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## Dye-sensitized photoprocesses in “silver stearate – silver bromide” system

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**Abstract.** The article provides a comprehensive description of spectral sensitization of photothermographic materials, showing a significant influence of dye molecules localized on the surface of silver stearate on the spectral sensitization process of photothermographic materials. It demonstrates that silver stearate effectively transfers dye molecules luminescence to the silver bromide microcrystal with a lightguide mechanism.

**Keywords:** spectral sensitization, photothermographic materials, luminescence, silver stearate, silver bromide, Rhodamine 6 G.

### Introduction

In addition to CCD and CMOS sensors, the photothermographic materials based on silver halide and silver salts of fatty acids (in particular silver stearate) compositions are used quite widely to record optical images (Goryaev 1991; Morgan 1993; Sahyun 1998). When preparing such photosensitive composition, silver bromide is synthesized on the surface of silver stearate (Goryaev 1994a; 2013). Spectral sensitization process can be achieved by adding various dye-sensitizers into this photothermographic composition. Therefore, it is possible to attain photosensitivity of such compositions in any optical spectral range (Goryaev 2011; 2013).

### Results and discussion

Dye molecules precipitate both on the surface of silver stearate and on the surface of silver bromide when this dye is adsorbed into photothermographic compositions. Silver stearate is a transparent dielectric in visible range (Goryaev, Smirnov 2012). Dyes adsorbed on different dielectric surfaces radiate with luminescence quantum yield of a few dozen per cent (Goryaev 2013). Therefore, a large quantity of luminescence light transmits through the silver stearate particle and hits the microcrystal of silver bromide. The luminescence of the dye adsorbed on silver stearate was investigated with the use of the “white standard” dilution method (Goryaev 1980; Goryaev, Smirnov 2015). Figure 1 shows the ratio of the luminescence technical yield of Rhodamine 6G adsorbed on the surface of silver stearate to the degree of dilution by “white standard” (magnesium oxide). The technical quantum yield increases at first and then becomes constant with decreasing concentration of the dyed sample in the magnesium oxide powder. The constant value of the technical yield is the true luminescence quantum yield of the adsorbed dye (Goryaev 1980).

In many sensitizing dyes, luminescence and absorption spectra strongly overlap (Goryaev 1981). Figure 2 shows the absorption and luminescence spectra of Rhodamine 6 G adsorbed on silver stearate.

Since absorption and luminescence spectra strongly overlap, the luminescence radiated by the dye molecules adsorbed on silver stearate is effectively absorbed by the dye adsorbed on the silver bromide surface. Therefore, luminescence light induces the photophysical and photochemical processes required for photographic process in silver bromide. The dye molecules adsorbed on silver bromide absorb luminescence light and become able to transfer energy directly to silver bromide according to the theory of the non-radiative resonant inductive energy transfer (Akimov, Cherkasov, Cherkashin 1980; Ermolaev, Sveshnikova, Bodunov 1996).

Consequently, the dye molecules adsorbed on silver stearate, as well as on silver bromide, exert significant influence on the spectral sensitization process, where silver stearate ensures sufficiently effective transmission of energy from dye molecules to the sensitivity centers of silver bromide. This is confirmed by the fact that the optimal concentration of dye in photothermographic compositions is substantially higher than in classic silver halide emulsions (Goryaev 2011; Goryaev, Kolesova, Timohina et al. 1992).

Efficient spectral sensitization has been observed (Goryaev, Kolesova, Timohina et al. 1992) in the compositions where silver bromide was synthesized directly on the surface of silver stearate. In this case, the optimal concentration of silver halide in relation to silver stearate is 10 mol%. The ratio for the volume concentration of silver bromide microcrystals is as follows:

$$c_{vol} = \frac{cMd'}{M'd} \quad (1)$$

where  $c$  is the molar concentration of silver halide,  $M$  and  $M'$  are the molecular masses of silver bromide and silver stearate respectively,  $d$  and  $d'$  are the density of silver bromide and silver stearate respectively. In case of  $M = 187.8$ ,  $M' = 391.3$ ,  $d = 6.47$ ,  $d' = 1.40$  and  $c = 0.1$ ,  $c_{vol}$  is 0.0104. Further assuming that the particles of silver halide and silver stearate are cubes, it is possible to estimate the ratio of the silver stearate surface area  $s'$  to silver halide  $s$ :

$$\frac{s'}{s} = 1.2 (c_{vol})^{-\frac{2}{3}} - 0.2 \quad (2)$$

Given this assumption and  $c_{vol} = 0.0104$ , the effective area of the silver stearate surface is 25 times greater than the effective area of the silver halide surface (Goryaev 1994b).

