

## MECHANISM OF SPECTRAL SENSITIZING OF THE EMULSION CONTAINING HETEROPHASE “CORE –SHELL” MICROSYSTEMS

The new approach to the process of spectral sensitizing of emulsions created on base of hetero-phase microcrystals of “non- photosensitive core — photosensitive silver-haloid shell” structure is offered. The distinctive feature of the given system is a possibility of sensitizer dye introduction on the “core-shell” border. Considering such spatial separation of dye adsorbed on a core by the shell of silver halide, the mechanism of sensitization, which provides the expansion of emulsion spectral sensitivity area, is offered.

### INTRODUCTION

Holographic emulsions based on silver halide till now are the most sensitive among all recording media and it attracts the permanent interest to them. These emulsions are suitable for recording of the reflecting and transmitting transparent volume holograms possessing both high diffraction efficiency, and high angular and spectral selectivity [1,2]. Nevertheless, in this sphere till now there are problems demanding the solution, one of which is expansion of emulsion spectral sensitivity range. In the given work the new approach to spectral sensitization of holographic emulsions is considered, which allows to expand a range of their spectral sensitivity considerably and to obtain single-layer emulsions, suitable for color and infrared holography.

### PROBLEM STATEMENT

In some cases, for example for recording of color holograms it is necessary to expand emulsion spectral sensitivity to all visible range. Moreover, for the solution of some technical problems it is necessary to have emulsion, which is sensitive to infrared (IR) area of spectrum. The latter problem is solved by introduction of the dyes absorbing light in near infrared area of a spectrum with generation of non-equilibrium charge carriers. However, used dyes are unstable even during storage at low temperatures, and they decompose to components, therefore such emulsions are insensitive and tend to fogging and degradation of the latent image.

Besides in usual AgHal emulsions, especially at exceeded concentration of dye, the IR sensitivity decreases because of so-called dyes self-desensitizing phenomenon of the second kind [3]. In this case, illumination quanta interaction with dye molecules excited by light with non- excited ones happens, and as the result, the luminescence of the nearest dye appears instead of generation of the free charge carrier. The solving of the problem could be achieved through spatial division of dyes interacting this way.

The similar situation arises also while using two or more dyes absorbing light in different areas of a spec-

trum. They also can interact with each other and desensitize the emulsion. For solution of this problem, the multilayered emulsions are used, each layer of which is sensitized by its dye, but such solution in the case of holographic emulsion is not optimal.

To solve both problems described above, it is possible to apply the model of emulsions based on hetero-phase micro-crystals of “non-photosensitive core — photosensitive silver-halide shell” structure [4].

Due to special features of hetero-phase micro-crystals structure the dyes — sensitizers could be absorbed not only on an external surface of silver-halide shell (as it is done traditionally), but also on the internal surface on the border core — shell surface [5], what allows to solve a problem of spatial separation of various dyes, and to increase their storage stability as well.

The goal of the given work is to study the features of the described above spectral sensitizing of photosensitive hetero-phase micro-crystals emulsions (including the holographic ones), and to create the working model of the electron-hole processes occurring in the emulsion when the latent image is created.

### MATERIALS AND METHODS

General scheme of synthesis process of emulsion with hetero-phase micro-crystals “core  $\text{CaF}_2$  —  $\text{AgBr}$  shell” is described in detail in [5]. Depending on purpose of emulsion the average size of microcrystals in them is:

~0.35 microns — emulsion intended for the photographic purposes (“photographic” emulsion); ~0.05 microns — emulsion intended for record of holograms (“holographic” emulsion).

For spectral sensitization of such emulsions we used three various dyes:

I — sodium salt of 3,3,3'-di- $\gamma$ -sulfopropyl-1,1'-diethyl-5,5'-dicarboethoximid-carbocyaninebetaine

II — pyridine salt of 3,3'-di- $\gamma$ -sulfopropyl-9-ethyl-4,5,4',5'-dibenzothiacarbocyaninebetaine

III — 1,1'-diethyl-quini-2,2'-cyaniniodide.

