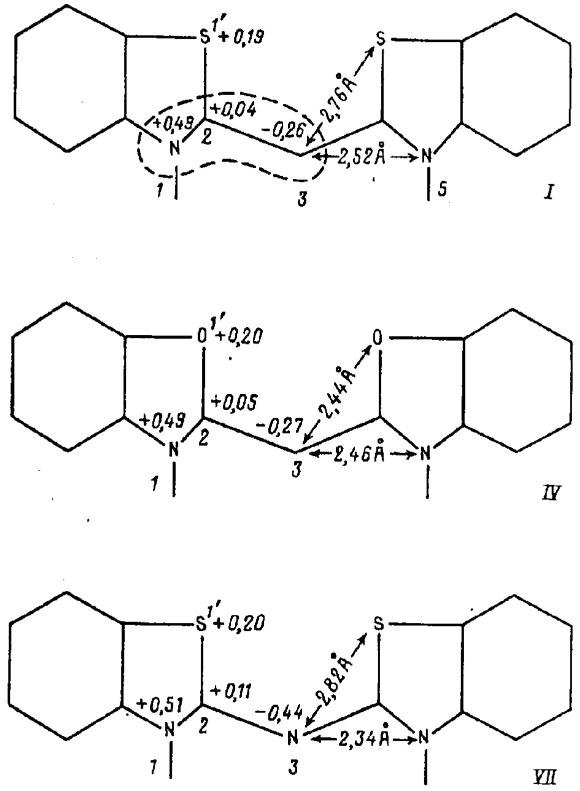
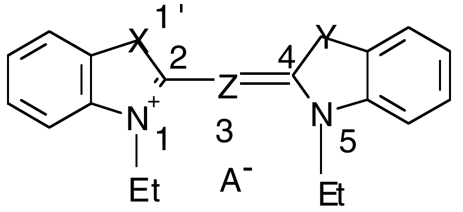


Figure 5. Molecular diagrams of monomethinecyanines and monoazacyanine.

Investigation of Adsorption of Monomethinecyanine Dyes

Because monomethinethiacyanines are able to desorb MB from (Ag,Au)S centers,[1,15] the dependence of specific adsorption of monomethinecyanines (MMC) on (Ag,Au)S centers on dyes structures was studied. Symmetrical and unsymmetrical MMC derivatives of benzoxazole, benzothiazole, benzoselenazole, benzotellurazole, benzoimidazole as well as monoazacyanine with the general formula of Scheme III



Scheme III

where X and Y = O, S, Se, Te, NMe; Z = CH and N, X^- – anion, were investigated.[4] Some results of the photographic action of MMC are given in Table IV. Dyes were added to emulsion before MB in alcohol solution in concentrations of 8×10^{-4} and 16×10^{-4}mol/mol AgBr.

According to the data in the Table IV symmetrical benzthiazolocyanine (I) and benzselenazolocyanine (II) exhibit the highest antifoggant effect. Unsymmetrical benzthiatellurazolocyanine is close to them in its activity. Benzoxazolocyanine (IY) has practically no antifoggant effect and benzoxathiazolocyanine (Y) has only a weak one. In contrast, benzthiaimidazolocyanine (YI) exhibits fog growth. The change of the methine group to nitrogen in benzthiazolomonoazacyanine (YII) strongly weakens the antifoggant activity of the dye.

As a hypothesis for explanation of the photographic activity of MMC, an assumption was made that the first condition of specific adsorption of dyes on (Ag,Au)S centers, resulting in MB desorption from that centers, is correspondence of the distances between charges in 1,3-dipoles in the dyes to the distances between Ag^+ and S^{2-} ions in the Ag_2S center lattice.[15,21] According to Ref. 22, distances between ionic rows in the lattice of Ag_2S formed on the AgBr plane of T-grains are equal to 2.58, 2.84, 3.08, and 3.96 Å. It is characteristic in this case that the first two values are significally less than the distance between Ag^+ and Br^- in the AgBr lattice (2.89 Å).The presence of significant charge densities in 1,3-dipoles represents the second condition of adsorption.

For verification of the hypothesis, calculations of the equilibrium geometry of some dyes were made by molecular mechanics with correction of force constants for bond orders.[4] Results are given in Table V. In addition calculations were made of π-charge distribution on atoms using the approximation of Pariser-Pople-Parr (PPP). Results are summarized in Table VI.

