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MECHANISM OF INCREASE IN EFFICIENCY OF PHOTOGRAPHIC IMAGE FORMATION

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INTRODUCTION

Photographic process as way of registration of optical information has found the broadest application in various areas of human activity, began from simple display of the world around until using of photographic methods in science and technology. At the same time at all stages of development of the photographic science by its main objective was the achievement of the maximum sensitivity of photographic materials. And, at early stages of development of the photography the sensitization of photographic materials was required only for reasons of reduction of time of exposure. In modern conditions, for example, at registration of the fast-proceeding processes and photography in the conditions of small illumination the sensitization is one of the main problems of the photo in spite of the fact that progress in improvement of properties of materials is available and the sensitivity of modern photographic materials is increased a million times in comparison with Dagerrotype.

The analysis of the existing ways of increase in photosensitivity of photographic materials as at synthesis of emulsions, and directly to or after exposure shows that the available processing methods of sensitization will not give significant gain of sensitivity. Intensive researches of ways of increase in efficiency of formation of the photographic image have led to uncommon decisions. As one of alternative decisions the replacement of photographic way of registration of information by means of silver halide materials on not photographic is offered. However, as shows long experience, the traditional photography with her modern level of development is rather competitive.

It is absolutely clear that purposeful search of ways of improvement of photographic characteristics of silver halide materials is impossible without deep understanding of the fundamental processes happening at formation of the latent photographic image. As the most universal and consistent model of photographic process now as most of authors is recognized the electronic and ion theory of Gurney-Mott. According to Gurney and Mott's theory, in the course of formation of the latent image it is possible to allocate electronic and ionic stages conditionally. At radiation of microcrystals the free electron, and in valence band – free hole arises light from the field of own absorption of silver halide in conduction band. Presence in microcrystals of defects according to Frenkel leads to the fact that electrons after repeated intermediate captures on small traps are localized on microcrystal surface in rather deep potential hole. Electron life time on such trap is enough for neutralization of interstitial ion Ag^+ with formation of atom of silver Ag_0. As a result of the subsequent reactions of electrons with silver ions on surface the steady group, silver atoms – the center of the latent image is formed. In order that the center of the latent image has not broken up and became developable, on surface of microcrystals in the course of chemical growth purposely create deep traps (centers of sensitivity). However such large center can be also the fog center if silver recovery happens due to catalytic interaction to electrons at developing.

Thus, in primary act of photographic process the divided free carriers moving to microcrystal surface are formed spatially. However, on it the electronic stage does not come to an end, and the electron can be lost for photographic process, and degradation of the absorbed energy can happen on various mechanisms (recombination to free hole, thermal dispersion, capture by small traps, interaction to the environment, etc.). Really, time of life of free electrons in silver halides is ~ (10^{-9} – 10^{-10}) with, and for neutralization by the electron of mobile ion of silver localized on deep trap with formation of atom Ag_0 10^{-5} s are necessary already. It should be noted that the more the trap depth, the more electron life time on it and, therefore, interaction probability with silver ion. Besides, small traps are filled earlier than deeper ones, therefore even in the presence of free electrons the formation of the centers of the latent image can be complicated because of localization of electrons on small traps. Moreover, on surface of emulsion microcrystals the competitive reactions of interaction with molecules of oxygen and moisture distracting electrons from photographic process can develop.

Follows from the above that is necessary for achievement of the maximum quantum yield of photographic process:

1. To strengthen action of the actinic rays absorbed by silver halide.
2. To keep photoelectrons for formation of the centers of the latent image, to exclude possibility of course of the distracting reactions.

It is possible to implement the first, for example, influencing photographic material strong ($E > 10^6$ V/cm) electric field under the influence of which sharp increase in concentration of free electrons in silver halide is observed. Extensive literature is devoted to research of action of electric fields on sensitivity (see the literary overview), however, the saved-up experimental material does not allow to explain consistently received results. Preservation of photoelectrons can be carried out, isolating surface of microcrystals from interaction with the environment, reducing thereby the probability of capture of carriers molecules of oxygen and moisture.

Free charge carriers at low temperature can participate in recombinational processes, and at room temperature – in formation of the latent photographic image.

The purpose of work is study by means of luminescent method of mechanisms of increase in efficiency of formation of the photographic image under the influence of strong electric fields and also at introduction to photographic emulsions of various hydrophobic ingredients. In this regard studying mechanisms of the processes happening at the specified ways of increase in efficiency of formation of the photographic image is represented very relevant task.

In work features of the low-temperature electroinduced luminescence (EIL) of silver halides arising under the influence of pulse electric field are studied. It is established that EIL and increase in efficiency of formation of the photographic image when exposure in stronger electric field are caused by multiplication of charge carriers in silver halides. By means of luminescent method the new – "insulating" – mechanism of supersensitization of silver halide photographic materials hydrophobic compounds is studied and reasonable.

Work consists of introduction, four chapters and the conclusion.

In chapter 1 the short literary overview of experimental results on influence of electric fields on sensitivity of photographic materials is given and the theory of ionization of semiconductors is stated. Also questions of increase in efficiency of spectral sensitization of silver halide photographic materials are considered.

In chapter 2 the test aggregate and the measuring technique of luminescent spectrums of silver halides is described. Besides, justification of application of luminescent method as research tool is given.

Experimental results on the electroinduced luminescence of silver halides and also their discussion are given in the chapter 3.

In chapter 4 results of research of the "insulating" mechanism of supersensitization of silver halide photographic materials are described.

In the conclusion short conclusions by the main results of work are given.

CHAPTER 1. SOME WAYS OF INCREASE IN EFFICIENCY OF FORMATION OF THE PHOTOGRAPHIC IMAGE

1.1. Mechanisms of supersensitization of silver halide photographic materials

Understanding of mechanisms of increase in efficiency of spectral sensitization – photographic materials will allow to carry out purposeful search of ways of improvement of their photographic characteristics.

One of ways of increase in spectral response of photographic layers is based on use of the phenomenon of supersensitization which is understood how the superadditive increase in sensitivity in some spectral spectrum caused by introduction to spectrally sensitized emulsion of small amounts of dyes or colourless component [1, page 266]. The specified substances (supersensitizers) at the same time can not sensibilize in the field of absorption of the main dye. Increase in spectral response when using colourless component in domestic literature is called activation [2, page 167]. The effect of supersensitization has been opened by Blok and Renwick [3] in 1920 who observed superadditive action of auramine and pinacianol at adsorption on AgHal-substrate. Authors have explained this phenomenon with interaction of two sensitizers therefore the effect of sensitization, bigger is observed, than at separate introduction of sensitizers to emulsion. In spite of the fact that the phenomenon of supersensitization has been open about 70 years ago, the theory of supersensitization remains one of the most important problems of the modern scientific photo. It is connected with the fact that all existing theories of supersensitization do not give rather complete idea of the processes happening at energy exchange of excitation between solid phase of silver halide and the adsorbed dye (see, for example, [4.5]).

Recently the problem of efficiency of spectral sensitization and supersensitization is discussed by B.I. Shapiro in terms of the probability of course of the secondary oxidation reduction reactions proceeding at light absorption by the adsorbed dye [6].

It should be noted that the supersensitization is rather complex process which can proceed in several stages and be carried out in each separate case on various mechanisms. The effect of supersensitization at the same time can be caused by the following reasons:

- bathochromic or hypsochromic shift of bands of absorption of sensitizer and supersensitizer (if the last is dye);
- emergence of new bands of light absorption;
- emergence of the new bands of absorption characteristic only of combined action of sensitizer and supersensitizer;
- increase in adsorption of dye in the presence of supersensitizer;

- decrease in the desensitization [1, page 267] caused by dye;
- increase in quantum yield of spectral sensitization without significant change of adsorptive properties of dye.

The most important of the specified effects is increase in efficiency of optical sensitization without light absorption change by dye as in this case the maximum quantum yield of supersensitization is reached [1, page 265]. Let's consider some existing views of the supersensitization mechanism.

1.1.1. Mechanism of excitons capture

The first attempt to explain the phenomenon of supersensitization was made by Vest and Carroll [7, 8] who observed growth of spectrally sensitized photosensitivity under the influence of the sterile basis of 2- (*n*-diethylaminostiril) petrolthiazol on J-aggregates of 1.1'-diethyl-2,2' -quinocyaniniodide. Also growth of spectrally sensitized photoconductivity at light absorption in J-band was observed of the sensitizing dye. Dye concentration at the same time much more exceeded concentration of supersensitizer. Authors have offered that the specified experimental results are the proof of action of supersensitizer as the agent promoting "splitting" of ordered structure of J-aggregates of dye. Really, it is known [8] that the isolated molecules of dye are more effective in processes of spectral sensitization, than the molecules aggregated in ordered layer with overlapping of wave functions. It is caused by degradation of excitation energy in layer of the interacting molecules (see, for example, [9-11]) where there can be excitons with big mobility and big time of life. Excitation energy at the same time can be spent for thermal fluctuations or for dye fluorescence. Supersensitizer, thus, breaking regular structure of J-aggregates of dye, can work as trap of excitons thanks to what the probability of energy exchange or carriers between silver halide and dye grows.

1.1.2. Hypothesis of partition of aggregates

In Rozenoff [10], Zuckerman [14.15] and Byrd [16] works the influence of supersensitizers on photochemical and photo-electric properties of J-aggregates of the polymethine dyes adsorbed on surface of silver halide microcrystals is investigated. Authors have established that molecules of supersensitizer brakes monomeric layer of molecules of dye on what specifies hypsochromic shift in J-band of the dye. At the integrated layer of dye and supersensitizer there are always molecules of the anti-sensitizers lowering quantum yield of sensitization. Various impurity or Dye-O_2 can serve like anti-sensitizers. Being built in layer of molecules of dye, the supersensitizer "switches off" anti-sensitizers from processes of deactivation of photoexcitation energy.

It should be noted, however, that recently by number of experiments [17-20] it is established that the hypsochromic shift of absorption band of dye under the influence of supersensitizer is caused by Coulomb interaction between molecules of sensitizer and supersensitizer.

1.1.3. Theory of supersensitization by means of energy transfer

This theory is based on the assumption that transfer of energy from dye to supersensitizer on inductive resonant mechanism is possible [21]. Such mechanism assumes possibility of excitation energy exchange between molecules of the organic matter which is at distance about 150-200 Å; at the same time overlapping of wave functions of the interacting molecules is necessary, and inductive and resonant interaction consists of the sum of interactions of outer electrons of the donor and acceptor of energy [11, page 13]. The theory of this phenomenon has been offered by Ferster [12] and generalized by Dexter [13] for cases dipole - dipolar, dipole - quadrupole and other types of interactions between molecules of the donor and acceptor of excitation energy. For small distance between the donor and acceptor dipole - quadrupole, quadrupole-quadrupole and dipole - dipole mechanisms of interaction give almost identical deposits to the total probability of inductive - resonant interaction. At big distances the dipole - dipole mechanism entirely dominates. At the same time the probability of power transmission is expressed through energy acceptor luminescent spectrum.

It should be noted that in practice two various mechanisms of supersensitization by power transmission are implemented:

- if the supersensitizer absorbs light in more short-wave spectral spectrum than dye, then there is power transmission from the excited singlet level of sensitizer on the excited triplet level of supersensitizer [22]. Such singlet - it is accepted to call triplet transfer of energy intercombinative conversion [23, page 505]. As time of life of the excited triplet state is significantly more than time of life of singlet state, intercombination conversion increases power transmission probability to silver halide;

- if the supersensitizer absorbs light in more long-wave area than dye, then excitation energy can be transferred by singlet – singlet mechanism from dye to supersensitizer. In this case electron life time in excited state also grows that leads to increase in efficiency of spectral sensitization.

1.1.4. Orientation model of supersensitization

Lifshits, Natanson and Levkoyev [24-27] investigated influence of surface-active and some other substances on efficiency of spectral sensitization. As spectral sensitizers the authors used number of the main and non-core polymethine dyes. It is established that some combinations of the specified compounds lead to increase in spectral response of silver halide emulsion without light absorption change by dye. On the basis of these results the authors draw conclusion that supersensitizers change adsorptive properties of dyes that is orientation of the adsorbed dye concerning AgHal microcrystals. At the same time power transmission probability from the sensitizing dye to silver halide significantly increases.

In Rister [20, 28] works the supersensitization of azomethine and other dyes by means of number of mercaptols which are not effective spectral sensitizers is studied. It is established that the specified compounds not only increase efficiency of spectral sensitization in dye M-band, but also promote the partition of J-aggregates. The author assumes that molecules of supersensitizer are adsorbed on surface of AgHal-microcrystals, thanks to Coulomb interaction with superficial ions of silver, isolating thereby molecules of the sensitizing dye from the surface of silver halide. At the same time more favorable conditions for excitation energy transmission are created to microcrystal of haloid silver that will be coordinated with the representations developed in works [24-27]. Besides, such arch structure complicates capture of the photoborn rise carriers molecules of dye [18].

It should be noted that within this model it is impossible to explain dependence of efficiency of supersensitization on ratio of concentration of the main dye and supersensitizer.