Infusion of such dyes in emulsion occurs as in molecular (M) and aggregated phases (J and H aggregates [6]). Wavelengths of absorption maxima of molecular

M and aggregated J and H phases of dyes I-III adsorbed on a surface of micro-crystals in halogen-silver emulsion are specified in the Table.

Table

Dye	H-band (nm)	M-band(nm)	J-band (nm)
I	508	519	-
II	-	630	680-690
III	-	545	578

It has to be marked that the long-wave part of absorption band of J-aggregates of dyes often extends up to 900 nm.

Spectral sensitization of hetero-phase emulsions using marked dyes was carried out stage by stage. Therefore, for experimental research three types of sensitized emulsion were prepared (symbolically a,b,c):

a) emulsion with hetero-phase micro-crystals "CaF<sub>2</sub> core — AgBr shell", prepared under the procedure described in work [5], was sensitized with dyes II or III in concentration 10<sup>-4</sup> mole of dye for mole CaF<sub>2</sub>, by traditional way (control emulsion);

b) to suspension containing homogeneous calcium fluoride particles of given size we added 10<sup>-4</sup> mole of dye II or III for mole on моль CaF<sub>2</sub>. These conditions provided practically full adsorption of dye on a surface of core CaF<sub>2</sub>. Then an AgBr shell was grown up on core CaF<sub>2</sub> with adsorbed dye II or III under the procedure [5];

c) "b" emulsion but additionally sensitized with the dye I in concentration 10<sup>-4</sup> mole of dye for mole CaF<sub>2</sub>;

For developing of obtained emulsions surface and deep developers [7] were used. Such ways of developing allow us to observe position of the centers of the latent image all over volume of halogen-silver shell of composite system. Surface developer — only those hetero-phase micro-crystals in which centers of the latent image are on external surface of AgBr shell can be developed. Deep developer provides partial dissolution of AgBr shell top layers. So thus we can develop those hetero-phase micro-crystals in which centers of the latent image are in volume of AgBr shell up to the surface of non-photosensitive core.

## RESULTS

On Fig. 1 results of the spectral sensitometric tests are presented, which are concerned to three mentioned above types ("a", "b", "c") of "photographic" emulsions, containing dye II. Concentration of dye was high enough for the existence in emulsion not only a molecular phases of dye, but also its J-aggregates. Exposure and processing of layers of the specified types of emulsions was carried out in spectral-sensitometer ISP-3 with the help of a standard technique [8].

As it follows from the data submitted on Fig. 1.A, for exposed emulsion "a" optical density after processing with the help of both surface and deep developers (curves 1, 1') in comparison with non-exposed emulsion "a" (curve 3) are practically equal, both in the absorption area of molecular dye II ( $\lambda_{\max} = 630$  nm) and in the absorption area of the J-aggregate of dye II ( $\lambda_{\max} = 690$  nm).

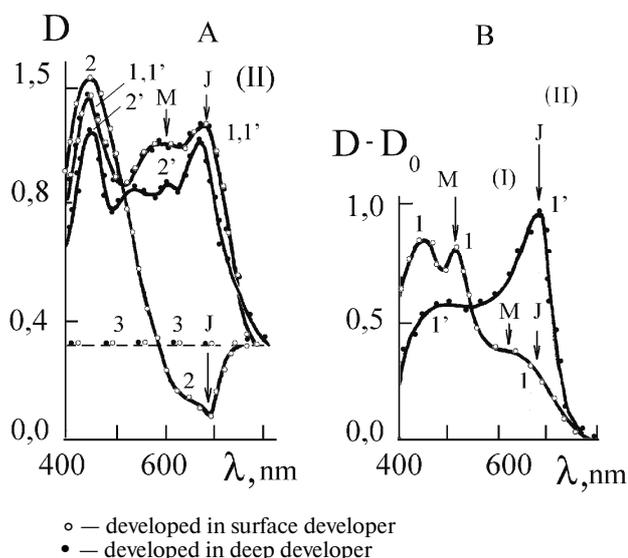


Fig. 1. A. Spectral distribution of optical density (D) of exposed layers of "photographic" emulsions "a" (1,1') and "b" (2,2') containing the dye II after development in surface (1,2) and deep (1', 2') developers. Bar line (3) marks the fog optical density of non-exposed and developed samples of emulsion "a" and "b" both in surface and deep developers. B. Spectral distribution of optical density (D-D<sub>0</sub>) of exposed layers of "photographic" emulsion "c" after developing in surface (1) and deep (1') developers, D<sub>0</sub> — fog optical density of non-exposed and developed both in surface and deep developers of emulsion samples "c".

