

Sensitization of Merocyanine Dyes of Tabular Microcrystals

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The effect of various concentrations of merocyanine dyes on photographic properties of AgBr tabular microcrystals with an AgBrI lateral shell has been investigated. Total photographic speed of photolayers is determined depending on the character of dye adsorption on the surface of microcrystals at the introduction of a dye after chemical sensitization. The greatest increase in photosensitivity is shown to be observed for the dye capable of forming j-units in the adsorbed state. The possibility to avoid desensitization in the area of characteristic absorption of silver halide by the introduction of a dye before chemical sensitization has been considered. Reflection spectra and spectral sensitivity of spectrally sensitized photolayers are determined. The relation between reflection spectra and spectral sensitivity of photolayers including the dyes is established.

Introduction

One of more prominent aspects in modern photography is increase in photographic speed of AgHal grains. To increase photographic speed of grains, it is necessary to form a limiting potential number of sites of latent image centers and thus, to increase quantum efficiency of a photographic process. The localization of a latent image allows us to increase the photographic response both in the area of AgHal characteristic absorption and in the spectral area.

During chemical sensitization, latent image centers are formed unselectively on an octahedral surface {111}. On the other hand, they are formed selectively on a cubic {100} surface, mainly, on surface defects or on the corners and edges of cubes. In the latter case a limited number of sensitivity and latent image centers are formed [1]. Now, in photographic technology for the preparation of photosensitive materials, tabular grains and grains of a complex structure, composition and habit are widely used. As is well known, tabular grains have two main parallel {111} surfaces and edges {100}. A traditional chemical sensitization of tabular grains results in a nonselective formation of the majority of sensitivity and latent image centers along the perimeter of the main surface, edges and corners [2]. Therefore, tabular grains require special methods for concentrating the latent image. One of these methods is to introduce substances – site directors – capable of controlling the topography of topochemical reaction products, the number of sites for sensitivity centers formation being limited and the efficiency of concentrating the latent image centers increasing.

Site directors include iodide, thiocyanate, azainden, mercaptotetrasol and j - aggregating dyes or their combinations. Most of the dyes are capable of being selectively adsorbed on {111} or on {100} surfaces that prevents a latent image from being formed on {111} or on {100} surfaces [1]. Also, by using the dyes as site directors it is possible to obtain an additional sensitivity increase due to spectral sensitization.

Methods

AgBr tabular grains with an AgBr_{0.96}I_{0.04} lateral shell were synthesized for our research. AgBr and AgBr_{0.96}I_{0.04} fine emulsions were synthesized by the controllable two-jet crystallization technique at the temperature 40°C. First, an aqueous solution of gelatin (with the concentration 1.5 %) was placed in the reactor. 1 mol AgNO₃ and KBr solutions were added into the reactor at the speed of 17 ml/min. For an AgBr fine emulsion the synthesis pBr value was kept constant and equal to 1.4, and for an AgBr_{0.96}I_{0.04} fine emulsion - equal to 3. AgBr tabular grains were synthesized by the method of physical ripening from a fine emulsion at T = 60°C, pBr = 1. To prepare tabular grains with a lateral shell the emulsion containing AgBr tabular grains was placed in the reactor at T = 66°C. The 1 mol KBr solution was added in order to adjust the pBr value to 3. Then a 10 % solution of KSCN in the quantity of 0.4 ml/gAg was added. After that an AgBr_{0.96}I_{0.04} fine emulsion was being added in the reactor by portions every 10 – 15 min. Physical ripening was carried out for 2 – 2.5 hs. at pBr = 1. Then aqua soluble salts were washed out from the emulsion by the method of precipitation and dispersion. After the dispersion process the final pBr in the emulsion was adjusted to 3 and the pH to 7.

Chemical sensitization was carried out at T = 60°C. Solutions of additives were introduced into a mixing up emulsion in the following sequence: the antifoggant KF-4026 - Na₂S₂O₃ (2.0*10⁻⁵ mol/molAg) - KSCN (4.0*10⁻² mol/molAg) - HAuCl₄ (1.88*10⁻⁵ mol/molAg).