1.1.5. Theory of supersensitizer's capture of holes

Recently, thanks to Gilman's works with colleagues [18, 29-32], the important step in understanding of mechanisms of supersensitization of the aggregating dyes is taken. Developing Vest and Carroll [7, 23] idea about capture of exciton, Gilman has offered the mechanism of capture of holes of dye supersensitizer. Gilman considers necessary, but insufficient condition for effective supersensitization that the highest filled molecular orbital of supersensitizer is located closer to vacuum level, than the highest busy molecular orbital of the sensitizing dye [30]. Such relative positioning of the specified energy levels of dye and supersensitizer creates favorable conditions for capture of hole of the photoexcited dye on the main level of supersensitizer. At the same time the probability of deactivation of excitation energy in dye molecule by electron-hole recombination decreases, and the photoelectron can be used for formation of the centers of the latent image. The supersensitizer in this case regenerates the main dye. Investigating supersensitization 1,1'-diethyl-2,2 '-cyanynchloryde the Ox by means of number of supersensitizers with oxidizing potentials from $E_{1/2}$ = +1.0 V to $E_{1/2}$ = +0.54 V, Gilman has established that the threshold of effective supersensitization for oxidation potential has made $E_{1/2}$ = +0.88 V. Note that the oxidation potential of the main dye at the same time was +0.99 V. Thus, according to Gilman's representations, effective supersensitizers are those which oxidation potential is located closer to vacuum level not less, than on 0.1 V concerning the potential of the sensitizing dye.

The mechanism offered Kollye [34] according to whom monomer of dye is supersensitizer of the J-aggregate of the same dye can be one of possible ways of supersensitization of the aggregating dyes within Gilman's model (at the same time monomer has to be oxidized easier, than the J-aggregate). Only in this case localization of photohole of dye at the main level of molecule of monomer is possible. In Kollye [34] work as luminescent method it is shown that monomer 5,5',6,6'`– tetrachlorine – 1,1',3,3' –

tetraetilbenzimidacarbocyanine supersensitize the J-aggregate of the same dye as monomer is oxidized easier, than the J-aggregate.

In Nelson’s [35] work the supersensitization of the pseudo-cyanine adsorbed on CdS-monocrystals in the J-aggregated state is investigated. Measurements of ionization energy of dye and supersensitizer have shown that thermal activation energy of photoconductivity for the semiconductor with composition dye + supersensitizer significantly (on 0.2 eV) is less, than for case of lack of supersensitizer. The author believes that it is caused by interaction of dye and supersensitizer and formation of charge-transfer complex. In that case at excitation of the "dye-supersensitizer" system the photoelectron moves from the highest filled level of supersensitizer to the lowest vacant level of dye. The energy shortage in 0.2 eV is spent at the same time for overcoming Coulomb forces of pushing away from outer electrons of dye, and the level of energy of the excited electron increases on 0.2 eV that increases the probability of hit of electron in CdS conduction band.

In conclusion it is necessary to stop at the works devoted to electrochemical research of the mechanism of spectral sensitization and supersensitization which were carried out on semiconductor electrodes. Such works have been carried out by Tribush and Gerisher [36-39] who investigated the supersensitizing action of some compounds of salvage type and have established that in the presence of the specified substances photo electromotive force and sensitized photocurrent increases. Authors connect this effect with salvage function of the specified compounds in relation to dye and, as a result, – with increase in probability of transfer of electron to silver halide.

In Watanabe's works with employees [40.41] results on rhodamine supersensitization by hydroquinone on CdS-electrode are received. Authors revealed that as a result of course of photocurrent quinone which is hydrochinone oxidate is emitted, that is the supersensitizing effect of hydroquinone is caused by capture of hole of dye.

1.1.6. Supersensitization of infrachromatic photographic materials

According to modern representations (see, for example, [5, 42]), the supersensitization ortho-and panchromatic dyes, especially in the J-aggregated state, is caused by acceptance of hole of dye supersensitizer [29.30]. However, in this way it is impossible to explain supersensitization of infrachromatic dyes under the influence of derivatives stilbene-0.0 '-disulphonic acids [43], tetraazainden [44] and triarilphosphine [45, 46] which are oxidized more difficultly, than the main dye [47.48]. In work [49] the supersensitizing action of di (n-anisil) - phenyl phosphine is investigated by means of luminescent method. It is shown that introduction to AgBrI emulsion of triarilphosphyne leads to reduction intensity of flash, stimulated IR-radiation in green band low-temperature (T = 77 K) luminescence. Authors connect such result with emergence of the positive surface-bound charge created by interstitial ions of silver at adsorption of triarilphosphyne which supersensitizing action consists in increase in absorption and increase in stability of the adsorbed dye. Thus, the specified mechanism differs from supersensitization across Gilman and will well be coordinated with the adsorptive model offered by I.I. Levkoyev with colleagues (see, for example, [24-27]). It is known also [47] that the efficiency of spectral sensitization infrachromatic dyes decreases when lengthening polymethine chain that is caused by growth of desensitization due to capture of photoelectrons dye ([I], page 256). At the same time the efficiency of supersensitization of infrachromatic dyes by means of some organic compounds increases at increase in number of methine groups [45, 46]. Thus, for explanation of supersensitization of infrachromatic dyes Gilman's mechanism of hole capture of dye supersensitizer is inapplicable.

In works [5.35] the offer that the supersensitizing action of the compounds stated above is connected with inhibition of the reactions of desensitization distracting photoelectrons from processes of formation of the latent image has been stated. Such reactions can be oxidation of dye with formation of Dye compounds with O_2 and also capture of photoelectrons molecules of oxygen and moisture. Besides, in case of infrachromatic dyes the supersensitizer can perform function of intermediate trap of photoelectron which passing conduction band, is localized on the center of the latent image.

If the photoemulsion layer is at low temperature, then the specified hydrophobic compounds can influence processes of radiating recombination. Therefore one of relevant tasks is studying influence of hydrophobic organic compounds on recombinational luminescence of microcrystals of photographic emulsions and the adsorbed dyes – sensitizers. The solution of objective will allow to specify the mechanism of increase in efficiency of spectral sensitization hydrophobic substances.

1.2. Influence of external electric field on photosensitivity of photographic materials

In spite of the fact that the photosensitivity of photographic materials for lifetime of the photo has grown approximately by 106 times, significant increase in photosensitivity by means of chemical and photographic methods for the last several decades did not manage to be reached [50, page 390]. Therefore search of essentially new ways of sensitization of ready layers before exposure (preliminary flare and hyper sensitization) has been carried out or – after exposure (latensification) [50, page 393]. Besides, Klein and Mateek it was offered to put to photolayer constant electric field of high voltage during exposure [51]. Authors connected sensitization with the shift of ions of silver to the centers of the latent image. Thus, the foundation has been laid for physical methods of impact on sensitivity of photographic materials directly in the course of exposure. In the subsequent works special attention (see, for example, [52]) has been paid to problem of management of sensitivity of external electric field as "inclusion" of photosensitivity only at the time of exposure opens new ways of use of silver halide photographic materials.

Besides, interest in behavior of photographic materials in electric field is caused by possibility of studying the fundamental processes happening at various stages of photographic process [53, 54]. However, in spite of the fact that for quarter of the century, starting with the publication of the known works Rotstein [55], rather big experimental and theoretical material on influence of electric field on photosensitivity, the mechanism of the specified phenomenon finally is saved up not found out.

In Rotstein's experiments the emulsion layer of industrial film of "Kodalit" which was placed between glass plates with transparent electrodes has been used. Synchronously with pulse flare (τ = 100 microsec) on electrodes gave field impulse (τ = 50 microsec) voltage $E = (1 \div 5)\ 10^6$ V / cm. As a result of action of electric field the increase in density of blackening and contrast of photographic layer was succeeded to observe Rotshtein. For explanation of the gained effect Rotstein has put forward two alternative mechanisms of influence of electric field on photosensitivity. According to the first mechanism, external electric field interferes with recombination of the photoborn rise charge carriers, increasing thereby the probability of capture of photoelectrons by the centers of sensitivity. Such assumption will be agreed with ideas of low quantum efficiency of formation of the centers of the latent image at initial stage [1, page 115]. Really, electric field can partially reduce the probability of course of the reactions distracting photoelectrons and ions of silver from formation of the centers of the latent image. The recombination, regression, electron capture by small traps in volume of microcrystals or in the environment can be such reactions.

In pulse electric field Rotstein connects the second mechanism of increase in photosensitivity with the fact that ionization by collision is resulted by avalanche reproduction ("multiplication") of electrons that leads to increase in total number of electrons in system. The author also assumed that the avalanche can develop not only in volume of microcrystals, but also in binding, providing developability of the grains having low quantum efficiency at these illumination. Increase in the steepness of the characteristic curve has to be consequence of it, that is, increase in contrast of photoemulsion layer, as was observed in Rotstein's experiments. Let's note that the nonlinear dependence of effects of the field on voltage calls into question justice of the second mechanism offered by Rotstein, and, on the contrary, the threshold nature of dependence of effect of the field of his voltage confirms hypothesis of multiplication of electrons in strong fields.

Researches of a number of authors (see, for example, [56-72]) have allowed to assume that electric fields voltage up to 1 MV/cm create more favorable conditions for formation of the centers of the latent image both due to reduction of recombinational losses, and owing to availability of electrotopographical effect [73, 74]. The maximum effect of the field (E <1 MV/cm), received by authors of the specified works, was about one order, and, on low-sensitive emulsions (FT-SK, FT-30) with rhodium chloride. Therefore more perspective way of increase in photosensitivity in electric field it is necessary to consider increase in concentration of free electrons in volume of microcrystals due to reproduction in strong (E> 10^6 V/cm) electric fields [75]. Authors of work [76] managed to increase sensitivity of X-ray film of Class -110 on two orders in pulse electric field intensity of 10^6 V / cm. Authors consider proofs of multiplication of carriers rather big size of the making multiple copies field and also substantial increase of sensitivity.

In further works the results confirming the specified mechanism of action of strong electric field are received:

- threshold nature of growth of photosensitivity under the influence of strong fields [77-81];
- dependence of threshold of multiplication on the size of emulsion microcrystals [82-84];
- extreme nature of dependence of effect of the field of time lag of light flash (method of "light probe") [85-88];
- action of repeated impulses of electric field on effect of increase in photosensitivity [89-90];
- dependence of level of the electroinduced veil on the back front of impulse of electric field [91].

It is necessary to recognize, however, that the listed above results are only the indirect evidence of avalanche reproduction of charge carriers under the influence of strong electric field. In work [92] by means of independent luminescent method the new effect called the electroinduced low-temperature luminescence is found. Coincidence of spectrums of the pulse photo and electroinduced luminescence of various photographic materials, the threshold nature of intensity of luminescent flash from electric field intensity and a number of other experimental results have allowed authors to consider multiplication of nonequilibrium carriers most of not consistent howl model of the electroinduced sensitization of silver halide emulsions.

[1)] For exception of injection of nonequilibrium carriers the electrodes separated from photoemulsion insulating joints.

For the first time emergence of luminescence of solid bodies under the influence of strong electric fields was observed Losev in 1923 and Destrio in 1936 . The exhaustive overview of electroluminescence of various crystals is made in work [93], however, it is necessary to dwell upon the theory of effect of Destrio since the phenomenon of electroinduced luminescence of silver halides described in this work can be considered, in some way, analog of the luminescence found by Destrio.

In Destrio's experiments the electroluminescence of the powdery zinc sulfide weighed in dielectric when imposing variation electric field was visually observed by average voltage of 10^5 V / cm. It has been established also that there is threshold value of field gradient necessary for occurrence of luminescence. At the same time the dependence of integrated superficial brightness (B) on effective voltage (U) with frequency of 50 Hz was described by the following formula:

$$B = A \cdot U^n \exp\left(-\frac{b}{U}\right) \tag{1.1}$$

where A, b and n – constants, and $n = 1 \div 3$. Besides, size B increased with growth of frequency.

Further experiments (see, for example, overview in [94], page 43) has been confirmed that the electroluminescence of crystalline phosphors under the influence of strong electric fields arises due to ionization by collision. For the quantitative description of the specified processes the Townsend's β–mechanism for breakdown of the gas discharge determined by ionization rate (α) on aggregate of length that is has been used by number of the ionizing events caused by one electron on centimeter of way in electric field. The dependence of ionization rate on electric field intensity is defined by way of creation of avalanche of nonequilibrium carriers. Processes of formation of avalanche at breakdown of dielectrics have been considered by Hippel [95], Frelikh [96] and in modified form for semiconductors – Shokley [97], Chuyenkov [98], Keldysh [99], Wolf [100] and some other authors. There are two mechanisms of multiplication of electrons in stronger electric field have been offered:

1. Ionization by collision happens similar to the category in gases which mechanism is described by Townsend. Here the electron gains the energy necessary for ionization of atoms of lattice, on some length of run between two collisions.
2. At repeated collisions with lattice atoms the electron keeps part of energy and in time between collisions gains additional energy therefore the drift speed of electrons increases and can become much more normal thermal. Energy of electron at the same time gradually increases to values at which perhaps avalanche reproduction due to ionization by collision.

