A Procedure of the Chemical Sensitization Rate Checking of AgCl Emulsion Microcrystals

Boris A. Sechkarev and Marina I. Ryabova State University of Kemerovo, Russia

Introduction

It is difficult to study the influence of chemical sensitization on a photosensitivity of AgCl microcrystals for microcrystals of size less then 0.5 μ m because of low intrinsic sensitivity of silver chloride. However, it is doubtless, that the Ag₂S and Ag_nAu sensitivity centers change a microcrystals surface state and their sensitometric properties. Especially the surface influence is appear by use of small microcrystals (d<0,2 μ m), where a surface/volume ratio much grows, and the superficial properties of micro-crystals determine a photoprocess efficiency. Emulsion AgCl microcrystals with d<0,2 μ m are widely used in high resolution photomaterials (phototechnical, aero-photographic films, etc.). Therefore the control of chemical sensitization efficiency for these micro-crystals is important.

Experimental Results and Discussion

We offer a way of the control of chemical sensitization efficiency of the small size AgCl microcrystals through an adsorption of reference spectral sensitizer. As a reference dye is chosen 1,1',3,3'-tetraethyl-5,5'-bis-(threefluoromethilsul-fonyl) imidocarbocy-aniniodide. A selection of dye for the chemical sensitization research is caused by results of a preliminary series of experi-ments. It is shown, that the dye adsorption on AgCl microcrystals is not accompanied by growth of a fog optical density on sensitized emulsion, (that is rather frequently observed at sensitization by carbocyanine dyes²). This dye also has narrow absorption band in a visible spectrum (λ =530 nm).

For determination of extinction factor dye under consideration is prepared water or water-alcohol solutions with concentration interval from 10^{-3} up to 10^{-6} mol/l. Spectra of dye solutions absorption are measured by use spectrophotometer "SPECORD UV VIS". Then optical density D of the maximum absorption band is determined. Extinction factor is calculated by the Ber-Lambert expression:

$\varepsilon = \mathbf{D}/(\mathbf{C} \times \mathbf{I})$

where: ε- extinction factor (l/mol×cm); D - optical density; C - dye concentration (mol/l); l- layer thickness (cm). Figure 1 shows an dye absorption spectrum. Extinction factor was determined for the narrow absorption band of λ =530 nm.

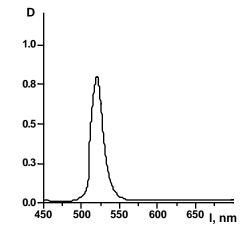


Figure 1. An dye absorption spectrum.

In a wide interval of temperatures (45-60°C) it is shown that the optimal conditions of carbocyanine dyes effective adsorption on microcrystals AgHal are pAg=7,0-8,5, pH=7,5. It was established, that the adsorption reaches saturation under these conditions in 20 minutes.

The dye adsorption is carried out on AgCl cubic {100} microcrystals (d=0,18 mm) at pAg=8,0 and t=58°C during 20 minutes. An adsorption isotherm of dye is obtained, which can be attributed to described Langmuer equation adsorption isotherms by it's form. On Fig. 2. the isotherms of a dye adsorption in coordinates C_{ad} (mol/g Ag) - C_{eq} (mol/l) and in Langmuer coordinates are presented. The adsorption isotherm in Langmuer coordinates allow to estimate value of the maximum adsorption. For our dye it is $C_{admax}=9\cdot10^{-6}$ mol/g Ag.

The measurement of adsorbed dye concentration on AgCl microcrystals surface after chemical sensitization were also carried out. Results have prove, that the degree of "filling" of a microcrystals surface remains nearly constant (accurate to an error of a method was 15%) regardless of a sensitization type (S, S+Au, Au). This is possible to make a conclusion, that the sensitivity centers are not centers of the dye adsorption on AgCl microcrystals as well as some other photographic active compounds.

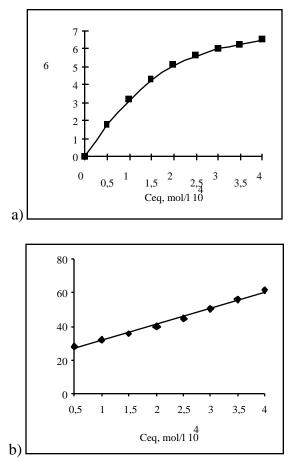


Figure 2. The dye adsorption isotherms: a) In C_{ad} , (mol/g Ag) coordinates; b) In Langmuer coordinates.

However, the sensitivity centers, formed at chemical sensitization, influence to dye adsorption conditions. On unsensitized AgCl crystals the dye adsorb mainly in monomolecular state, but on the sensitized emulsions an j-aggregation is observed. A jband in a adsorbed dye reflection spectrum changes depending on a degree of an emulsion microcrystals sensitization intensity.

Exposing of unsensitized microcrystals with adsorbed dye results to saturation of microcrystals by electrons, which are captured mainly on fog centers. If the dye is adsorbed on chemically sensitized microcrystals, the electrons of dye are captured by inner sensitivity centers, that results in increase of a photosensitivity.

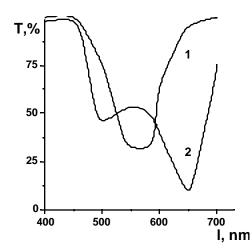


Figure 3. Reflection spectra of adsorbed on AgCl microcrystals reference dye: 1) unsensitized grains; 2) sensitized grains.

Since the dye has Γ anion there is the reasonable question whether observed sensitivity growth is the consequence of a AgCl crystals surface conversion? For this purpose a conversion of a crystals surface is carried out in concentration, appropriate iodide concentration of used dye. It is found, that the injection of iodide in concentration [I]=4 $\cdot 10^4$ mol/mol Ag does not influence on sensitivity of chemically sensitized emulsions and results only in growth of fog optical density.

Conclusions

1. The concentration of adsorbed dye on chemically sensitized AgCl microcrystals remains constant and not depends on a sensitization type.

2. The investigated dye adsorbs mainly as j-aggregate on sensitized AgCl microcrystals.

3. The efficiency of chemical sensitization can be judged by adsorbing the investigated dye on AgCl crystals in constant surface concentration $8 \cdot 10^{-5}$ (mol/m²).

References

- 1. A. N. Latishev., et. al., J. Sci. and Applied Photogr. and Cinematogr., 27: 274-277 (1982).
- B. I. Shapiro, et al, J. Sci. and Applied Photogr. and Cinematogr., 33: 256-254 (1988).
- 3. J. R. Dyer, Prectice-Hall ins., enclearvood cliffs., NY, 1970.
- 4. B. A. Sechkariov, Y.A.Breslav, et al., IS&T's Congress, Beijing, China, 1990, pp.357-359.
- 5. B. I. Shapiro, L. V. Tolstova, *Proceeding of IS&T's 49th* Annual Conference, Minneapolis, USA, 1996, pp.348-350.