Spectral sensitization was carried out before or after chemical sensitization. When spectral sensitization was carried out after chemical sensitization the emulsion was chemically sensitized up to the optimum the value of photographic speed with the minimum optical density of the fog. The concentration of the dyes added into the emulsion was 1.0*10⁻⁵, 5.0*10⁻⁵, 1.0*10⁻⁴, 5.0*10⁻⁴, 1.0*10⁻³ mol/molAg. For this purpose alcohol-working solutions with the concen-

tration $1.0 \cdot 10^{-3}$ mol per liter were used. Then the samples were stored at constant temperature for half an hour for the reaction of adsorption to take place, and then they were coated on the triacetate support. When spectral sensitization was carried out before chemical sensitization, spectral sensitizers were added into the emulsion in the same quantities and were stored in the reactor for 30 minutes at $T = 60^\circ\text{C}$. Then chemical sensitizers were added into the emulsion. Sampling was made every 15 minutes. The duration of chemical sensitization was 1 - 1,5 h. The choice of dyes for our research was prompted by the literary data on the studies of the adsorption of dyes on various types of the surface of AgBr grains [1]. For spectral sensitization the following three dyes were selected: one of the dyes was capable of being adsorbed mainly on the octahedral surface of grains $\{111\}$, the second of them - capable of being adsorbed mainly on the cubic surface $\{100\}$ and the third one - capable of forming extended J - units. The dyes are presented in Table 1.

The exposure of chemically and spectrally sensitized samples was carried out on the sensitometer PHSD-41, the measurements of optical density of darkening were made on the densimeter DP-1M. Chemical photographic processing was performed under standard conditions using the developer UD-2. Then, sensitometric tests were made and main photographic characteristics were defined.

To interpret the results on spectral sensitization, the present authors studied the reflection spectra of the dyes adsorbed on tabular grains with the help of the spectrophotometer Spekord-M40 and determined spectral sensitivity of photolayers with dyes by the spectrosensitometer ISP-73.

Table 1. Basic characteristics of dyes.

Dye №		λ_{max} , nm	Type of adsorption	Formula
№	№			
1	X	526	Adsorbed mainly on the cubic surface $\{100\}$	
2	XI	570	Adsorbed mainly on the octahedral surface $\{111\}$	
3	XII	570	Capable of forming extended j-units	

Results and Discussion

This study of photographic characteristics of tabular grains with a lateral shell depending on the ability of the dye to be adsorbed on various surfaces of a microcrystals was made

by means of dyes having five different concentrations. Chemical sensitization preceded spectral sensitization. The photographic characteristics: photographic speed by the criterion 0.2 ($S_{0,2}$) and 0.85 ($S_{0,85}$), optical density of fog (D_0) of photolayers prepared on the basis of AgBr tabular grains with an $\text{AgBr}_{0,96}\text{I}_{0,04}$ lateral shell, sensitized dyes, are presented in Table 2.

As seen from Table 2, Dye №X adsorbed mainly on the cubic surface possesses a sensitizing effect. Total photographic speed of a photolayer in comparison with spectral unsensitized photolayers increased two times as much at the concentration of the dye $1.0 \cdot 10^{-5}$ mol/molAg and is $S_{0,85} = 115$, $S_{0,2} = 33$ at $D_0 = 0.08$.

Dye №XI adsorbed mainly on the octahedral surface of tabular grains, increases total photographic speed in the $5.0 \cdot 10^{-5}$ - $1.0 \cdot 10^{-3}$ mol/molAg concentration range. When the concentration of the dye in the emulsion is $1.0 \cdot 10^{-3}$ mol/molAg photographic speed is the greatest ($S_{0,85} = 331$, $S_{0,2} = 100$ at $D_0 = 0.12$), that corresponds to increase in photographic speed twice as much in comparison with the photolayer without a dye

Table 2. Photographic characteristics of spectrally sensitized photolayers on basis of AgBr tabular grains with an $\text{AgBr}_{0,96}\text{I}_{0,04}$ lateral shell.