The first mechanism of acceleration has been theoretically considered by Shokley [97], Chuyenkov [98] and Wolf [100] who have received for ionization rate (α) the following dependence on field gradient:

$$\alpha \sim \exp\left(-\frac{b}{E}\right) \tag{1.2}$$

where b – the constant depending on ionization energy of this substance and length of free run of charge carriers. Besides, it was supposed that the average length of free run of electrons does not depend on speed and energy of optical phonons ($h\omega$) it is comparable with energy (ε), which is received by electron, accelerating in electric field. For size ε the ratio is fair:

$$\varepsilon = eEl_1 \tag{1.3}$$

where e – elementary charge, E – electric field intensity, l_1 – the way passed by electron without dispersion on phonons. Chinoves [101] has received coincidence of experiment to formula (1.2) for silicon in the field of weak fields ($E < 4 \cdot 10^5$ V/cm) in the assumption that

$$h\omega = eEl_1 \tag{1.4}$$

The second mechanism is implemented for strong electric fields when electrons after each collision with atoms of lattice keep part of energy (ε), acquired in electric field. In this case it is possible to call carriers with high energy hot and to calculate ionization rate, using the theory of breakdown of dielectrics offered by Frelikh [96]. Such calculation has been done by Wolf [100] and it has turned out that for strong fields ($h\omega << eEl$) ionization rate is connected with electric field intensity as follows:

$$\alpha \sim E^{-1} \exp\left(-\frac{C}{E^2}\right) \tag{1.5}$$

where C – the size, constant for this substance. The threshold energy of ionization received by Wolf for silicon was equal 2.3 eV that considerably exceeds width of forbidden band.

Ratios (1.2) and (1.5) have been received in the assumption that length of free run of carriers in valent semiconductors does not depend on speed that is obvious, is not carried out in case of strong electric fields. In the presence of hot carriers not only acoustic, but also optical lattice vibrations are excited that will lead to increase in peripheral speed of carriers, and, it can be much more thermal. Has allowed to be discharged Chuyenkov [98] taking into account initiation of optical lattice vibrations for valent semiconductors dependence $\alpha(E)$, similar (1.5) for this temperature. Having used as criterion of transition from weak fields to stronger ratios

$$h\omega = eEl\ , \tag{1.6}$$

where l – length of free run of electrons, it is possible to estimate voltage of the making multiple copies field which is equal $4 \cdot 10^4$ V/cm ([94], page 58).

For crystals with some share of ionic bond Chuyenkov [102] has received dependence of probability of ionization on voltage of external electric field of the following look:

$$\omega(E) = E^n \exp\left(-\frac{const}{E^{\theta(E)}} \right) \tag{1.7}$$

where $I < \theta < 2$, n – the constant depending on dielectric permittivity. In case of strong electric fields ($eEl >> h\omega$) the dependence (1.7) will be transformed in

$$\omega(E) = E^2 \exp\left(-\frac{const}{E^2} \right) \tag{1.8}$$

It should be noted that the theories of ionization by collision of Shokley and Wolf which are described ratios (1.2) and (1.5) are special cases (1.8) for weak ($eEl << h\omega$) and stronger ($eEl \cong h\omega$) fields, respectively. The results received for crystals with some share of ionic bond (ZnS, ZnO, SiC) are well described by formula (1.5) ([94], page 61).

The phenomenon of photon multiplication in optical spectral spectrum found in alcali halide crystals [103-106] has allowed authors to draw conclusion on doubling (in case $h\nu > 2E_g$) and trebling (in case $h\nu > 4E_g$) quantum yield of low-temperature luminescence. In works [I07-110] as direct experiments on studying spectrum of excitation low-temperature (4.2 J) bands of luminescence 2.35 eV in the area (2.7 ÷ 11) eV it is shown that at energy of photons $h\nu > 3E_g \div 4E_g$ reproduction of electron-hole couples is observed. In works [62, 63] the calculation of function of distribution of electrons for energy and reproduction coefficient for AgBr-microcrystals of the radius of 0.7 microns is carried out that has allowed to estimate the threshold field: $E_{\text{thresh}} \geq 3 \cdot 10^5$ V/cm.

Thus, the analysis of literary data shows that the most consistent mechanism offered for explanation of action of electric field on photographic sensitivity should be considered reproduction of charge carriers due to ionization by collision in strong electric fields.

CHAPTER 2. EXPERIMENTAL SETUP AND MEASURING TECHNIQUES OF LUMINESCENT SPECTRUMS OF SILVER HALIDES

Registration of luminescent spectrums and its excitation in the spectrum of lengths of waves to from 400 to 1200 nm was carried out on the original installation (Fig. 1) allowing to carry out the following operating modes:

- automatic recording of spectrums of fluorescence and phosphorescence at excitation by monochromatic light with the wavelength from 400 to 1200 nanometers;
- automatic recording of spectrums of fluorescence and phosphorescence at pulse excitation by the radiation of the nitric laser ($\lambda = 337$ nanometers);

- observation of influence of additional infrared illumination on intensity of luminescence in the modes of fluorescence and phosphorescence;
- automatic recording of spectrums of relative quantum yield of fluorescence and phosphorescence;
- registration of kinetics of increase and attenuation of luminescence at single pulse excitation by laser radiation.

All listed operating modes can be carried out in the spectrum of values of temperatures from 77 to 300 K.

The exciting light of xenon lamp DKsSh-1000 (S1) is focused by the system of quartz lenses L1 on entrance crack of the monochromator UM-2 (M1). The flexible quartz light guide C1is pressed to output crack of the monochromator M1 on which the image of entrance crack is projected. The output of the C1 light guide is fixed in the special holder (1) allowing by means of micromovements and rotation –the light guide around own axis to choose the optimum provision of bunch of exciting light on sample.

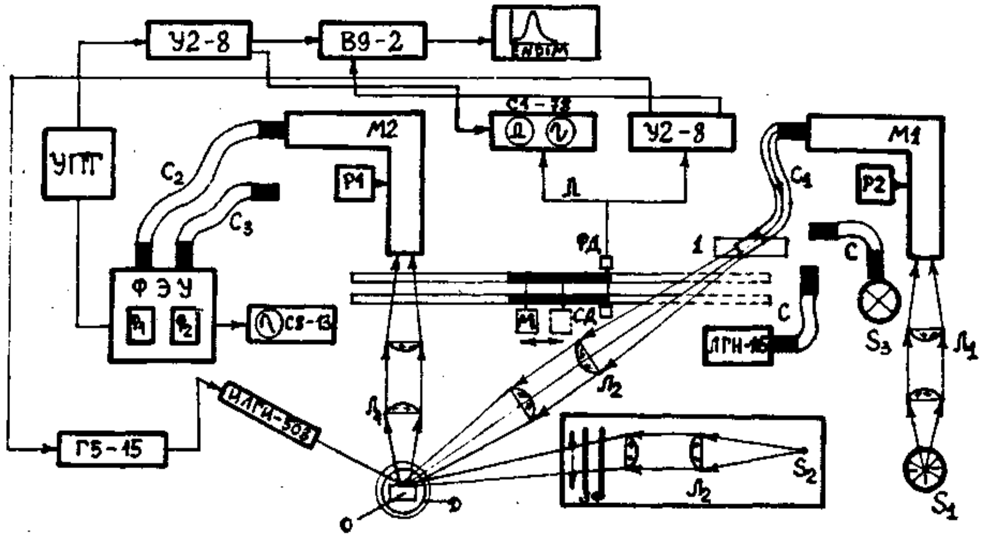


Fig. 1. Flowchart of experimental setup.

Besides, by replacement of the corresponding light guides (C), fixed in the holder (1), it is possible to excite luminescence LGN-105 laser He-Ne light (λ = 632.8 nanometers) or mercury lamp of DRSh-250 (S2). Further the monochromatic light after the system of lenses L2 gets on the sample (O) which is in dewar (D) with liquid nitrogen. For reduction of dispersion of exciting light and luminescent emission on external wall, the Dewar placed in tight glass glass from which before each measurement pumped out water vapor by means of the vacuum booster pump. Luminescent emission from sample gathers the system of lenses L4 on entrance crack of the monochromator M2 by means of which scanning of luminescence of sample in spectrum is made. The block of photodetectors contains photoelectronic multipliers (FEU-79 (F1) and FEU-83 (F2)) on spectral spectrums from 400 to 800 nanometers and from 700 to 1200 nanometers, respectively. Light guides C2 or C3 transfer radiation in the studied spectral spectrum from the monochromator M2 on the photocathode of the corresponding photoelectronic multiplier transforming light signal to electric. For increase in ratio the signal/noise of measurement was carried out on alternating current, modulating signal the disks rotating on motor M axis. Here the measuring technique of phosphorescence described by Levshin is used ([113], page 80), however the mode of phosphorescence is provided by simultaneous overlapping of exciting light and the luminescence generated samples and possibility of change of dark and light intervals. Motor M is fixed on the rider moving on optical bench and has two fixed positions for work in the modes of measurement of fluorescence and phosphorescence (to the phosphorescent mode there corresponds shaped designation of the motor in fig. 1). Relative displacement of disks around spin axis allows to change dark interval between impulses of exciting light and the beginning of measurement of luminescence. In our experiments the impulses of light had duration $\tau \approx 0.02$ ms, the dark interval made $\tau \approx 0.2$ ms. On the rider with the motor there is optoelectronic couple (photo and light-emitting diode) forming the clock pulse given on GZ-15 generator entrance for start of the nitric ILGI-503 laser at excitation of luminescence by light wavelength $\lambda = 337$ nanometers. Duration of laser impulse is (10±2) ms, the spectrum of delays of the generator – from 0 to 1.2 ms. The basic signal formed by opto-couple after frequency and phase selection and strengthening by means of the selection U2-8 amplifier arrives also on entrance of the synchronous detector B9-2 that allows to compare basic and useful signals not only on frequency, but also on phase and to allocate constant component of signal for graphic display of dependence of intensity of luminescence on wavelength. The specified display is carried out as follows. On entrance of the two-dimensional ENDIM 620.01 recorder from the output of the synchronous detector B9-2 the signal corresponding to intensity of luminescence is given. To change of wavelength of luminescence there corresponds the alternating stress removed from rheochords (P1 and R2) which are strictly connected with drums of the monochromators M1 (in case of record of spectrum of excitation) or M2 (in case of record of luminescent spectrum) which gives in on the second entrance of the two-coordinate recorder. The useful electric signal removed from FEM moves on the preliminary direct current amplifier (DCA) executed on chip of K 544 UD 8B with strengthening coefficient $K_{amplif} = 70$ and the level of the noise brought to entrance – 90 dB. The coefficient of strengthening is constant in frequency spectrum from 0 to 100 kHz.

For studying influence of additional infrared illumination on intensity the luminescence has been used the technique described in work [114]. The KGM 12-100 halogen glow lamp (S3) which radiation focused by quartz lens LZ, passing through the silicon filter (F) and mechanical lock (3), got on sample that allowed to investigate influence of constant long-wave (λ> 900 nanometers) illuminations on intensity of stationary luminescence of silver halides and also kinetic characteristics of luminescence was source of infrared light (availability of flash, clearing of luminescence, time of establishment of stationary level, the phenomenon of flare growth of luminescence, etc.). The flare growth was measured by the technique described in work [115], but the signal was registered by means of the two-coordinate recorder allowing to carry out development on time with various speeds. All measurements described above were taken in the mode "infinitely long" excitation ([113], page 71, that is such duration at which balance between the radiation and absorption of crystalline phosphor is established. The research of kinetics of increase and attenuation of luminescence was conducted in the mode of "instant" excitation ([113], page 71), that is having considerably the smaller duration, than the period of decay of luminescence. Luminescent spectrums at the specified excitation were removed on points with single start of the pulse laser. The signal with FEM was given on entrance of the memorable C8-I3 oscilloscope, and then photographed.

Temperature measurements were taken in all the modes described above, using the sample holder of special design providing thermostabilization of sample in the course of measurements. For temperature monitoring used copper – the constantan thermocouple with which signal was given on the KSP-4 recorder.

Observation and research of low-temperature luminescence were conducted on the experimental complex consisting from:

- luminescent installation (fig. 1);
- the small spectrum figurative installation consisting of the generator of surge voltages, the setting generator and the electrical power aggregate;
- the special holder for the sample allowing to put high-voltage impulses of voltage of various polarity to various photographic materials and monocrystals.

The high-voltage block developed at department of physics of Moscow Engineering Physics Institute allowed to form impulses of special form by duration ~ 300 nanoseconds and with an amplitude up to 30 kV [117]. Synchronization of laser and electric impulses carried out the generator of the setting GZI-6 impulses. The sample was clamped between two electrodes: copper grid with size of cell (50 x 50) microns and the polished plate from stainless steel. For exception of injection of carriers the electrodes isolated from sample clear triacetate film. For reduction of probability of breakdown of sample under the influence of field impulse before measurements the photographic materials kept in liquid dielectric (ethanol or glycerin).

The impact of the electroinduced processes on sensitivity of photographic materials at temperatures from 77 to 320 K was investigated by the technique described in work [118].

CHAPTER 3. THE ELECTROINDUCED LUMINESCENCE OF MONOCRYSTALS AND EMULSION MICROCRYSTALS OF SILVER HALIDES

Progress in understanding of mechanisms of forming of photosensitive solid phase of silver halides, various ways of sensitization and formation of the image have allowed to make certain progress in improvement of quality of photographic materials and to bring closer their photographic characteristics to limit therefore it is absolutely clear that essentially new ways of sensitization were necessary for creation of industrial photolayers with higher production characteristics. One of ways of the solution of objective was management of photosensitivity by means of exposure in electric field. However, purposeful search of the most effective ways of application of any given way of impact on substance requires understanding of the fundamental processes happening at the same time.