For the exposed emulsion "b" developed with surface developer (curve 2) in comparison with non-exposed emulsion "b" (curve 3), on wavelengths  $\lambda > 600$  nm, the reduction of optical density (enlightenment) occurs and main part of this enlightenment falls on the absorption area of J-aggregate of dye II ( $\lambda_{\max} = 690$  nm). Application of deep developer in a case of exposed emulsion "a" (curve 2'), in comparison with non-exposed emulsion after processing with deep developer (curve 3), shows an increase of optical density in the absorption band of both molecular dye II (band M,  $\lambda_{\max} = 630$  nm) and in the absorption area of J-aggregate of dye II (band J,  $\lambda_{\max} = 690$  nm). However, if for emulsion "a" this increase occurs almost equally both in a band M and in band J, in case of emulsion "b" an increase of absorption in band J occurs in the much greater degree than in band M. If we compare between each other exposed emulsions "a" and "b" with sensitized dye II, in a case of emulsion "b", the expansion of a spectral range of a photosensitivity in long-wave area (see curves 1 and 2' in long-wave area) is observed.

For "photographic" emulsion "c" Fig. 1 B, after processing in surface developer (curve 1) the increase of the optical density in the absorption field of a molecular band of dye I ( $\lambda_{\max} = 519$  nm) is observed as well as small increase of the optical density in the absorption field of dye II both in molecular ( $\lambda_{\max} = 630$  nm) and in J-aggregated ( $\lambda_{\max} = 690$  nm) phases. Application of deep developer results in reduction of absorption in M band of dye I and essential increase of optical density in absorption band of J-aggregates of dye II ( $\lambda_{\max} = 690$  nm) (curve 1').

The same spectral sensitometric tests were carried out for "holographic" emulsions (types "a" and "b"). Experimental data of such researches are presented at Fig. 2.

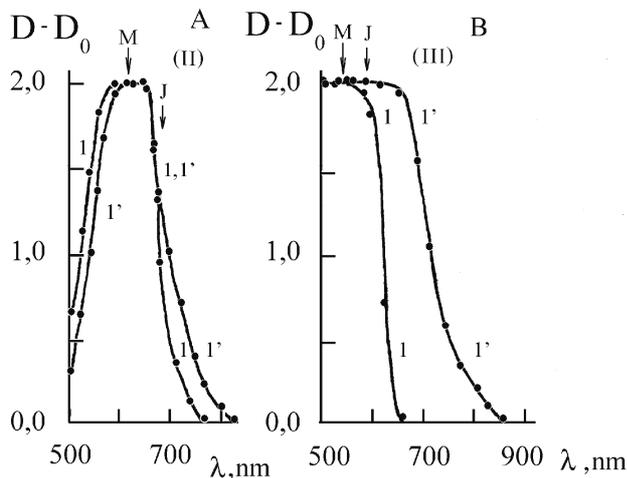


Fig. 2 A. Spectral distribution of optical density ( $D-D_0$ ) of exposed layers of "holographic" emulsions "a" (1) and "b" (1') with dye II after development in deep developer. B. Spectral distribution of optical density ( $D-D_0$ ) of exposed layers of "holographic" emulsion "a" (1) and "b" (1') with dye III after development in deep developer

$D_0$  is the optical density of a fog of non-exposed and developed in deep developer emulsion samples "a" and "b".

From Fig. 2 one could see, that the sensitization both with dye II and dye III of "holographic" emulsion of "b" type in comparison with emulsions of "a"

type sensitized by the same dyes results in expansion of emulsion sensitivity spectral area in long-wave part of a spectrum. If for dye II this displacement is insignificant, for dye III it is essential. It should be mentioned that for "photographic" emulsion of "b" type the expansion of the spectral sensitivity in long-wave region in comparison with to emulsion of "a" type is also observed.