C(dye), mol/molAg	Dye №	Photographic characteristic		
		$S_{0,2}$	$S_{0,85}$	D_0
0	X	18	60	0,1
$1.0 \cdot 10^{-5}$		33	115	0.08
$5.0 \cdot 10^{-5}$		30	95	0.09
$1.0 \cdot 10^{-4}$		21	55	0.11
$5.0 \cdot 10^{-4}$		8	20	0.90
0	XI	57	160	0.08
$1.0 \cdot 10^{-5}$		49	125	0.21
$5.0 \cdot 10^{-5}$		52	154	0.21
$1.0 \cdot 10^{-4}$		64	180	0.21
$5.0 \cdot 10^{-4}$		81	200	0.19
$1.0 \cdot 10^{-3}$	101	330	0.12	
0	XII	57	160	0.08
$1.0 \cdot 10^{-5}$		38	105	0.08
$5.0 \cdot 10^{-5}$		60	155	0.11
$1.0 \cdot 10^{-4}$		80	300	0.17
$5.0 \cdot 10^{-4}$		152	595	0,20
$1,0 \cdot 10^{-3}$	91	400	0,57	

The above results show that the greatest photographic speed can be achieved when using Dye №XII, capable of forming extended j-units. The greatest increase in photographic speed is observed for the concentration $5.0 \cdot 10^{-4}$ mol/molAg ($S_{0,85} = 595$, $S_{0,2} = 153$ at $D_0 = 0,2\text{ед}$), that corresponds to increase in photographic speed almost four times as much.

For spectrally sensitized photolayers with the maximum photographic speed we received spectrosensitograms in the 400 - 1000 nm range and reflection spectra. Spectrosensitograms and reflection spectra for Dye №XII are shown in Fig. 1.

As seen from Fig. 1.a., the desensitization effect in the area of characteristic absorption of AgHal absorption is observed for adsorbed Dye № XII. For low exposures ($H = 1/9H_0$) the photolayer has the greatest photographic speed at 600-650 nm that corresponds to the adsorption of the dye in j-state (Fig. 1.b). Desensitization effect is also observed for Dyes №X and №XI.

In order to increase absorption in the area of characteristic absorption of spectrally sensitized photolayers, spectral sensitization was carried out with Dye № X before chemical. Dependencies of photographic characteristics of photolayers from the duration of chemical sensitization using Dye №X with the concentrations $1.0 \cdot 10^{-5}$ and $1.0 \cdot 10^{-4}$ mol/molAg preceding chemical sensitization are given in Fig. 2 (a, b).

As seen from Fig. 2, when adding the spectral sensitizer with the concentration $1.0 \cdot 10^{-5}$ mol/molAg before chemical sensitizers (it corresponds to 15 min in Fig. 2.), photographic speed of a photolayer amounts to 60 by the criterion 0.85, that is much less than for a photolayer with the introduction of the dye after chemical sensitization ($S_{0.85} = 115$, tab. 2.). The photolayers obtained after the introduction of Dye №X with $1.0 \cdot 10^{-4}$ mol/molAg both before and after carrying out the chemical sensitization have $S_{0.85} = 60$.

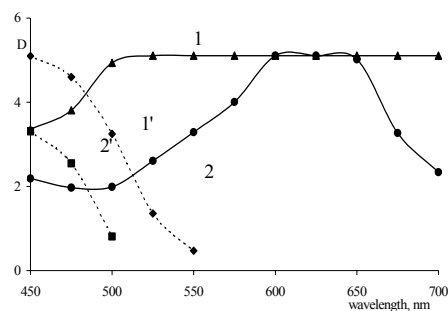
The results on the effect of light with different wavelengths in the 450 - 550 nm range on spectral sensitivity of the photolayer sensitized by Dye №X added before chemical sensitization, in the quantity of $1.0 \cdot 10^{-5}$ mol/molAg, are given on Fig. 3 (curves 1 and 2). Curves 1' and 2' correspond to the reference sample at the same exposures.