For studying the mechanism of influence of pulse electric field on photosensitivity of photographic materials we have conducted comparative research by means of independent methods – luminescent and photographic. Such choice is caused by the fact that else in 1955 Matossi and Nadelmen [116] observed radiation burst in ZnS-phosphorus weighed in dielectric. The specified luminescence arose at recombination of nonequilibrium carriers in the field of the volume charge created due to crystalline phosphor polarization. Therefore studying the low-temperature electroinduced luminescence of silver halides described by authors of work [92] was one of tasks of work. It is connected with the fact that found V.M. Belous and N.G. Dyachenko [119, 120] the effect of influence of long-wave light on luminescence of silver halides has offered new prospects of application of luminescent method for clarification of mechanisms of the electron-hole and ionic processes happening at light absorption. Besides, the luminescent technique has gained further development [121] that has allowed to prove Meydinger's assumption [122, page 9] and Berg [122, page 77] that the low-temperature luminescence and photolysis (at the room temperature) microcrystals of photographic emulsions are the competitive effects which are mutually excluding each other and to offer luminescent method as the tool for research of ionic processes in silver halides. From everything told obviously that detection of luminescence of silver halides under the influence of electric field was extremely important experimental result allowing to expand and concretize significantly idea of the electroinduced processes in silver halides.

3.1. The electroinduced luminescence of microcrystals of photographic emulsions

Preliminary series of experiments on detection of the electroinduced luminescence of microcrystals of AgBrI-emulsions has shown that increase in electric field intensity (both constant, and variable with frequency of 50 Hz) to some threshold values (~ 10^5 V/cm) inevitably leads to breakdown of samples. At the same time at the time of breakdown of samples the green luminescence localized in the place of development of avalanche visually is found. Such result, apparently, has been connected with weakening of the external field due to electronic and ionic polarization and, as a result, – sharp reduction of the internal effective field. Application of short-term impulses of the field has allowed to find the low-temperature electroinduced luminescence of silver halides [92].

In our experiments industrial highly sensitive photographic materials have been investigated: RM-1, RM-V, RF-3, RF-1 and others. Photographic layers 150 microns thick were affected in liquid nitrogen by pulse electric field 30 kV lasting $5 \cdot 10^{-6}$ sec. and an amplitude of 20 ÷ 30 kV that led to emergence of luminescent flash. The oscillograms reflecting temporary dependence of intensity of the electroinduced RM-V photolayer luminescence for different lengths of waves of spectrum of radiation are presented on fig. 2. Total time of highlighting at action of the pulse field did not exceed 10^{-3} sec. In spectrum of the electroinduced luminescence of not exhibited layers of RM-V two bands with $\lambda = 550$ and 680 nanometers are observed (fig. 3, curve 1). After preliminary flare of layer only one short-wave band remains (fig. 3, curve 2). Similar bands are registered also in spectrum of low-temperature photoluminescence of layer of PM-B at excitation by the radiation of the pulse laser (fig. 3, curve 3). Intensity of the photo and electroinduced luminescence for convenience of display are brought to one scale as the intensity of photoluminescence for all studied materials was 2 –3 orders higher than intensity of the electroinduced luminescence. Change of intensity (I_λ) luminescent flash from voltage (E) of the pulse electric field enclosed to sample has threshold character. Dependences I_λ and effect of increase in photosensitivity S_E/S_0 from E are presented on fig. 4. Value of effect of the field defined on formula $\eta = S_E/S_0$.

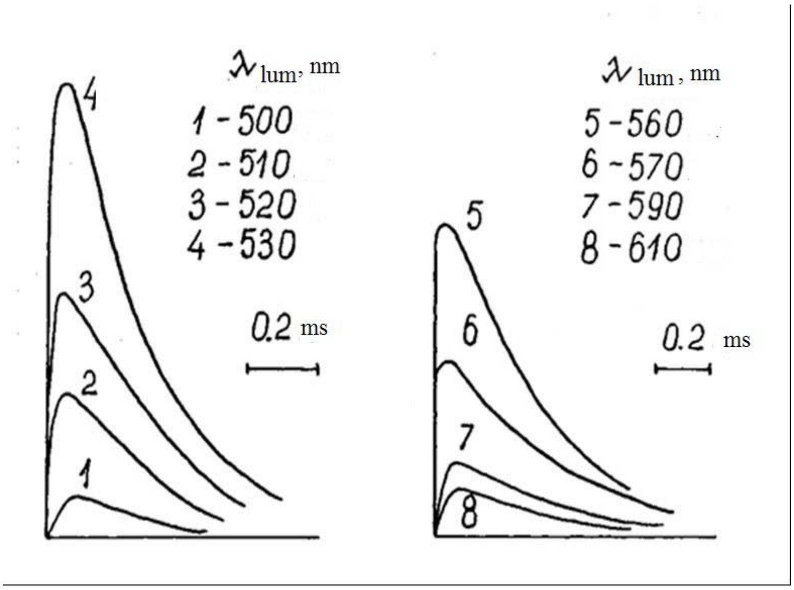


Fig.2. Time dependence of intensity of the electroinduced RM-V film luminescence on wavelength.

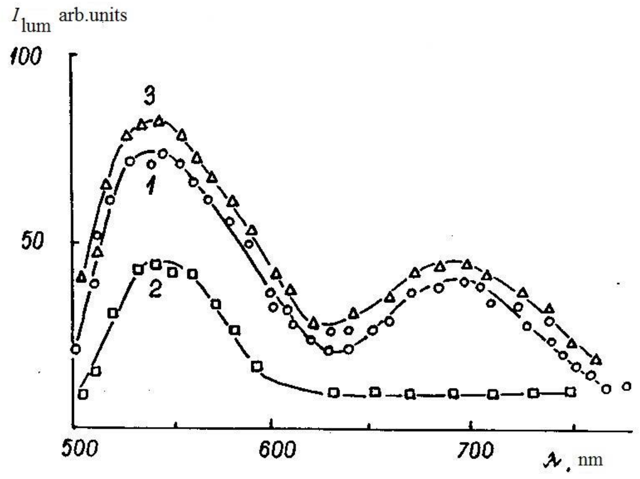


Fig. 3. Spectrums photo (3) and RM-V electroinduced (1, 2) luminescences of photolayer before (1) and after (2) exposure.

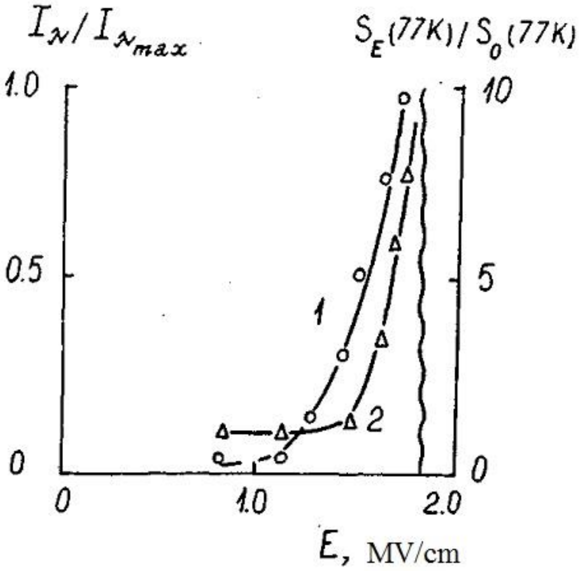


Fig.4. Dependence of intensity (I_λ) the electroinduced luminescence (1) and effect of increase in photosensitivity of film of RM-V of electric field intensity. λ_{max} = 550 nm.

Formula

$$\eta=S_E/S_0 \qquad (3.1)$$

where S_E and S_0 – sensitivity of photographic material when exposure with the field and without it, determined by the set blackening density over veil level by criterion 0.85. Photographic materials exhibited at temperature of liquid nitrogen laser radiation synchronously with field impulse.

Provided on Fig. 2 – 4 data allow to assume that the electroinduced luminescence is caused by radiating recombination of the carriers created in silver halide lattice as a result of ionization by collision, and the specified effect is luminescent analog of the phenomenon of increase in photosensitivity in the making multiple copies electric field. The drawn conclusion is confirmed by results of the experiments executed on various photographic emulsions. As one would expect, the probability of excitation of the electroinduced luminescence in electric field of certain voltage is much more for coarse-grained photoemulsions, than for fine-grained. This result correlates with data of work [82] in which authors specify that for films Photo 130 and PT-1 with average size of microcrystals 0.8 and 1.2 of micron the beginning of multiplication of electrons is observed at voltages fields 3.5 and 2.0 MV/cm, respectively. In our experiments it is established also that size I_λ the it is more, than more dielectric permittivity of binding.

3.2. Research of polarizing effects in the phenomenon of the electroinduced luminescence of silver halide photographic emulsions

Impact of external electric field on electron-hole and ionic processes leads to change of photosensitivity of photographic materials. When field gradient is sufficient for reproduction of electron-hole couples in microcrystal, considerable gain of photosensitivity is observed [55]. If under the influence of electric field the nonequilibrium carriers are only displaced to surface of microcrystals and the specified spatial redistribution of charge carriers reduces the probability of concoction of electrons at the centers of sensitivity, then in that case there is deterioration in photographic characteristics of light-sensitive medium. The 3rd this case the negative effect of the field is observed (see, for example, [56,123,124]). In works [125-130] it has been established that the effect of increase in photosensitivity in external electric field significantly depends on electronic and ionic polarization of emulsion microcrystals. As the phenomenon of the electroinduced luminescence of photographic emulsions [92] found recently is caused by radiating recombination of electron-hole couples created and multiplied by electric field, in this work the impact of electronic and ionic polarization on the electroinduced luminescence of AgBrI emulsions is studied.

As it has been found out [125-128] earlier, action of pulse electric field with the maximum voltage $E = 10^6$ and duration $\sim 10^{-7}$ with on photographic emulsion at the room temperature leads 10^6 V/cm to ionic polarization of silver halide microcrystals that does not allow to investigate separately contribution of electronic polarization to the total process defining change of photosensitivity. With lowering of temperature the ionic mobility of silver decreases, and at temperature of liquid nitrogen the strong pulse electric field duration even 10^{-5} with does not cause ionic polarization.

In the first series of experiments the impact of electronic polarization on the electroinduced luminescence has been studied. The film of the Russian Federation-3 was affected by impulse of voltage with an amplitude up to 30 kV with periods of building-up and recession $0.3 \cdot 10^{-6}$ with and $5 \cdot 10^{-6}$ with, respectively. For exception of injection luminescence [131] the film was isolated from electrodes. After influence of impulse of voltage there is flash of the electroinduced luminescence with time of razgoraniye 10-4 with and duration ~ 10^{-3} sec. In spectrum of the registered luminescence the green band with $\lambda_{max.}$ = 540 nm is observed. Change of intensity is presented on Fig. 5 (I_λ) the electroinduced luminescence on the wavelength of 540 nm at consecutive giving of impulses of electric field on sample. Impulses of voltage gave with interval from 1 to 10 min. From the given dependence of size I_λ from number (N) of impulses of external electric field follows that consecutive influence of the first seven impulses of voltage at an interval of 1 min., leads to reduction of intensity of luminescence then the stationary level of luminescence does not change. It is connected with the fact that at consecutive unipolar excitation there is polarization of microcrystals caused by the shift of electrons and holes to near-surface area with the subsequent their localization that partially reduces effectively operating field in microcrystals.

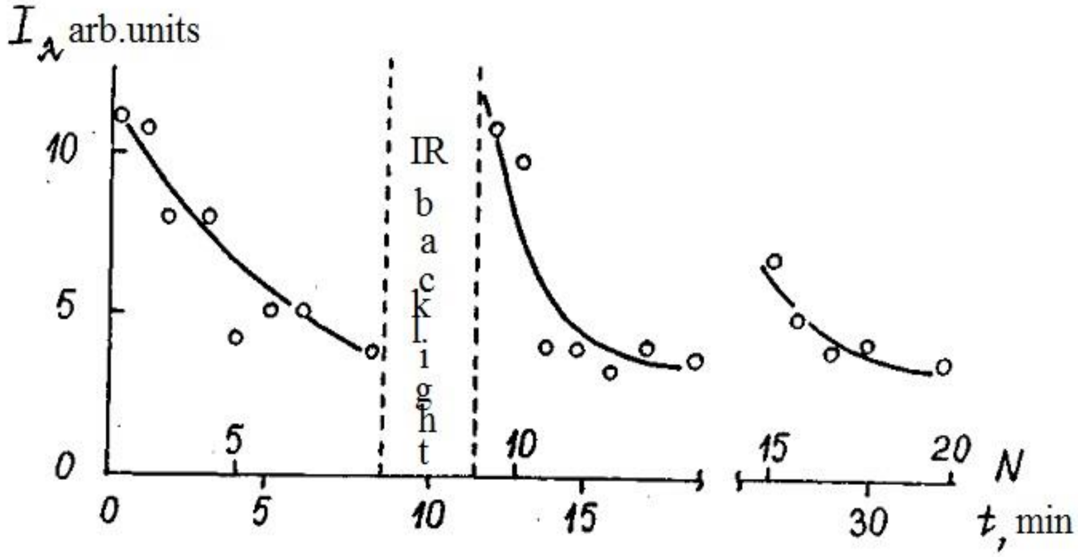


Fig. 5. Dependence of intensity (I_λ) the electroinduced luminescence on the wavelength of 540 nm from consecutive impact of surge voltage on film of the RF-3. On abscissa axis are postponed order number (N) of impulses and time (t) of their receipt is relative the first.