Observed spectral sensitivity displacement both for "photographic" and "holographic" emulsions occurs up to 900 nm and it is natural to assume that it is caused by absorption of J-aggregates of dye. The reason of this effect (in case of emulsion of type "b") is the greater efficacy of generated in J-aggregates non-equilibrium carriers of charge use for latent image creating. It could occur due to the spatial division of molecular dye and J-aggregates of dye by AgBr cover because molecular dye is basically adsorbed on external surface of a cover and J-aggregate of dye — on internal surface. Spatial division of various phases of dye eliminates interaction at photo-excitation of the J-aggregate, which leads only to a recombination luminescence of molecular dye, instead of charge free carriers generation in silver halogenide [9].

Increase of  $\text{CaF}_2$  dye concentration adsorbed on core at spatial division of the molecular and aggregated dye by AgBr cover is accompanied, besides the expansion of spectral sensitivity area, by decrease of fog level on the cover external surface (see Fig. 3).

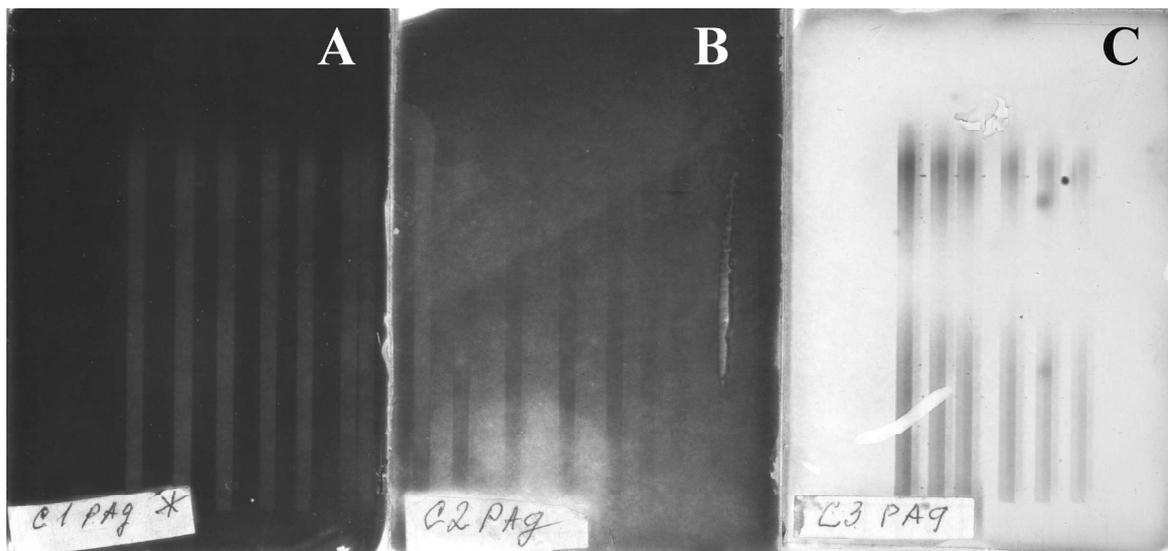
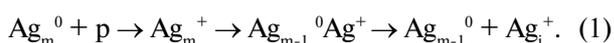
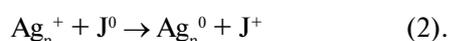


Fig. 3 Spectral sensitograms of emulsions developed by deep developer containing dye II in different concentrations (a mole dye /mole AgBr): A- $2 \cdot 10^{-5}$ ; B -  $4 \cdot 10^{-5}$ ; C -  $6 \cdot 10^{-5}$

Seen fogging decrease on an outer surface of AgBr shell results from reaction [10]



Occurrence of the holes on an outer surface of a shell is caused by the following reason. Adsorption of J-aggregate of dye II on an interior surface of a shell is accompanied by reaction



As it has been established by us in [11], the main level of the J-aggregate of dye II lays below the level of

a valence band top of AgBr, therefore the hole is localized on J + transfers in valence band AgBr



Then the hole in valence band migrates to an outer surface of AgBr shell and provides the reaction (1).