According to the data of the Table V all monomethinecyanines are nonplanar because of steric hindrances created by bulk heteroatoms and other groups. Substitution of the methine group by nitrogen atom in dye YII is accompanied by planarization of the molecule.

Calculations of π-electron density (Table VI) testify to the availability in MMC molecules of characteristic 1,3-dipoles with positive charges on nitrogen atoms or

TABLE IV. Photographic Action of Investigated Dyes

No. of Dye	X	Y	Z	D_{dye}	ΔD	D_{dye}	DD
		$C = 8 \times 10^{-4}$mol/mol AgBr				$C = 16 \times 10^{-4}$mol/mol AgBr	
I	S	S	CH	0.47	1.53	0.37	1.63
II	Se	Se	CH	0.43	1.57	0.35	1.65
III	S	Te	CH	0.80	1.20	0.35	1.65
IY	O	O	CH	2.00	0.00	1.72	0.28
Y	S	O	CH	1.91	0.09	1.60	0.40
YI	S	NMe	CH	2.54	-0.54	2.91	-0.91
YII	S	S	N	1.79	0.21	1.53	0.47

Note: $D_o = 0.22$, $D_{MB} = 2.00$; $A^- = I^-$ for dyes I – YI; $A^- = ClO_4^-$ for dye YII.

TABLE V. Distances (Å) and Angles (Degrees) in Monomethinecyanines Molecules

Dye	N_1 - Z	N_5 - Z	X - Z	X - Y	φ_1	φ_2
I	2.52	2.52	2.76	3.54	76	127
IY	2.46	2.46	2.44	3.13	53	130
Y	2.52	2.46	2.78	3.30	59	129
YII	2.34	2.34	2.82	3.31	10	132

Note: φ_1 is an angle between heterocycles; φ_2 is an angle between $C_2 – Z – C_4$.

TABLE VI. Distribution of π-Charges in the Monomethinecyanine Molecules

Dye	N_1	N_5	X	Y	Z	C_2	C_4
I	+0.49	+0.49	+0.19	+0.19	-0.26	+0.04	+0.04
III	+0.50	+0.50	+0.20	+0.14	-0.25	+0.05	+0.04
IY	+0.49	+0.49	+0.20	+0.20	-0.27	+0.05	+0.05
Y	+0.50	+0.47	+0.20	+0.20	-0.26	+0.05	+0.04
YI	+0.44	+0.52	+0.16	+0.52	-0.35	+0.01	-0.02
YII	+0.51	+0.51	+0.20	+0.20	-0.44	+0.11	+0.11

on heteroatoms X (and Y) and with negative charge on the methine carbon atom. In Fig. 5 molecular diagrams of benzthiazolomonomethinecyanine I, benzoxazolomonomethinecyanine IY, and benzthiazoloazacyanine YII are given.

Independent of the dye type, we find that on the nitrogen atoms about one-half positive charge is localized and on heteroatoms X and Y (excluding dye YI) about one-fifth of the charge. On methine carbon atom in the dyes I – Y about one-fourth negative charge is localized. In the case of electron-donor NMe group positive charge of that group is increased as well as negative charge on the methine carbon. Especially negative charge in thiaazacyanine YII is increased. Hence in molecules studied there are 1,3 and 1^1,3 dipoles.

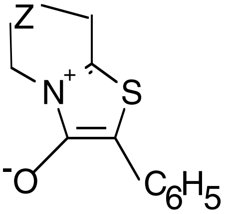
According to the data of Table V distances in 1,3 dipoles ($l_{N\text{-}Z}$) and in 1^1,3 dipoles ($l_{X\text{–}Z}$) significantly depend on the dye type. Attention is drawn to the fact that in transition from I to IY, shortening of the distances in the 1,3 and 1^1,3 dipoles is observed (see Fig. 5). By contrast, in dye YII at the shortening of the distance in the 1,3 dipole, the length of the 1^1,3 dipole is increased. Therefore, both dyes lose selective adsorption on (Ag,Au)S centers.

In spite of the fact that calculated bond lengths should be taken only as speculative values it can see that the distances in the 1,3 and 1^1,3 dipoles of benzthiazolomonomethinecyanine I (2.52 and 2.76 Å) correlate reasonably with the distances between Ag^+ and S^{2-} ions in Ag_2S clusters (2.58 and 2.84 Å).[22] For benzoxazolomonomethinecyanine IY, distances are significantly shorter (2.46 and 2.44 Å).