The electronic nature of polarization is confirmed by the fact that after radiation of sample infrared light (λ> 900 nanometers) which releases electrons and holes from localization levels, the intensity of luminescence at the subsequent giving of impulse of electric field is restored to initial. The described results are presented on Fig. 5 – between the eighth and ninth impulses of voltage photoemulsion layers irradiated with infrared light within three minutes. Reduction of electronic polarization of microcrystal happens also at storage of sample. So, for example, increase in duration of interval between the 14th and 15th impulses up to 10 minutes has led to partial recovery of intensity of luminescence (Fig. 5).

Results of experiments in which after series of unipolar impulses the polarity of connection of electrodes changed well will be coordinated with the offered explanation. Dependences of the electroinduced luminescence on consecutive influence of impulses of voltage with interval of 0.5 min. are presented on Fig. 6. Each subsequent series of impulses moved at influence of the field with the polarity opposite to the previous series. It has turned out that, first, when changing polarity of electric impulses the intensity of luminescent flash from the first impulse in each subsequent series is more, than in previous, and secondly, in each series of measurements the unipolar influence reduces intensity of luminescent flash to the same level. Such result demonstrates that when giving five unipolar impulses of external electric field the identical electronic polarization is reached. Therefore, the increase in intensity of flash of luminescence caused by change of polarity cannot be connected only with growth of voltage of the effective internal field, and is defined by increase in number of electron-hole couples participating in avalanche development. For understanding of the described effect it is important to mean that each influence of unipolar impulse of electric field promotes the shift and localization of charge carriers at edges of microcrystal and therefore at change of polarity of electric field the efficiency of process of reproduction of charge carriers increases.

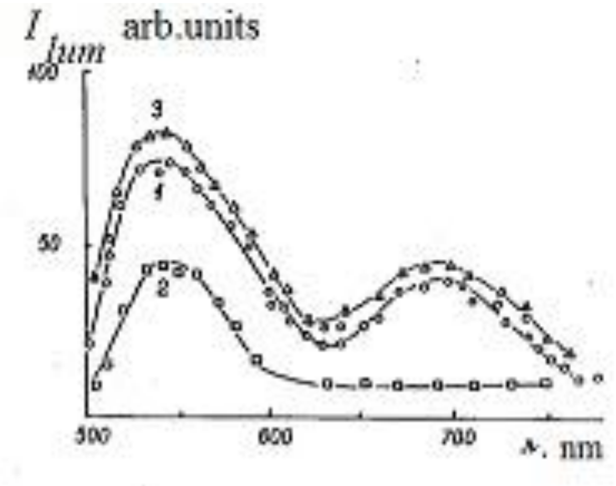


Fig 6. Dependence of intensity (I_λ) the electroinduced luminescence from consecutive impact of surge voltage on film of the RF-3. Later each five measurements the polarity of impulses was changed for opposite. On axis abscissae the order number (*N*) of measurement is postponed.

For clarification of impact of ionic polarization on efficiency of the electroinduced luminescence of emulsion microcrystals experiments in which samples were affected not only short-term pulse, but also constant electric field have been made. Voltage sources have been connected in such a way that constant electric field created potential difference on sample to 5 kV. The total potential difference on sample depended on polarity of impulse of voltage. The received results are presented in the form of dependence of intensity of the electroinduced luminescence on consecutive action of number of impulses of the field with interval of 0.5 min. in Fig. 7. The experiment was made as follows. Influence of the first five impulses was investigated in the absence of constant electric field, and - at simultaneous imposing constant and pulse water the subsequent. Constant electric displacement which polarity was opposite to surge voltage, has caused increase in intensity of luminescence (Fig. 7, see results of 6 –11 measurements). It is connected with the fact that constant electric field leads to ionic polarization of microcrystals, – which strengthens the external pulse field.

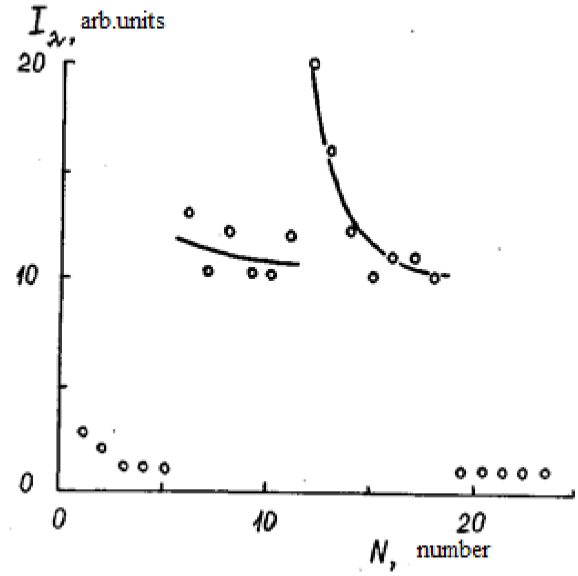


Fig. 7. Dependence of intensity (I_λ) electroinduced luminescence on the wavelength of 540 nm from consecutive impact of surge and constant voltage on film of the RF-3. On abscissa axis number (*N*) of measurement is postponed.

After 11-th impulse the polarity of connection of electrodes to sample has been changed that has led to additional increase in intensity of luminescence at the subsequent 12-14 impulses, and after the 15th impulse the intensity of luminescence has matched the intensity observed of 7-11 impulses. The similar effect is described above (see fig. 6) and connected with increase in number of the primary electrons participating in avalanche development. Since the 19th impulse, the polarity of constant voltage matched polarity pulse that has led to total disappearance of luminescence. The impossibility of excitation of luminescence is connected with reduction of the effective internal field of microcrystal because of ionic polarization. The drawn conclusion is confirmed by the fact that additional infrared illumination does not change action of constant electric field to the electroinduced luminescence. As is well-known [132, 133], external electric field creates photoelectret and thermoelectret conditions of emulsion silver halide microcrystals. Follows from results of the made experiments that the electret condition and the low-temperature electroinduced luminescence of silver halides arising in the course of influence of electric field are the competitive mutually excluding phenomena.

3.3. The electroinduced luminescence of monocrystals of silver halides

In spite of the fact that now the most probable mechanism of the electroinduced sensitization of silver halide photoemulsions should be considered avalanche reproduction of carriers in strong electric fields, the question of the nature of the specified reproduction remains open. Really, reproduction of carriers can result from ionization by collision of ions of lattice or the impurity centers created in microcrystal. Simple calculation shows that the second process demands smaller energy, but its implementation requires accumulation of considerable concentration of products of chemical sensitization of atomic and molecular or cluster dispersion. Increase of number of free carriers under the influence of strong electric field is equivalent to increase in exposure of photoemulsion layer, increase in density of blackening of the shown image is consequence of what. At temperature of liquid nitrogen the increase in concentration of nonequilibrium carriers has to be followed by growth of intensity of recombinational luminescence. However to such assumptions results of comparative research of influence of strong electric field on photosensitivity primitive and chemically sensitlized contradict emulsion. In work [84] it is established that on primitive emulsions the size of effect of sensitization is much higher, than on the emulsions subjected to chemical sensitization that contacts dispersion of electrons on impurity centers.

For specification of the mechanism of avalanche reproduction the low-temperature electroinduced luminescence of silver halide monocrystals of various galogen structure has been studied. As objects of research the monocrystals of AgBr, AgBrI and AgClI which are grown up by the Stokbarger's method have been chosen. Alloying with iodine was carried out at addition to AgBr and AgCl fusion of small amounts of AgI; samples had thickness ~ 5 10^{-4} m. In spectrums of the electroinduced luminescence of monocrystals of AgBr and AgBrI the same bands, as in photoluminescence spectrums are observed at excitation by the radiation of the pulse nitric laser (λ = 337 nm). For example spectrums of the photo and electroinduced luminescence for AgBr monocrystal +0.1 molar % AgI are given in Fig. 8. Let's note that the integrated intensity of the low-temperature electroinduced luminescence of all studied monocrystals is much higher, than for photoemulsions (~ 10^3 times) that can serve as the proof of matrix nature of reproduction. Comparison of the results presented on Fig. 8 and in Fig. 3 demonstrates that in spectrums of the photo and electroinduced AgBr monocrystal luminescence + 0.1 mol. % of AgI and AgBrI emulsion the wide band of luminescence caused by the pair iodic centers [110] prevails. As the photoluminescence was excited by light from the field of own absorption of silver halide in the specified experiments, coincidence of the described spectrums gives strong reason to assume that in stronger electric field the reproduction of carriers happens due to ionization by collision of anions and cations of lattice, and the arising holes are localized further at the impurity levels of radiating recombination. At the same time it must be kept in mind that the nonequilibrium carriers created by the field are displaced to electrodes, and their recombination occurs after removal of external voltage. The movement of carriers in the field of volume charge defines sharp increase of intensity of flash of the electroinduced luminescence.

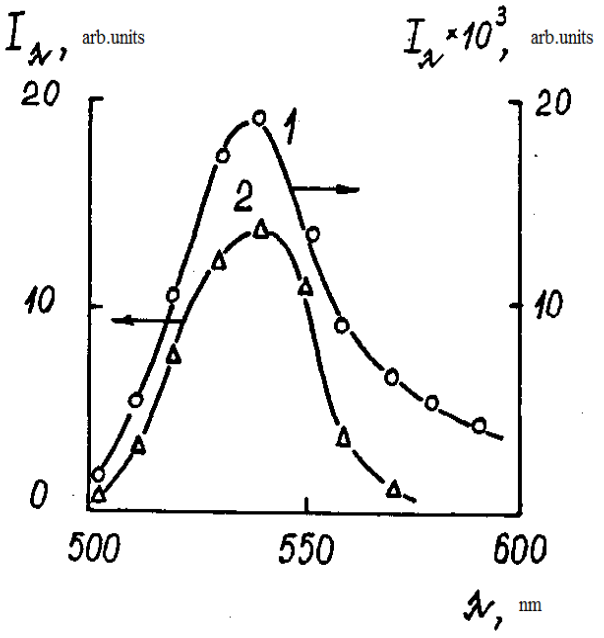


Fig. 8. Spectrums photo (1) and AgBr electroinduced (2) luminescences of monocrystal AgBr +0,1 mol. % AgI.

The drawn conclusion well is confirmed by results of experiments on studying luminescent properties of monocrystals of AgCl + 0.1 mol. % AgI. Unlike AgBr and AgBrI, spectrums of the photo and electroinduced luminescence kristallaAgClI do not match (Fig. 9).

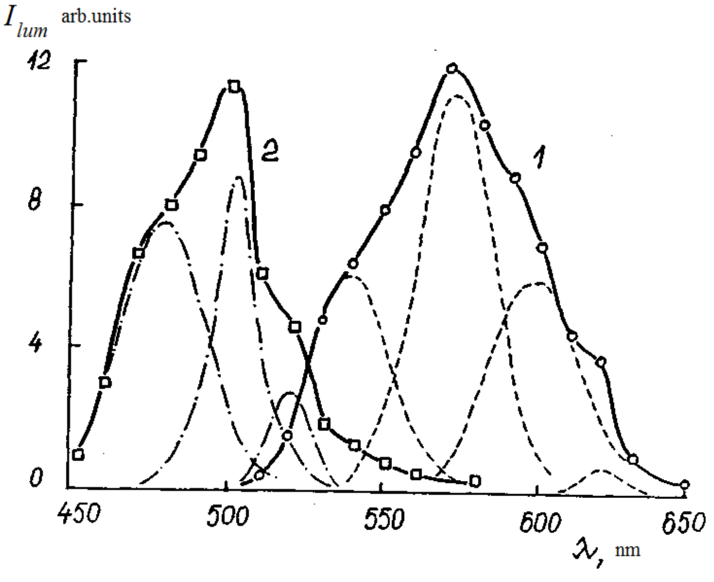


Fig. 9. Spectrums photo (1) and AgCl electroinduced (2) luminescences of monocrystal + 0.1 mol. % AgI.

Influence of the external field leads to emergence of the bands characteristic of nominally clean AgCl, with $\lambda_{max.}$ = 480 and 500 nm which are not observed in photoluminescence spectrum (Fig. 9, curves 1 and 2; here the contours of separate bands received by the so-called "relay" method described in work [134] are given in the drawing). The specified bands are caused by uncontrollable impurity of ions of bromine and purposely entered impurity of ions of iodine (luminescence of the excitons localized on impurity). As it has been established [135, 136] earlier, observed at 4.2 K band with $\lambda_{max.}$ = 500 nanometers Ag^{2+} *e* is caused by the radiation of the autolocalized exciton $Ag^{2+}e$.