To prove our assumption, we carried out the low-temperature research of the luminescence of these emulsions. On Fig. 4, one could see the spectra of low-temperature ( $T = 77 \text{ K}$ ) luminescence and excitation of a luminescence not only in "holographic" emulsions of type "b" but also as an intermediate stage of its preparation: — before we cover  $\text{CaF}_2$  core with

adsorbed on them dye II with a AgBr shell. These luminescent studies were performed under such conditions: time of sample excitation and time of its luminescence registration are equal, and they equal to  $10^{-4}$  s and dark interval is  $1.1 \cdot 10^{-3}$  s at the modulation frequency of 400 Hz.

As it follows from the mentioned luminescent data, the phosphorescence of molecular dye II ( $\lambda_{\max} = 800$  nm) (curve 1) is excited by light not from the absorption area of molecular dye ( $\lambda_{\max} = 630$  nm), but from absorption area of J-aggregate of dye II ( $\lambda_{\max} = 630$  nm) (curve 1'). This fact proves the presence of the interaction between excited dyes, which result in emulsion desensitization. After AgBr shell is created, the phosphorescence of molecular dye II under excitation of the J-aggregate of dye disappears, and there emerges a luminescence with  $\lambda_{\max} = 700$  nm (curve 2). Excitation of this luminescence (curve 2') is both caused by absorption AgBr of a shell ( $\lambda_{\max} = 430-450$  nm) and absorption of molecular dye ( $\lambda_{\max} = 630$  nm) as the excitation of the luminescence from absorption area of the J-aggregate of dye II is absent.

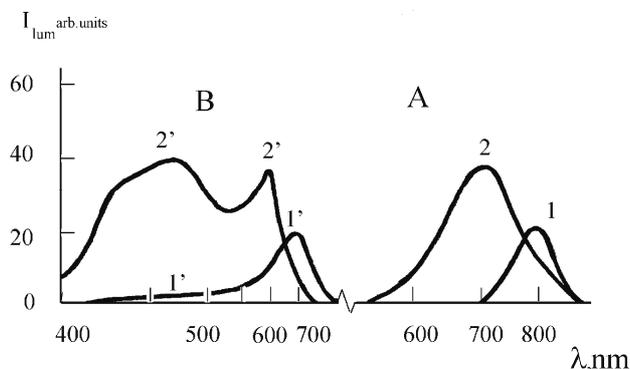


Fig. 4. Spectra of low-temperature T 77 K luminescence (A) and excitation of luminescence (B) of "holographic" emulsion of "b" type at the intermediate stage of its preparation: curves 1, 1' — when we do not create AgBr shell on  $\text{CaF}_2$  core with adsorbed on them dye II; curves 2, 2' — "holographic" emulsion of type "b" with dye II

Spectra of a luminescence (A) were obtained at the excitation with  $\lambda = 690$  nm — curve 1 and with  $\lambda = 450, 630$  nm — curve 2; Spectra of excitation (B) were given for a luminescence at  $\lambda = 800$  nm — curve 1' and on  $\lambda = 700$  nm — curve 2'.

As after AgBr shell creation, the luminescence of molecular dye at excitation of the J-aggregate of dye has disappeared, hence, it testifies that self-desensitizing action of dye caused by their interaction is eliminated and thus, it provides the significant displacement of spectral sensitivity of emulsion of type "b" in the long-wave area.

## DISCUSSION

Earlier in [12], it was shown the basic opportunity of covering of the dye adsorbed on non-silver  $\text{CaF}_2$  core by AgBr shell without specification of an aggregate phases of dye and its role in the process of an spectral sensitization. The comparison of the luminescent and sensitometric results, proves the existence of interaction between the molecular and J-aggregated dye on

core  $\text{CaF}_2$ . For a case of hetero-phase micro-crystal, we assumed that the shell divides interaction among the molecular and aggregated phases of dye that results in observable expansion of area of spectral sensitivity of various composite of the system.