As seen from Fig 3, desensitization effect in the area of characteristic absorption by silver halide disappears when the dye is added into a chemically unsensitized emulsion both at big, and small exposures ($D = 4.5$ for a photolayer with the dye (curve 1) and $D = 3$ for a photolayer without the dye (curve 1') at $H = 1/3H_0$).

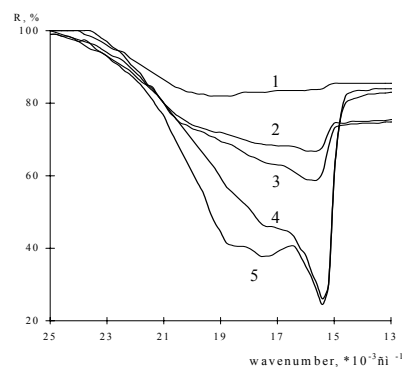
Dependencies of optical density of darkening from the wavelength of light attacking a photolayer chemically sensitized for 30 min in the presence of Dye №X with the concentration $1.0 \cdot 10^{-5}$ mol/molAg added before chemical sensitization are represented in Fig. 4.

There is no desensitization effect in the area of AgHal characteristic absorption when continuing chemical sensitization (Fig. 4). However, increase in photographic speed in the area of AgHal characteristic absorption does not result in total photographic speed increase (Fig. 2a). It is likely to be due to the dye's adsorption on AgHal's free surface in a molecular state without forming J-units. The given assumption is verified by the reflection spectra of photolayers (Fig. 5.) obtained after Dye №X is added into the primitive emulsion (curve 1) followed by chemical sensitization proceeding for 30 min (curve 2).

The maximum of absorption for introducing the dye before chemical sensitization is observed at 526 nm (19000 cm^{-1}) corresponding to a molecular state of the dye on the surface of microcrystals (Table 1). The maxima corresponding to J-aggregation (18200 cm^{-1}) and to the H-state of the dye (19600 cm^{-1}) are not observed.



a)



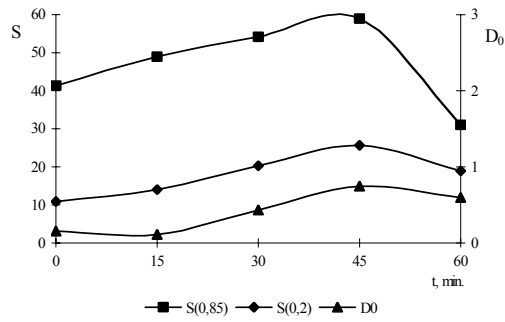
b)

Figure 1.: a) Dependence of optical density of darkening from the wavelength of incident light on a photolayer with Dye №XII: 1' - $C(\text{dye}) = 0, H = 1/3H_0$; 2' - $C(\text{dye}) = 0, H = 1/9H_0$; 1 - $C(\text{dye}) = 5.0 \cdot 10^{-4}, H = 1/3H_0$; 2 - $C(\text{dye}) = 5.0 \cdot 10^{-4}, H = 1/9H_0$;

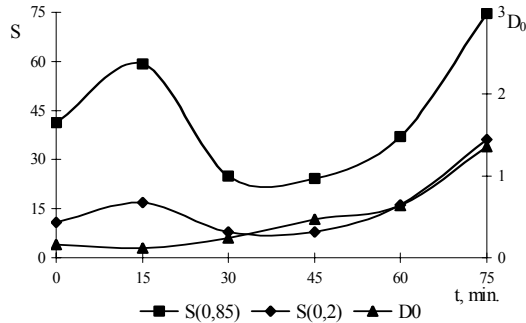
b) Reflection spectra of Dye №XII adsorbed on $\text{AgBr}/\text{AgBr}_{0.96}\text{I}_{0.04}$ tubular grains. The concentration of the dye in a photolayer is: 1 - $1.0 \cdot 10^{-5}$, 2 - $5.0 \cdot 10^{-5}$, 3 - $1.0 \cdot 10^{-4}$, 4 - $5.0 \cdot 10^{-4}$, 5 - $1.0 \cdot 10^{-3}$ mol/molAg.