At light absorption by silver chloride the autolocalized exciton results from recombination of free electron (e) with the autolocalized hole (Ag^{2+}). Emergence intensive low-temperature (T=77K) luminescences of the autolocalized excitons in AgClI monocrystals at action strong ($E > 10^6$ V/cm) electric field unambiguously demonstrates the reproduction of charge carriers connected, in particular, with ionization by collision of Ag cations which are in lattice sites Ag^+. At the usual (not laser) density of excitation the luminescence of the autolocalized excitons in AgC1 is observed only in areas T <40 K [110]. Emergence of band of the electroinduced luminescence with $\lambda_{max.}$ = 500 nm even at T = 77 K on high concentration of the autolocalized holes created in strong electric fields (Ag^{2+}) and free electrons which radiating recombination causes emergence of luminescence of the autolocalized excitons. The additional proof of reproduction of carriers in the stronger field due to ionization by collision of anions and cations of lattice of silver halide is as well the fact that at the threshold nature of dependence of intensity (I_λ) luminescent flash from voltage of external electric field (Fig. 10) the threshold value, E_p, is much less for monocrystals, than for photoemulsions (compare Fig. 4, curve 1 and Fig. 10).

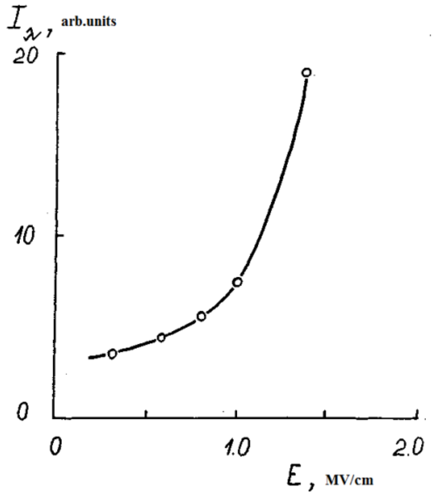


Fig. 10. Dependence of intensity (I_λ) the electroinduced AgCl +0.1 mol. % AgI monocrystal luminescence from voltage (*E*) of electric field. λ_{max}=500 nm.

The electrons multiplied by the field participate not only in radiating recombination with holes, but also in formation of the latent photographic image. The identical nature of the processes leading to increase in concentration of nonequilibrium charge carriers in the phenomena of the electroinduced luminescence and sensitization is confirmed also by comparison of dependences (I_λ) and η from voltage of the electric field attached to photoemulsion layer. As one would expect, increase (I_λ) it is observed only at the electric field strengths exceeding some threshold value, and the nature of dependences $I_\lambda = f(E)$ and $\eta = f(E)$ is identical (Fig. 11).

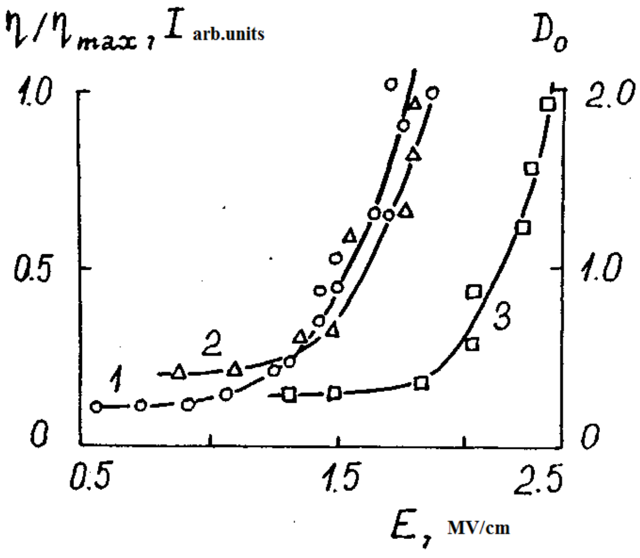


Fig. 11. Dependences of intensity of the electroinduced luminescence (1), sizes $\frac{\eta}{\eta_{\max}}$ (2) and density of fog (3) from voltage of the field attached to photoemulsion layer.

3.4. Features of luminescence of silver halides at pulse excitation by electric field and radiation of the laser

Action of pulse electric field on photoluminescence of silver halides depends on extent of synchronization of the moments of inclusion of exciting radiation and impulse of voltage and also on concentration of the nonequilibrium carriers created by light. For clarification of features of luminescence at such excitation the next experiment has been made. The luminescence of film of RM-1 was excited the radiation of the nitric laser, and electric field was included in various moments of highlighting of flash of photoluminescence. It has turned out that if the impulse of voltage is put to layer of photographic emulsion when the distant stage of attenuation of photoluminescence is registered, then, irrespective of the level of ultra-violet excitation and amplitude of the field, there is addition instant value of intensity photo $(I)_1$ and electroinduced $(I)_2$ luminescence (Fig. 12). If the impulse of voltage moves at the moments corresponding to initial stage of flash of photoluminescence, then action of the field already depends on intensity of exciting light. So, at increase in the specified level on three orders effect of stimulation of luminescence we weed (fig. 13) is replaced by effect of clearing (Fig. 14). At initial stages of flare-up of flash of photoluminescence total action photo and electroinduced excitation superadditive. It is important to emphasize that increase in intensity of photoluminescence under the influence of impulse of the field is observed on those exposures which correspond to formation of the centers of the latent photographic image (Fig. 12, 13).

Results of the described series of experiments well will be coordinated with the developed ideas of the shock mechanism of reproduction of charge carriers in silver halides in external electric field [92, 135]. In case of high concentration of electronic and strong couples created by light (~ 104 couples in one emulsion microcrystal of the average size of 1 micron) shielding of external electric field results from polarization of microcrystal, and the effective internal field in microcrystal is insufficient for implementation of ionization by collision of ions of crystal lattice. Therefore the external field will only displace electrons and holes to opposite sides of microcrystals with possible localization them on deep traps that will lead to decrease in acts of radiating recombination and, as a result, - to clearing of luminescence (fig. 14). At the room temperature the described process can be followed by negative effect of the field. If in microcrystal there is rather small concentration of nonequilibrium electrons and holes (for example, at small levels of excitation when in each microcrystal 10-100 electron-hole couples, or at distant stages of attenuation of photoluminescence are created at any of the excitation levels used by us), then reproduction of charge carriers in stronger electric field is possible that is followed by flash of the electroinduced luminescence (fig. 12, 13).

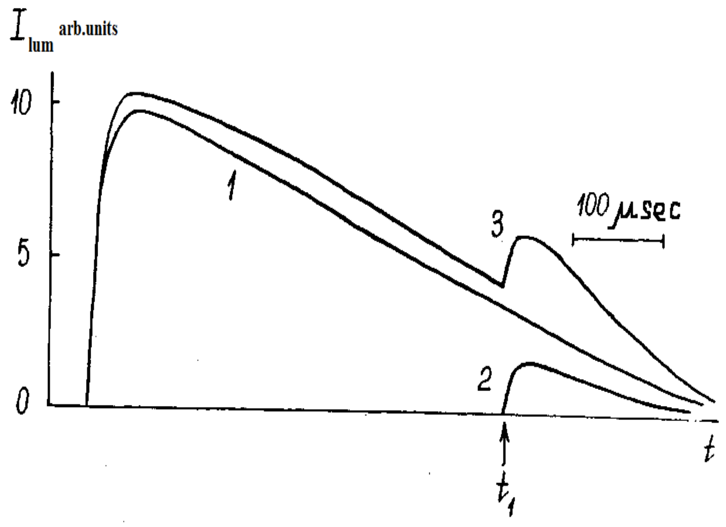


Fig. 12. Temporary dependence of intensity (I_λ) luminescence (λ_{max} = 540 nm) of AgBrI microcrystals of film RM-1 at pulse excitation by the radiation of the laser (1) and electric field (2). Curve 3 – change of intensity of photoluminescence at additional inclusion of pulse electric field; t_1 – moment of inclusion of the field.

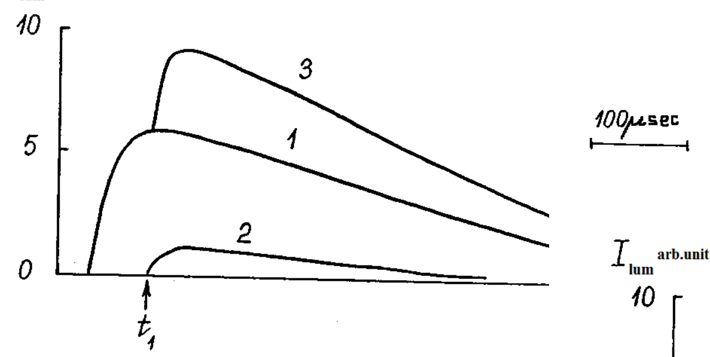


Fig. 13. The same that in Fig. 2.

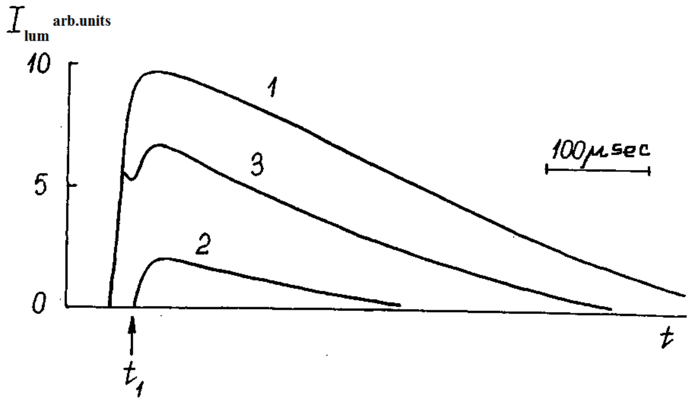


Fig. 14. The same that on Fig. 2, 13, but the intensity of laser excitation is increased by 10 times.

For quantitative assessment of action of the field it is in the case under consideration convenient to enter the following sizes:

I_1' - intensity of photoluminescence at the time of (t_1) of inclusion of electric field;

I_2 - the maximum intensity of the electroinduced luminescence;

I_3 - the maximum intensity of total luminescence when electric field acts on certain stage of highlighting of photoluminescence.

As it was noted above, in case of the weak level of excitation at action of the pulse field at initial stage of flash of photoluminescence

$$I_3 > I_1' + I_2$$

and at distant stage of decay of luminescence $I_3 = I_1' + I_2$

The specified ratio of sizes I_1', I_2 and I_3 in the first and in the second cases, obviously, it is connected with the following reason. It is known that the luminescence of the pair iodic centers in AgBrI microcrystals results or recombinations of free electron with the hole localized on the pair iodic center, or at recombination with this hole of the electron localized on some center [136]. Radiation on both mechanisms leads to appearance of relatives under the spectral provision of the bands of luminescence which are in the green site of spectrum and, radiation at distant stages of attenuation is connected, generally with donor-acceptor recombination.

The origins of green luminescence of AgBrI microcrystals described above allow to explain the nature of impact of electric field on photoluminescence. Really, course of processes of redistribution of electrons and holes on small and deep traps is characteristic of initial stage of flash of photoluminescence. From small traps the charge carriers can be released by electric field and are switched on in process of avalanche reproduction. Therefore in this case

$$I_3 > I_1' + I_2$$

On distant se attenuation stages the luminescence arises at recombination of the localized electron with the localized hole. If the field used in our experiments cannot affect recombination of donor-acceptor couples connected by Coulomb force, then conditions of reproduction of charge carriers in stronger electric field will significantly not differ from those which correspond to unexcited microcrystal. In this case addition of the intensity photo and electroinduced luminescence is observed, that is

$$I_3 = I_1' + I_2$$

AgCl monocrystal luminescence research +0.1 mole % AgI at pulse excitation by the radiation of the laser and electric field has allowed to reveal some features. It is established that at any of the used excitation levels $I_3 > I_1' + I_2$ and, besides, this ratio is carried out for any interval (Δt) between the moment of inclusion of laser radiation and giving of impulse of voltage (it is natural that Δt is chosen smaller, than duration of flash of photoluminescence). It was necessary to expect that simultaneous combined action of impulses of light and the field will lead to separate excitation of blue luminescence of matrix of AgCl and also green luminescence of the pair iodic centers and centers which are available in the "self-activated" [137] samples AgClI. However, at the specified way of excitation the luminescence other than considered is observed. For clarification of the mechanism of this phenomenon the monocrystal was irradiated with single impulses of light, and then gave field impulse with various delays (Δt = 0 – 1000 microsec). Dependences are given in Fig. 15 I_3 from wavelength for two intervals Δt: $2.0 \cdot 10$ microsec (initial stage of flash of photoluminescence, curve 1) and $5,0 \cdot 10^2$ microsec (stage of attenuation of flash of photoluminescence, curve 2). It has turned out that at change Δt there is redistribution of intensity in luminescence bands, and at increase Δt sharply the intensity of the band caused by the pair iodic centers increases, and at Δt = 500 microsec are observed luminescence in blue and green sites of spectrum, comparable on intensity.