It should also be noted that for the case of holographic emulsions with hetero-phase micro-crystals spatial separation of the molecular and aggregated dye by shell contributes to the effective separation of photo-excited non-equilibrium charge carriers. Separation of non-equilibrium charge carriers, in the case of composite system, could be illustrated by occurrence of an enlightenment in spectral area  $\lambda > 600$  nm for emulsion "b", when we develop it in the surface developer (Fig.1, curve 2). Observed enlightenment testifies that the quantity of the centers of the latent image located on AgBr shell surface of emulsion "b" micro-crystals after the exposure and development in surface developer, decreases in comparison with non-exposed emulsion. The greatest reduction takes place when illumination is made in an absorption band of J-aggregates of dye. As to our opinion, such reduction could proceed under the schemes, offered in reactions (1) — (3). As far as we have already determined, J-aggregates of dye are located basically on an internal surface of AgBr shell adjoining micro-crystals' core, when absorbing the light by J-aggregates, the generated holes migrate through a AgBr shell to its surface and there they result in destruction (reduction, neutralization) of the centers of the latent image, i.e. in "enlightenment". The AgBr shell presence provides translation of free holes of the J-aggregate of dye, adsorbed on core  $\text{CaF}_2$  through all thickness of the shell, leads to reduction of a fogging and causes the substantial increase of the diffraction efficacy of such emulsions. It could be used for the creation of "direct positive" images.

The ability of hetero-phase micro-crystals halogen silver shell to separate interacting phases of the dye can be used for spatial separation of different sensitizer dyes, which application earlier was complicated because of their interaction resulting in emulsion desensitization. Such dyes' separation allows to replace the multilayered emulsions with single-layered emulsions, which spectral sensitivity is determined by the dyes, which are located on different surfaces of a AgBr shell without desensitization effect.

## CONCLUSIONS

As a result of the studies of the newly modified emulsions and discussion of the experimental results we can state the follows:

1. The spectral sensitization of composite system "non-photosensitive core — halogen silver shell" allows adsorbing the sensitizer dye not only on external, but also on an internal surface of halogen silver shell.
2. It is determined, that halogen silver shell effectively separates the aggregated and interacting molecular dye phases (aggregated dye on non-photosensitive core and molecular dye on a surface of halogen silver shell), that eliminates effect of dye self-desensitization and results in expansion of area of emulsions with hetero-phase micro-crystals spectral sensitization.

3. Dyes' spatial separation allows to replace the multilayer emulsions with the single layer one with the spectral sensitivity determined by dyes at different surfaces of AgBr shell without desensitization effect.

#### References

1. Б.И. Шапиро Теоретические начала фотографического процесса. М.: Эдиториал УРСС. 2000, 209 с.
2. Патент 27837 України Спосіб виготовлення галогенсрібно-фотографічної емульсії. В.М. Білоус, Д.Г. Ніжнер, В.П. Чурашов.
3. В.М. Белоус, Л.И. Манченко, А.Ю. Попов, А.В. Тюрин, В.П. Чурашов, Ю.Б. Шугайло Фотографическая эмульсия с гетерофазными микрокристаллами — новая среда для записи глубоких трехмерных пропускающих голограмм// Оптика и спектроскопия. 1999, т.86, №2, с. 344-348.
4. А.Ю. Попов, Л.И. Манченко, А.В. Тюрин, Ю.Б. Шугайло Регистрация и воспроизведение световых пучков с топологическими дефектами // Сборник "Фотоэлектроника" вып.9, Одесса 2000, "Астропринт", с.126-129.
5. D.G. Nizhner, V.M. Belous, V.P. Churashov Preparation and Properties of Photographic Emulsions with Heterophase Microcrystals Comprising Nonsilver Cores and Silver Halide Shells// Imaging Science and Technology. 1999, v. 39, N 1, p. 56-66.
6. F. Dietz Zum stand der Theorie der spektralen Sensibilisierung //J. für Signalforschungsmaterialien. 1998, bd. 6, N 4, s. 245-266; N5, s. 341-361.
7. К.В. Чибисов Фотографическое проявление. Москва. 1999. "Наука". С 208
8. Ю.Н. Гороховский Спектральные исследования фотографического процесса. Москва. 1960. Изд. физ. — мат. литературы. С 390
9. А.В. Тюрин, В.П. Чурашов, С.А. Жуков, Л.И. Манченко, Т.Ф. Левицкая, О.И. Свиридова Взаимодействие молекулярных и полимолекулярных форм красителя// Оптика и спектроскопия. 2008, т. 104, № 1, с. 97-103.
10. А.В. Тюрин, В.П. Чурашов, С.А. Жуков, О.В. Павлова Механизм антистоксовой люминесценции галогенсеребряной эмульсии сенсibilизированной красителем// Оптика и спектроскопия. 2008, т. 104, № 2, с.237-244.
10. James, T.H. The Theory of the Photographic Process. // 1997, New York: Editorial Macmillan, 456 pp.
11. В.М. Белоус, Д.Г. Нижнер, Н.А. Орловская, П.Г. Херсонская Заращивание адсорбированного красителя оболочкой галогенида серебра в гетерофазных микрокристаллах// Журн. научн. и прикл. фото- и кинематографии. 1999, т. 34, № 4, с. 299-301.
12. Belous V.M., Nizhner D.G., Orlovskaya N.A., Khersonskaya P.G. Growth of the Adsorbed Dye by Halogen-Silver Core in Hetero-Phase Micro-crystals//Journal of Scientific and Applied Photo-and Cinematography 1999. v. 34. № 4. p. 299