Most likely, Dye №X is adsorbed on the entire surface of grains, not only on the surface {100}. During the further introduction of chemical sensitizers, the entire surface of grains is occupied by the dye in a molecular state and the efficiency of chemical sensitization is reduced, while the optical density of the fog grows because of the fast growth of a limited number of sensitivity centers. Increase in the dye concentration does not result in total photographic speed increase (Fig. 2.b).

Thus, it can be concluded that it is more expedient to use Dye №X after chemical sensitization when the sensitivity centers are already formed.



a)



b)

Figure 2.: a) for Dye № X with the concentration $1.0 \cdot 10^{-5}$ mol/molAg;

b) for Dye № X with the concentration $1.0 \cdot 10^{-4}$ mol/molAg.

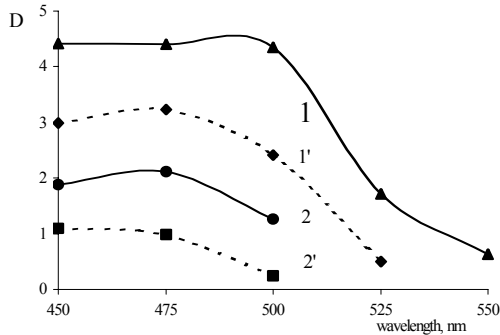


Fig.3. Dependence of optical density of darkening from the wavelength of incident light on a photolayer with Dye №X: 1' - C (dye) = 0, $H=1/3H_0$; 2' - C (dye) = 0, $H=1/9H_0$; 1 - C (dye) = $1.0 \cdot 10^{-5}$, $H=1/3H_0$; 2 - C (dye) = $1.0 \cdot 10^{-5}$, $H=1/9H_0$.

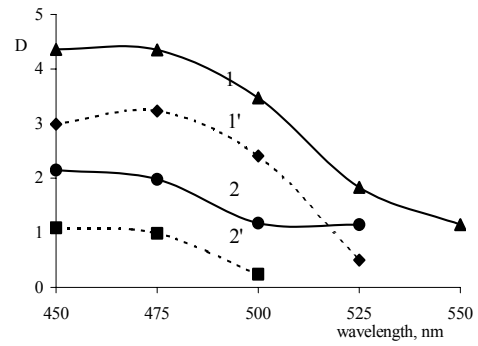


Fig.4. Dependence of optical density of darkening from the wavelength of incident light on a photolayer with Dye №X: 1' - C (dye) = 0, $H=1/3H_0$; 2' - C (dye) = 0, $H=1/9H_0$; 1 - C (dye) = $1.0 \cdot 10^{-5}$, $H=1/3H_0$; 2 - C (dye) = $1.0 \cdot 10^{-5}$, $H=1/9H_0$.

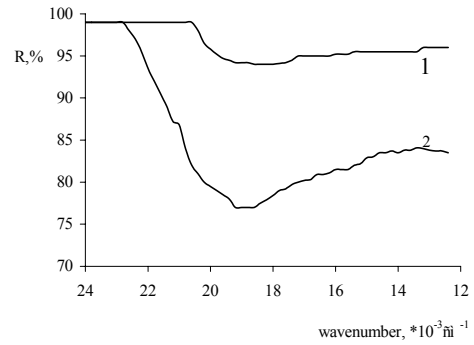


Fig.5. . Reflection spectra of photolayers with Dye №X, added before and/or after chemical sensitization: 1 - before the addition of chemical sensitizers; 2 - after the addition of chemical sensitizers.

Reference

1. US Patent Application, 002006849, Eastman Kodak Company, 2002
2. Maskasky J.E. // J.Imag.Sci. 1988. - V.32, - №4. - p.160-177.

Biography

Anton P. Prostenko was born in Blagoveschenck (Russia) on January 20, 1980. In 2001 he graduated from Kemerovo State University, the Chemistry faculty. Now he is a post-graduate of Kemerovo State University, the Physics faculty. His field of research is mass crystallization processes of silver halides, the author of 13 scientific publications.