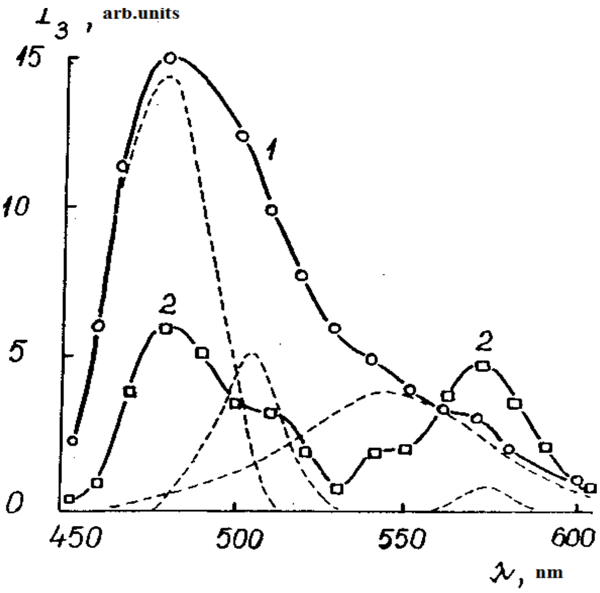


Fig. 15. Spectral distribution of size I_3 at AgCl monocrystal + 0.1 mole % of AgI for two intervals Δt (microsec): $2,0 \cdot 10$ (1) and $5,0 \cdot 10^2$ (2).

The given results can be explained as follows. After radiation of sample the pulse radiation of the laser creates rather high concentration of electrons and holes which are taken various centers differing in concentration, section of capture and recombination for charge carriers and also energy of thermal release of charge carriers from them. In the course of redistribution of charge carriers on levels channels of recombination turn on various. At late stages of attenuation of photoluminescence the radiating recombination of electrons with the holes localized on the pair iodic centers prevails (band with $I_{max.}$ = 570 nm) that is confirmed by presence in the specified band of flash of luminescence at infrared illumination. The external field creates additional concentration of electrons and displaces nonequilibrium charge carriers to electrodes, but is not capable to release holes. Therefore at removal weeding electrons, generally recombine with these localized holes that leads to increase in intensity of luminescence of the pair iodic centers in comparison with the luminescence determined by other channels of recombination. The experimental results given on Fig. 14 and 15 allow to assume that the levels causing luminescence with $I_{max.}$ of =480 and 570 nm have the greatest efficiency. It is possible to call the specified channels of recombination "fast" and "slow", respectively, and temporary permission of spectrums of the photo and electroinduced luminescence allows to estimate time of tunnel relocalization of hole for the pair iodic center.

CHAPTER 4. STUDYING "INSULATING" MECHANISM OF THE SUPERSENSITIZATION OF PHOTOGRAPHIC EMULSIONS

Now a number of methods of increase in efficiency of spectral sensitization of photographic layers by means of additional introduction to the painted emulsion of various organic compounds is known. If at the same time the added substance does not sensibilize in the field of absorption of the main dye and total action both component superadditive, then such substance is called supersensitizer, and the phenomenon of increase of spectral response – supersensitization [1, page 265].

Process of spectral sensitization of photographic emulsions can be conditionally divided into two stages – appearance of electron in emulsion microcrystal after light absorption by the adsorbed dye (D) and participation of this electron in formation of the latent photographic image. The oxygen molecules adsorbed on surface of microcrystals of photographic emulsions can capture the electrons generated by light from conduction band of silver halide [138, 139]. In the presence of moisture the course of the following reactions is possible [140]:

$$O_2 + e \rightarrow O_2^- \qquad (4.1)$$

$$O_2^- + H^+ \rightarrow HO_2^{\cdot} \qquad (4.2)$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (4.3)$$

Reactions 4.1 – 4.3 reduce creation probability of catalytically active centers in silver halide that significantly influences processes of formation of the latent image, aging and storageability of photographic materials [141]. It is absolutely clear that the specified reduction of concentration of electrons in conduction band of microcrystals of silver halide at the expense of the desensitizing effect of oxygen has to lead to reduction of intensity of low-temperature recombinational luminescence.

It is known also [142, 11] that molecular oxygen in ground state effectively extinguishes both fluorescence, and phosphorescence of organic molecules. Therefore the luminescence of some sensitizing dyes adsorbed on surface of microcrystals of photographic emulsions is partially extinguished by oxygen. Thus, if to isolate surface of emulsion microcrystals from interaction with oxygen and moisture, then it is possible to expect increase in concentration of electrons in conduction band of silver halide and at the excited levels of the adsorbed dyes and, as a result of it, – increases of intensity of low-temperature luminescence of silver halide and dyes. It is necessary to expect that at the room temperature the isolation of surface of microcrystals from the environment can affect efficiency of spectral sensitization.

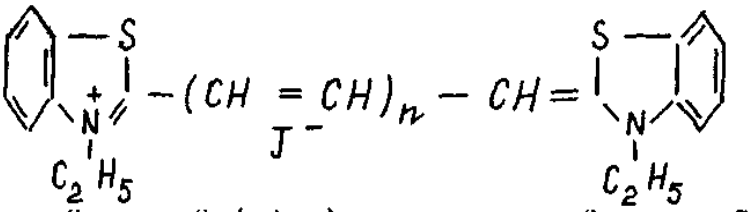
In works [143-145] it was offered to enter hydrophobic substances which form "insulating" laying between surface of microcrystal and binding into photographic emulsion. Availability of such laying, really, promotes increase in efficiency of spectral sensitization of photographic process and also increase in the intensity excited on recombinational to the mechanism of low-temperature luminescence of silver halide and the adsorbed dye [143].

The luminescence of dye arises according to the scheme

$$\text{Dye} + e + p \longrightarrow \text{Dye}^+ + e \longrightarrow \text{Dye} + h\nu_{\text{lum}} \qquad (4.4)$$

where e and p – the electron and hole created at excitation by light from the field of own absorption of silver halide.

As the "isolating" substances the following organic compounds have been chosen: With, N - diphenylnitron (I); C - (O-chlorophenyl), N-phenylnitron (II); C-phenyl, N - (n-tolyl) nitron (III); C - (n-gletoxyphenyl), N - (n-tolyl) nitron (IV); C - (O-chlorophenyl), N - (n-tolyl) Nitron (V); and also azo- and azoxybenzene. Photographic and luminescent researches were conducted on primitive monodisperse AgBr-emulsions (microcrystals had octahedral facet and the average size of 0.07 microns, concentration gelatin of 3%, the maintenance of AgBr of 0.2 mol/l), received by method of controlled two-jet emulsification at *p*Br =1.5. The spectral sensitization was carried out introduction of thiapolycarbocyanine of the following formula:



(4.4)

with various length (*n*) of polimethyne chain. The sensitizing dyes and supersensitizers entered into emulsion in the form of spirit solution in concentration, respectively, 5 mol/mol of AgBr and 10^{-5} (0.01 –1.0) 10^{-2} mol/mol AgBr.

For clarification of role of various nitron in processes of supersensitization preliminary experiments on influence of the specified compounds on luminescent properties of water and gelatinous solutions of spectral sensitizers have been made. In Fig. 16 and 17 for example spectrums of excitation of luminescence of dyes are given to 10% solutions gelatin before (Fig. 16, 17, curves 1) and after (Fig. 16, 17, curves 2). From the provided results it is visible that addition in gelatinous solution of dyes C, N–diphenylnitron leads to hypsochromic shift of band of excitation of luminescence of dyes. Such result can be explained as follows. In the homogeneous gelatinous environment the part of energy of molecules of dye is spent for interaction with gelatin molecules, and nitron, owing to the water repellency, reduce efficiency of intermolecular interaction of dyes and gelatin. It is possible to assume, therefore, that already in the homogeneous environment there is "isolation" of molecules of dye from gelatin.

Further influence of hydrophobic compounds on luminescent properties of primitive AgBr - emulsions has been investigated. The studied organic compounds have unequal impact on luminescent AgBr-emulsion properties, and on fig. 18 for example, luminescent spectrums of the specified emulsions at introduction are given C, N - diphenylnitron in various concentration. It has turned out that the concentration dependence of effect of increase in intensity of spectrum luminescence has extreme character for all hydrophobic substances, and the maximum effect is observed for azoxybenzene.

Hydrophobic organic compounds differ from the known supersensitizers in weak electron- and hole -acceptor properties and are characterized by rather big electrochemical potentials of oxidation and reduction in solutions. For clarification of nature of adsorption of the specified compounds on surface of microcrystals (that is whether is "insulating laying continuous) the next experiments which results are presented on fig. 19 and 20 have been made. Apparently on fig. 19a and 19b, presence C, N-diphenylnitron in primitive AgBr-emulsion does not change the nature of the extinguishing action of methylviologen to luminescence. It is known what methylviologen is powerful trap of electrons and the effective quencher of luminescence, in particular, at excitation by light from the field of own absorption AgBr. Follows from Fig. 19a that C, N-diphenylnitron does not interfere with penetration of molecules of methylviologen to surface of microcrystals of silver halide.

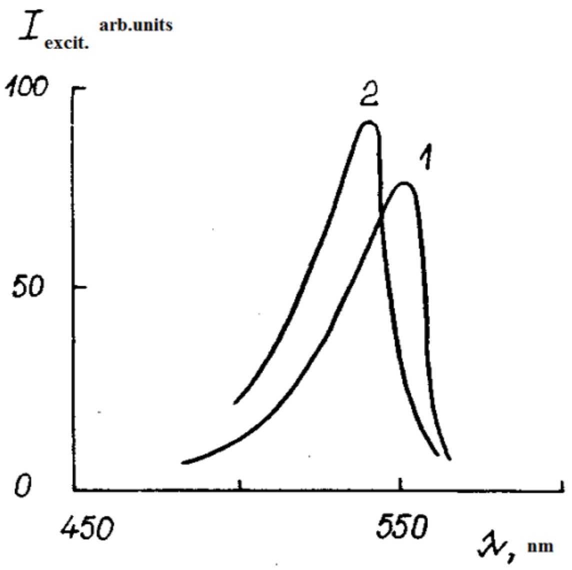


Fig. 16. Spectrums of excitation of luminescence of gelatinous solution of 2.2’-diethylthyacarbocyianinyodide before (1) and after (2) additional introductions C, N-di-phenylnitron. $\lambda_{max.}$ = 615 nm.

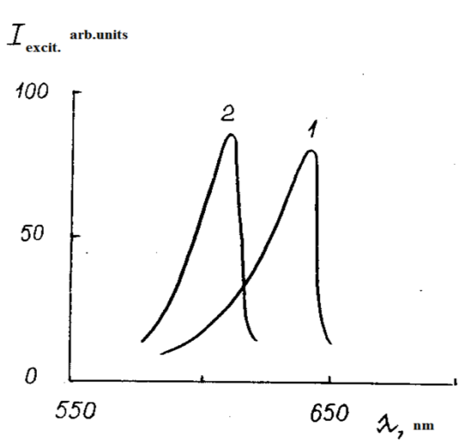


Fig. 17. Spectrums of excitation of luminescence of gelatinous solution of pyridinic salt 3.3’- di-γ-sulfopropyl-9-ethyl-4,5,4’, 5 '-dibenzothiacarbo cyanynebethain (1) and later (2) additional introductions C, N-diphenylnitron. $\lambda_{max.}$ =700 nm.

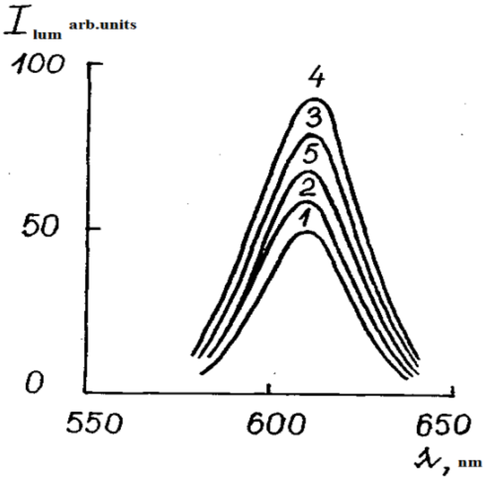


Fig. 18. Luminescent spectrums of AgBr-emulsion before (1) and after (2-5) introductions C, N-diphenylnitron in various concentration (mol/mol AgBr). λ_{ex} = 400 nm. 1 – test specimen; 2 – 3·10^{-4}; 3 – 10^{-3}; 4 – 3 ·10^{-3}; 5 – 10^{-2}.

In Fig. 20b the evolution of luminescent spectrums AgBr-emulsii is shown, to the subjected chemical sensitization within 2 hours at presence With, N-diphenylnitrona. For comparison luminescent spectrums of control emulsion without Nitron are given in fig. 20a. As it appears from the provided data, results were identical, that is introduction of Nitron has not affected kinetics of maturing AgBr-emulsii. Besides, it is necessary to emphasize that maturing, despite availability of the "isolating" laying, proceeds practically about tone speed. Therefore, the cover from With, N-diphenylnitrona is not continuous.

The comparative research of the specified organic compounds with various degree of water repellency is of undoubted interest. Luminescent spectrums AgBr-emulsii, containing various nitrona in concentration of 3 mol/mol of AgBr 10-3 are given in fig. 21. All nitrona promote increase in intensity (I) of ospectrum luminescence AgBr-emulsin (λmax = 610 nanometers) though increase I when using various nitron it is not identical.