UDC 621.315.592

*Tyurin A. V., Popov A. Yu., S. A. Zhukov, Yu. N. Bercov*

#### MECHANISM OF SPECTRAL SENSITISATION OF EMULSION CONTAINING HETEROPHASE "CORE –SHELL" MICROSYSTEMS

The new approach to the process of spectral sensitization of emulsions created on a base of hetero-phase micro-crystals of "non-photosensitive core — photosensitive silver-halide shell" structure is offered. Distinctive feature of the given systems is a possibility of sensitizer dye introduction to "core-shell" border. Considering such spatial separation of dye adsorbed on a core by the shell of silver halide, the mechanism of sensitization which provides the expansion of emulsion spectral sensitivity area is offered.

**Key words:** sensitisation, heterophase microsystems, emulsion.

УДК 621.315.592

*А. В. Тюрин, А. Ю. Попов, С. А. Жуков, Ю. Н. Берков*

#### МЕХАНИЗМ СПЕКТРАЛЬНОЙ СЕНСИБИЛИЗАЦИИ ЭМУЛЬСИИ, СОДЕРЖАЩЕЙ ГЕТЕРОФАЗНЫЕ МИКРОСИСТЕМЫ "ЯДРО — ОБОЛОЧКА"

Предложен новый подход к процессу спектральной сенсibilизации эмульсий, созданных на основе гетерофазных микрокристаллов состава "несветочувствительное ядро — светочувствительная серебрено-галогидная оболочка". Отличительной технологической особенностью данного процесса является введение красителя сенсibilизатора на границу раздела "ядро-оболочка". С учетом этой особенности — пространственного отделения оболочкой галогенида серебра красителя адсорбированного на ядре — предложен механизм сенсibilизации, обеспечивающий расширение области спектральной чувствительности эмульсии.

**Ключевые слова:** сенсibilизация эмульсии, гетерофазные микросистемы.

УДК 621.315.592

*О. В. Тюрин, А. Ю. Попов, С. О. Жуков, Ю. М. Берков*

#### МЕХАНИЗМ СПЕКТРАЛЬНОЇ СЕНСIBILІЗАЦІЇ ЕМУЛЬСІЇ, ЯКА ВМІЩУЄ ГЕТЕРОФАЗНІ МІКРОСИСТЕМИ "ЯДРО — ОБОЛОНКА"

Запропоновано новий підхід до процесу спектральної сенсibilізації емульсій, створених на основі гетерофазних мікрокристалів складу "несвітлочутливе ядро — світлочутлива срібно-галогідна оболонка". Технологічною особливістю даного процесу є введення барвника сенсibilізатора на границю розподілу "ядро — оболонка". З урахуванням цієї особливості — просторового розподілу оболонкою галогеніда срібла барвника адсорбованого на ядрі — запропонований механізм сенсibilізації, що забезпечує розширення області спектральної чутливості емульсії.

**Ключові слова:** сенсibilізація емульсії, гетерофазні микросистеми.