In monoazacyanine YII the distance in the 1^1,3 dipole (2.82 Å) is close to the distance in the Ag_2S cluster while the 1,3 dipole distance is significantly less (2.34 Å) than the minimum interion distance in Ag_2S clusters.That dye, in spite of maximum charges in the 1,3 dipole, is photographically weakly active. Shortening of the 1,3 dipole, despite correspondence of the distance in the 1^1,3 dipole with the Ag_2S lattice, is probably a main reason for less activity by the unsymmetrical benzthiaoxazolomonomethinecyanine Y in comparison with I. Therefore, we believe that correspondence between the intercharge distance in 1,3 dipoles ("N-CH"-dipoles) and interion distance in sulfide-silver clusters is mainly responsible for the specific adsorption of monomethinecyanines on Ag_2S centers. With distances of the order of 2.5 – 2.6 Å, specific adsorption of organic compounds on (Ag_2S) and (Ag,Au)S centers is possible.

Interaction of Mezoionic Derivatives of Thiazole with (Ag,Au)S Centers

For verification of the hypothesis about 1,3 dipole interaction of organic compounds with (Ag,Au)S centers, six mezoionic derivatives of thiazole of the general formula of Scheme IV with clearly defined 1,3-dipole structure were synthesized and investigated. In that compound, N and O atoms form 1,3 dipoles:

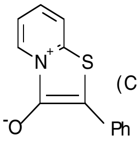


Scheme IV

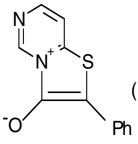
where Z is a group of atoms, forming the pyridine ring (C-21), or pyrimidine (C-22), quinazoline (C-23), quinoline (C-24), quinoxaline (C-25) and benzothiazole (C-26).

Results of the photographic action of compounds C-21 – C-26 on MB fog are given in Table VII. According to the data of Table VII these compounds indeed produce an antifoggant action. Maximum antifoggant action, close to that of the monomethinecyanine is characteristic for C-23 – C-26, including rings of quinazoline, quinoline, quinoxaline, and benzothiazole, respectively. Compounds C-21 and C-22 with the pyridine and pyrimidine rings exert less effect on the MB fog. Quantum-chemical calculation of equilibrium geometry for compound C-24 which has maximum antifoggant effect have shown that the distance in the 1,3 dipole is 2.63 Å, i.e., is close to the interionic distance in the Ag_2S lattice (2.58 Å). In the less strongly adsorbing compound, C-21, this distance is somewhat greater, 2.70 Å, which probably produces the decrease in the antifoggant properties of this substance.

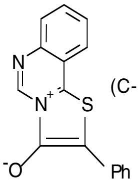
It should be pointed out that according to the quantum-chemical calculations on TAI molecules possessing specific adsorption on Ag_2S centers also there is a characteristic 1,3 dipole including oxygen of the oxy-group and the nearest nitrogen of heterocyclic ring. Therefore, an additional argument is that the reason for specific adsorption is agreement of the 1,3 dipole length in organic compounds with the distance in the Ag_2S or (Ag,Au)S lattice.



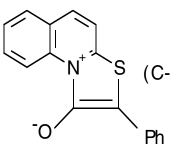
(C-21)



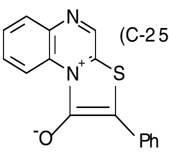
(C-22)



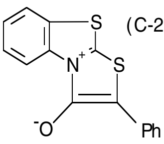
(C-23)



(C-24)



(C-25)



(C-26)

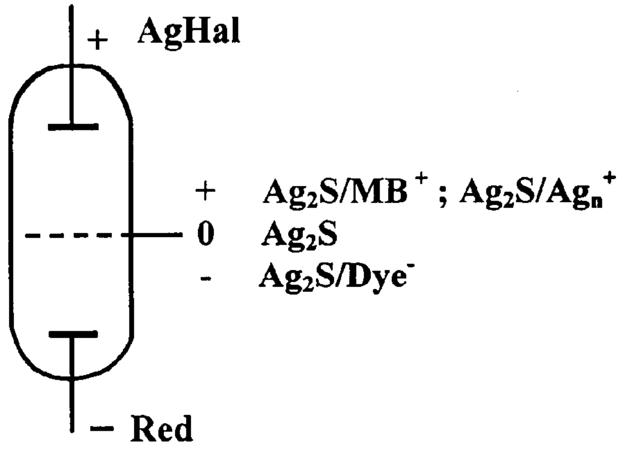


Figure 6. Triode model illustrates Ag_2S center function ("grid") in the regulation of development current; Ag_2S/MB^+: Ag_2S center with adsorbed MB^+; Ag_2S/Ag^+_n: latent image center; Ag_2S/Dye^-: Ag_2S center with adsorbed anionic cyanine dye.