Electronic microscope scanning has indicated that particles of silver stearate are oblong prisms (Fig. 3). The base length of these prisms is 3 to 5 times less than their height. The cube crystals of silver bromide were detected on the prism particles of silver stearate. In this case  $\frac{s'}{s} \approx 30$ . Thus, the above estimate is quite consistent with the optimal concentration values of sensitizing dyes observed in the experiments in photothermographic compositions that are almost two orders of magnitude greater than the values for traditional photographic emulsions (Goryaev, Kolesova, Timohina et al. 1992).

A luminescence light hits on the surface of the AgBr microcrystal via the lightguide mechanism shown in Fig 4. It is worth noting that the luminescence light of dye molecules hits the silver halide microcrystal both directly and when reflected from the interior face of a silver stearate particle. The reason for this is that silver stearate has a relatively high refractive index of 1.515 (Goryaev, Smirnov 2012). In turn, the refractive index of the environment (with polyvinyl butyral as the binder) is 1.485 (Kabanov 1974).

As a result, the luminescence light in silver stearate attains total internal reflection at angles of incidence of about 75° to 80°. At the interface of silver stearate and silver halide—the refractive index of silver bromide in visible range is over 2.2 (White 1972)—the luminescence light efficiently passes into AgBr. Thus, the silver stearate particle, similarly to a lightguide, focuses the light emitted by the dye localized on the silver stearate surface to a significant degree (Goryaev 1994b). In turn, this luminescence light is effectively absorbed by silver bromide sensitized by dye; the effect of the luminescence light of the dye molecules on silver stearate becomes significant. It is interesting to note that the adsorbed dye Rhodamine

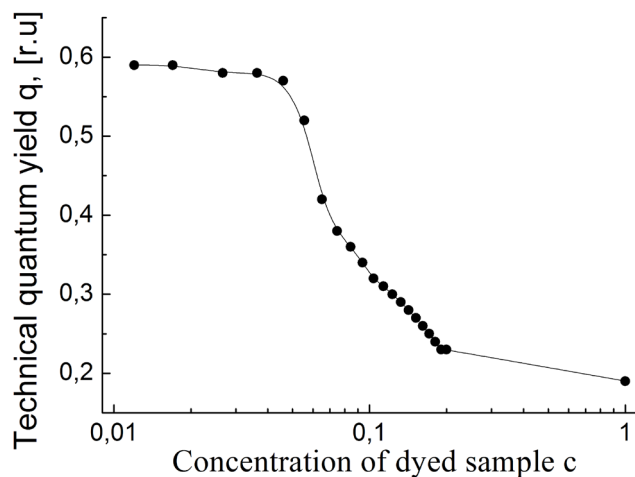


Fig. 1. The dependence of the luminescence technical yield of Rhodamine 6G adsorbed on the surface of silver stearate on the degree of the dilution by "white standard" (magnesium oxide).

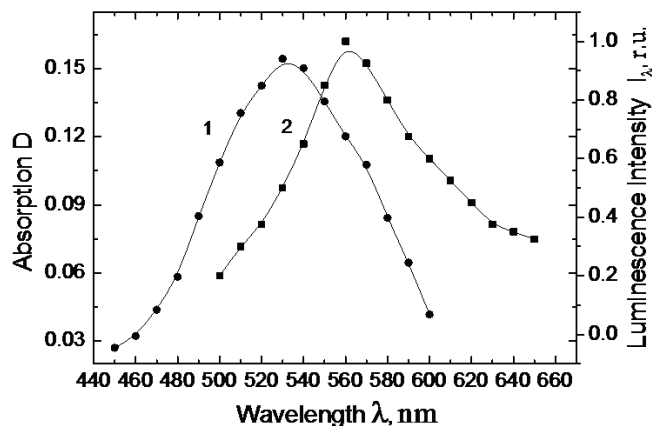


Fig. 2. Absorption (1) and luminescence (2) spectra of Rhodamine 6 G adsorbed on silver stearate surface

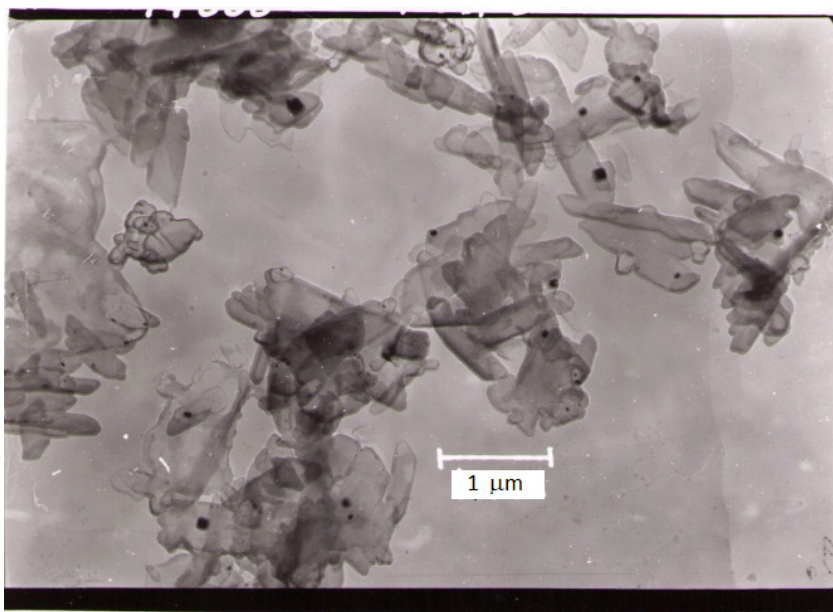


Fig. 3. Electron microphotographs of the silver stearate particles with the AgBr microcrystals located on its surface. The zoom is 14000x

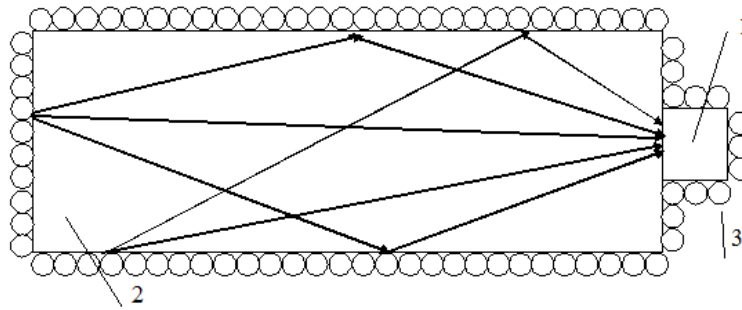


Fig. 4. Lightguide mechanism scheme of spectral sensitization of photothermographic materials. 1 – AgBr, 2 – silver stearate, 3 – adsorbed dye molecules.

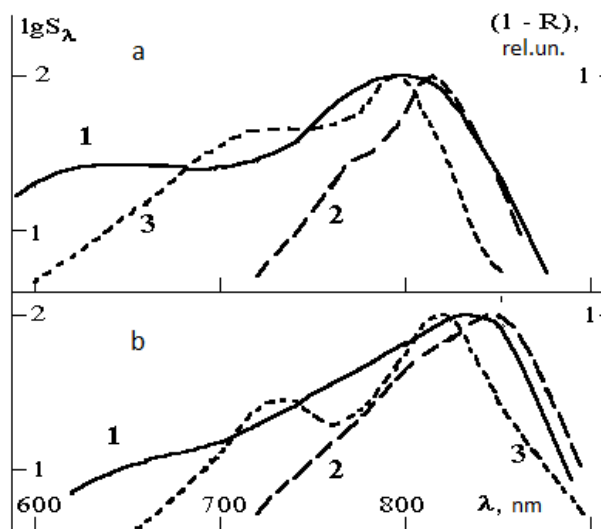


Fig. 5. Dependences of the spectral sensitivity of the photothermographic films based on silver bromide and silver stearate (1) and traditional silver-bromide emulsions (2) sensitized by no. 1389 (a) and no. 722 (b) dyes, the diffuse reflective spectra of these dyes (3)

6G increases the dielectric permittivity of silver stearate (Smirnov, Castro, Goryaev et al. 2017), which leads to an increase in the role of the lightguide sensitization mechanism. In order to estimate the contribution of dyes adsorbed on a non-light-sensitive organic silver salt to the process of spectral sensitization, a study into the spectral sensitivity of photo layers and absorption of dyes was carried out (Goryaev 1998). Figure 5 shows the dependences of the spectral sensitivity of the photothermographic films based on silver bromide and silver stearate (curve 1) and traditional silver-bromide emulsions (curve 2) sensitized by the same infra-chromatic dyes (Goryaev, Shapiro 1997). Also, the diffuse reflectance spectra of these dyes adsorbed on silver stearate are presented (curve 3).

Usually, the spectral dependence of the sensitivity  $S_\lambda$  of photographic materials follows the course of the light absorption by adsorbed dyes, except in cases of simultaneous adsorption of the various aggregate forms of dye. Therefore, the spectral dependence of the sensitivity of the silver-bromide emulsion (curves 2, Fig. 5) corresponds to the absorption spectrum of the dyes adsorbed on AgBr. Figure 5 shows that the position of the absorption bands of the dyes adsorbed on silver bromide and silver stearate differs significantly, and the spectral sensitivity of photothermographic composition is determined by the superposition of their absorption spectra. A qualitative comparison of the spectral dependences shown in fig. 5 allows for the conclusion that the contributions of the dyes adsorbed on silver bromide and the dyes adsorbed on silver stearate in the spectral sensitization process are approximately equal.

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