TABLE VII. Photographic Action of Mezoionic Derivatives of Thiazole

Compound	$D_{comp.+MB}$	ΔD
C-21	1.40	0.60
C-22	1.60	0.40
C-23	0.45	1.55
C-24	0.27	1.73
C-25	0.36	1.64
C-26	0.40	1.60

Note: $D_o = 0.14$; $D_{MB} = 2.00$; compounds concentration is 8×10^{-4} mol/mol AgBr.

"Triode" Model of Ag_2S Centers

For clarity MB and other electron-acceptor dye fogging action as well as specific adsorption of organic substances with 1,3 dipoles on Ag_2S centers could be considered in the "triode" model.[15] The triode model in photographic processes on AgHal and first of all in spectral sensitization was proposed by Levy.[23,24] In the present work, the triode model is applied to a dark process of development. The triode model is shown in Fig.6. According to the "triode" model negative charge on the cathode is produced by reducing agent Red (developing agent) and positive charge on the anode is produced by silver halide. Ag_2S centers provide a "grid." Charge on the grid controls a current between cathode and anode, i.e., the AgHal developing process. For intensifying of the current, the charge on the Ag_2S centers should be positive. In the case of methylene blue, the positive charge on the Ag_2S centers is produced by adsorbed MB^+ cation (Ag_2S/MB^+), which results in significant current increase and, as a consequence, fogging. On irradiation of AgHal grains on Ag_2S centers the positive charge is also produced by the silver particles of Ag^+_n centers of latent image (Ag_2S/ Ag^+_n). It therefore accelerates electron transfer from Red to AgHal.

In the case of selective adsorption of organic substances on Ag_2S centers at the cost of MB^+ desorption, the positive charge is decreased and as a result the fog is decreased. TAI appears to act in the same manner as well as some monomethinecyanines and mezoionic thiazole derivatives. An especially strong antifoggant effect should be forthcoming if the adsorbed substance has negative charge. In the triode model this is equal to the triode closing (Ag_2S/Dye^-). Indeed, as was shown in Refs. 1 and 15, in the presence of anionic dyes, in particular triethylammonium salt of 3,3'-di-(γ-sulfopropyl) thiacyanine, fog level of the layers with MB^+ decreased

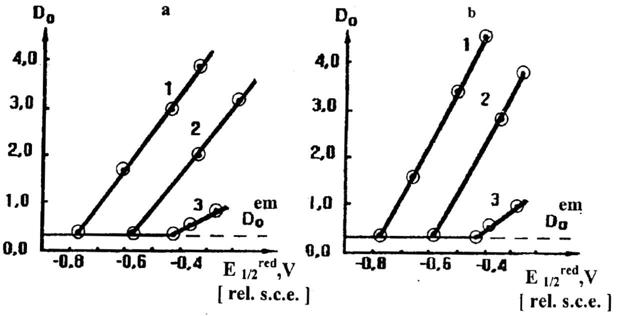
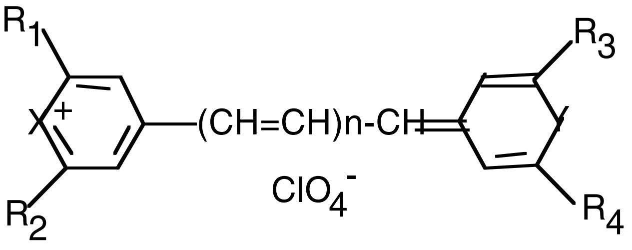


Figure 7. Dependence of the fog level, D_o, on $E^{red}_{1/2,dye}$ for the dyes with the structure of Scheme V with different length of polymethine chain: 1, $n = 0$; 2, $n = 1$; 3, $n = 2$. Dye concentrations: a, 2.5×10^{-5}; b, 5×10^{-5} mol/mol AgBr.

to a value even less than the fog level of samples without MB. Of note is that fog decreases in the case of cationic thiacyanine I on its adsorption on Ag_2S centers appear to be determined by the low electron affinity of monomethinecyanines in spite of their positive charge.[16] Therefore organic substance adsorption could control the catalytic properties of Ag_2S and (Ag,Au)S centers.

Dependence of Fogging Action of Electron-Acceptor Dyes on Their Electron Affinity

As electron-acceptor dyes pyrylo-, thia-, and selenapyrylocyanine dyes were used with the structure of Scheme V:



Scheme V

where X,Y = O, S, Se; R_1–R_4 = Ph, CH_3; $n = 0, 1, 2$, as well as methylene blue, pinacryptol green, Janus green, and phenosafranine. Electron affinity was characterized as $E^{red}_{1/2}$ (relative to SCE in acetonitrile).

According to results, dependence of the fog level, D_o, from $E^{red}_{1/2,dye}$ is complicated and is determined by various factors. In particular, it is limited by not only $E^{red}_{1/2}$ but by dye structure and above all by polymethine chain length (n) as well. In the dyes of Scheme V with equal length of polymethine chain (n = 0, 1 or 2) but with different heteroatoms, regular growth of D_o is observed with an increase in electron affinity of the dye (Fig. 7). Hence, dye adsorption on (Ag,Au)S centers is connected with polymethine chain length.

According to the data of Fig. 7, for the dyes with constant n linear dependence of D_o on $E^{red}_{1/2,dye}$ is observed over a definite interval of $E^{red}_{1/2,dye}$. The dependence has threshold-like character; i.e., up to the definite limiting value of $E^{red}_{1/2,lim} = -0.75$ to -0.80 V (versus SCE), the fogging process is not observed. In this case the limiting potential $E^{red}_{1/2,lim}$ value depends on n and increases as chain elongation occurs. For the second dye series, including methylene blue, pinacryptol green, Janus green, and phenosafranine, dependence of D_o on $E^{red}_{1/2,dye}$ also has theshold-like character ($E^{red}_{1/2,lim} = -0.76$V). Summarizing the results on fogging action of two sets of dyes, we can deduce that for good adsorbing electron-acceptor dyes the limiting potential of fogging for the investigated AgBr emulsion with S+Au sensitization could be localized around $E^{red}_{1/2,lim} = -0.75$ to -0.80 V (versus SCE).

Limiting potential $E^{red}_{1/2,lim}$ corresponding to beginning of fog formation could be useful for evaluating the sensitivity center electron level positions. Because they are not foggants, the sensitivity center potentials must be more negative than the potential for the onset of fog, $E^{red}_{1/2,lim}$.

According to the literature[5,20] potentials of conduction band (CB) bottom and valence band (VB) top are $E_{CB} = -1.34$ V and $E_{VB} = +1.26$ V (versus SCE). Hence, when taken into account that $E^{red}_{1/2,lim} = -0.75$ to -0.80 V, the potential of the (Ag,Au)S center has to be more negative, i.e., the depth of centers below the conduction band bottom is $\Delta E \leq 0.54 - 0.60$ eV, consistent with the data of Refs. 25 through 29.

Notice that a stable foggant effect ($D \cong D_{MB}$) of electron-acceptor dyes was observed at $E^{red}_{1/2,dye} = -0.40$ to -0.50 V (rel. s.c.e.). Therefore, the potential of development centers (latent image centers and fog centers) has to be equal or be more than this value, and their depth below the conduction band bottom is $\Delta E \geq 0.84 - 0.94$ eV. According to Dähne,[30] the depth of Ag_4 centers of latent images is $\Delta E \leq 1.2$ eV, and according to Kawasaki *et al.*,[31] the depth of Ag_4 centers of latent images on AgBr grains with S sensitization is $\Delta E = 1.3$ eV. Hence, on the basis of investigation of fogging processes of photographic emulsions by electron-acceptor dyes adsorbing on (Ag,Au)S centers it may be concluded that:

1. S+Au sensitization centers are located no deeper than 0.54 – 0.60 eV below the AgBr conduction band bottom.
2. Development centers are located on the depth about 0.84 – 0.94 eV or deeper below the AgBr conduction band bottom.

Summary

The history of photographic emulsion development is connected with creation of impurity centers of sensitivity. Impurity centers produced in the process of sulfur sensitization act as a catalyst for the latent image formation process. They are distinguished in their physicochemical properties from the basic light-sensitive substrate, silver halide. Just that distinction in the properties forms the basis of specific adsorption of organic substances on Ag_2S and (Ag,Au)S centers. Because of specific adsorption, alteration of catalytic center function is possible. This alteration provides information about microscopic impurity centers with an enormous amplification factor, characteristic of the photographic process. The method of "chemical microscopy" offers new possibilities for investigating small particles on AgHal grain surfaces. It is no less important that this method permits purposeful change of the properties of photographically active centers.

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