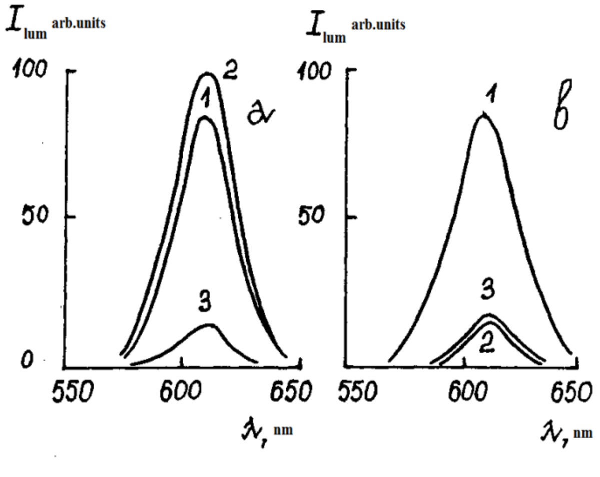


Fig. 19. AgBr-emulsion luminescent spectrums before (1) and after (2.3) consecutive introductions of solutions C,N-diphenylnitrone and methylviologen (a) and methylviologen, and then C,N-diphenylnitrone (b). Concentration C, N-diphenylnitron and methylviologen 3·10^{-3} mol/mol AgBr and 10^{-5}, respectively.

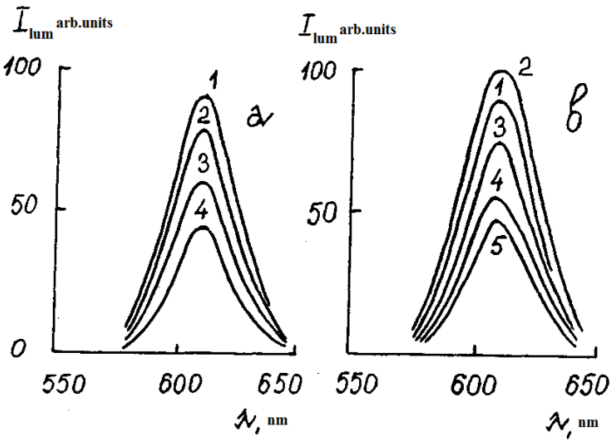


Fig. 20. Luminescent spectrums AgBr-emulsion without C,N-diphenylnitron (a) and with additional introduction of C, N-diphenylnitron (b) (C=3·10-3 mol/mol AgBr). Curves 2,3,4 in Fig. (a) and 3,4,5 in Fig. (b) correspond to 30, 60 and 120 minutes of maturing.

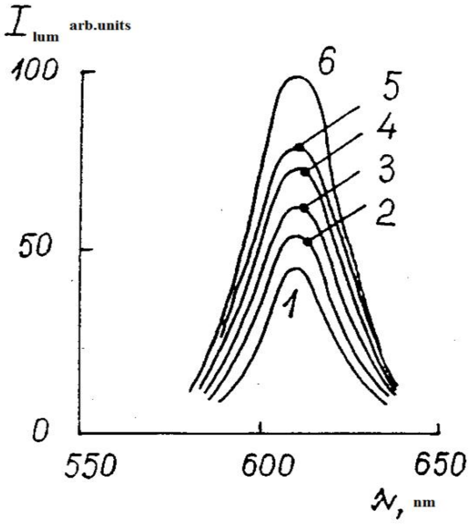


Fig. 21. Luminescent spectrums AgBr-emulsion to (1) and after introduction of various (2-6) (I-V) nitrons: 1 - test specimen; 2 - I; 3 - II; 4 - III; 5 - IV; 6 - V.

Besides, it has been established that in the same case there is also increase of intensity of the flash of luminescence stimulated by infrared light. Such result will be coordinated with the assumption that the hydrophobic substances adsorbed on surface of emulsion microcrystals interfere with loss of photoelectrons on reactions 4.1 - 4.3 and by that increase intensity of low-temperature recombinational luminescence and size of the light summ localized on deep traps.

The similar result is received and for spectrally sensibilized emulsions – addition of spirits of various nitron leads to increase in intensity, both ospectrum luminescence of silver halide, and fluorescence of the adsorbed dye. For example luminescent spectrums AgBr-emulsion, sensitized 3,3'-diethyl-thiatricarbocyaniniode and containing hydrophobic compounds I-V are given in Fig. 22 – 26 spectrums of luminescence of bromic silver emulsions, sensibilized 3.3 '-diethyltiacarbocyanyneiodide(Fig. 23), 3,3 '-diethylthiadicarbocyaninidide (Fig.24), 3,3'-diethyltiatricarbocyanineiodide (Fig.25) and 3,3'-dietilthiatetracarbocyanineiodide (Fig. 26) and the studied nitron containing some from are given in Fig. 23. In spectrums of luminescence of the specified emulsions the fluorescence bands described in literature [18] are observed. The luminescence in this case is caused by recombination of free electrons about radical cation of the adsorbed dyes.

It should be noted that the increase in intensity of low-temperature luminescence observed on experience can be determined by weakening of suppression of luminescence by the ionic mechanism [146] when binding superficial mobile ions of silver hydrophobic compounds. For verification of this assumption the corresponding experiments which have shown that the studied hydrophobic substances do not change the nature of temperature suppression of luminescence of AgBr and the adsorbed dye have been made. The received results will be coordinated with the known data that hydrophobic compounds are poorly adsorbed on microcrystals, and their interaction with surface of solid phase and dye is much worse, than with gelatinous. Besides, as it was specified earlier, availability in AgBr-emulsii compounds I-V does not influence process of chemical maturing (fig. 20 a, b).

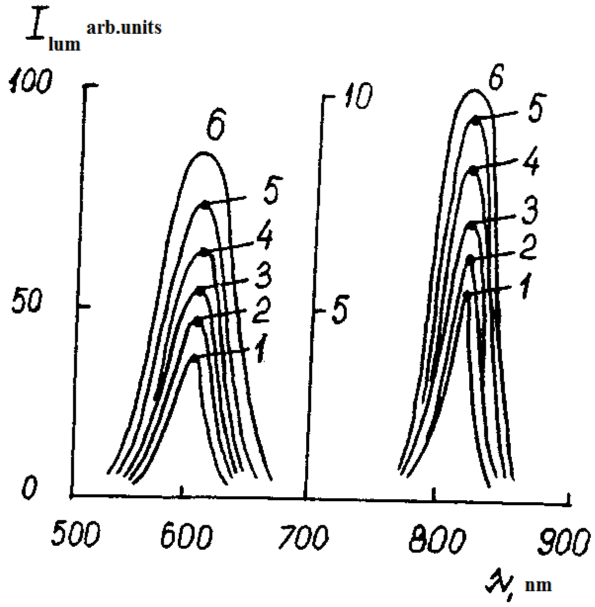


Fig. 22. Luminescent spectrums AgBr-emulsion, sensitized 3,3'-diethylthiatricarbocyaniniodide ($5 \cdot 10^{-5}$mol/mol of AgBr), to (1) and after introduction of various (2-6) (I-V) nitrons: 2-I; 3 - II; 4 - III; 5 - IV; 6 - V.

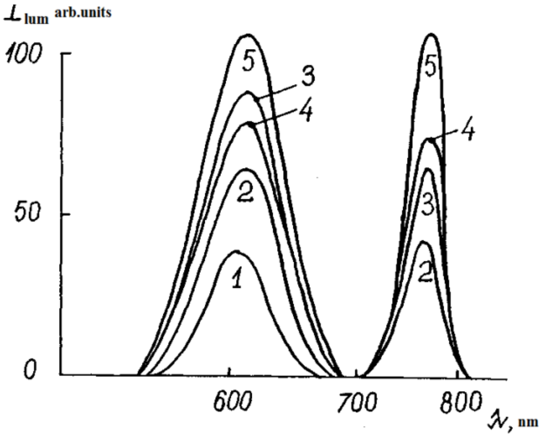


Fig. 23. Luminescent spectrums of bromic silver emulsion to (1) and later (2) introductions 3.3 '-diethyl tiakarbo cyanine iodide (5 mol/mol of AgBr 10-5) and additional introduction of solutions (10^{-3} mol/mol of AgBr) of azoxybenzene (3), azobenzene (4) and C, N-diphenylnitron (5).

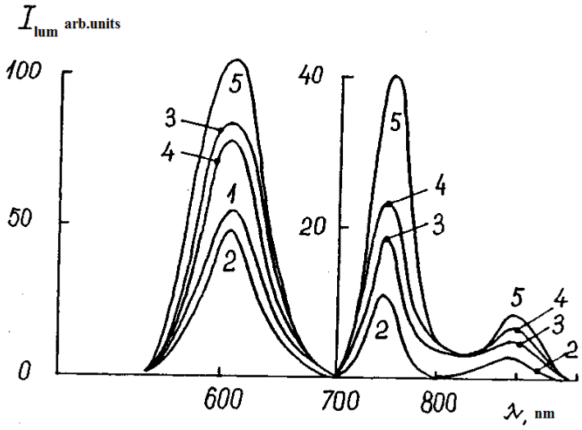


Fig. 24. Luminescent spectrums of bromic silver emulsion to (1) and later (2) introductions 3,3'-diethyl thiadicarbocyanyniodide ($5 \cdot 10^{-5}$mol/mol AgBr) and additional introduction of solutions (10^{-3} mol/mol AgBr) of azobenzene (3), azoxybenzol (4) and C, N-diphenylnitron (5).

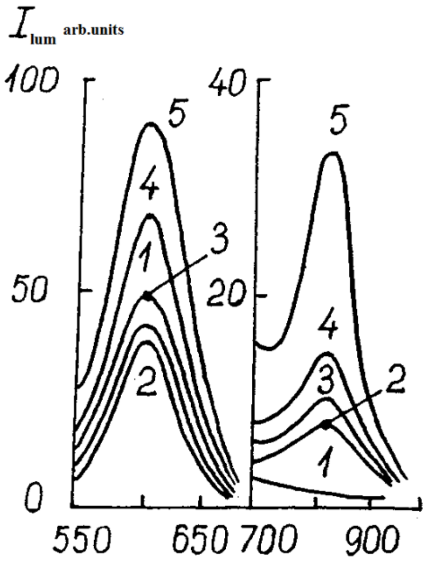


Fig.25.Luminescent spectrums of bromic silver emulsion to (1) and later (2) introductions 3.3 '-diethylthiatricarbocyanineiodide (10^{-5} mol/mol AgBr) and additional introduction of various concentration (3-5) (10^{-3} mol/mol AgBr) C, N-diphenylnitrone: 3-1.0; 4-3.0; 5-10.0.

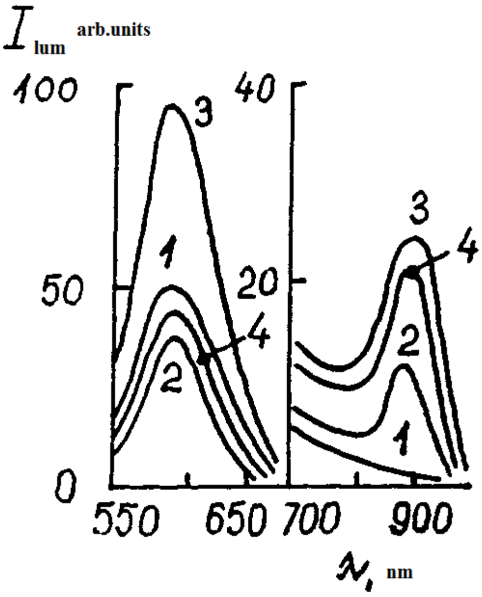


Fig. 26. Luminescent spectrums of bromic silver emulsion before (1) and after (2) introduction of 3.3'-diethyl thiatetracarbo cyanyniodide (10^{-5} mol/mol AgBr) and additional introduction (3,4) spirit solution with various concentration (10^{-3} mol/mol AgBr) C, N-diphenylnitrone: 3 - 1.0; 4 - 10.0.

For quantitative assessment of increase in intensity of luminescence of the AgBr-emulsion containing various hydrophobic substances it is possible to enter size

$$\mu = \frac{I - I_0}{I_0} \tag{4.6}$$

where I_0 and I – maximum bands of luminescence of intensity of silver halide at absence (I_0) and availability (I) nitron. The dependence of size is given in Fig. 27 μ for ospectrum band of luminescence of AgBr-emulsion from concentration (C) various nitron which are contained in emulsion. The similar dependences characterizing change (μ_2) to intensity of fluorescence 3.3'-diethylthiatricarbocyanyneiodide(band with λ_{max} = 820 nm) at change of concentration hydrophobic compound I-V, are presented on Fig. 28.

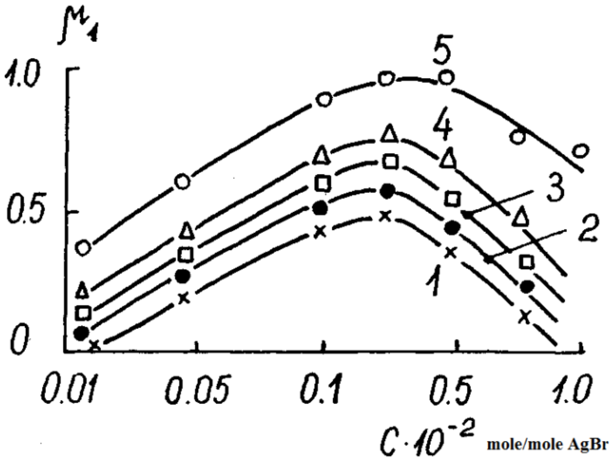


Fig. 27. Dependence of size μ_1 for ospectrum band ($\lambda_{max.}$ = 610 nm) luminescences AgBr-emulsion from concentration of various nitron. Curves belong to various (1-5) (I-V) nitrons, respectively.

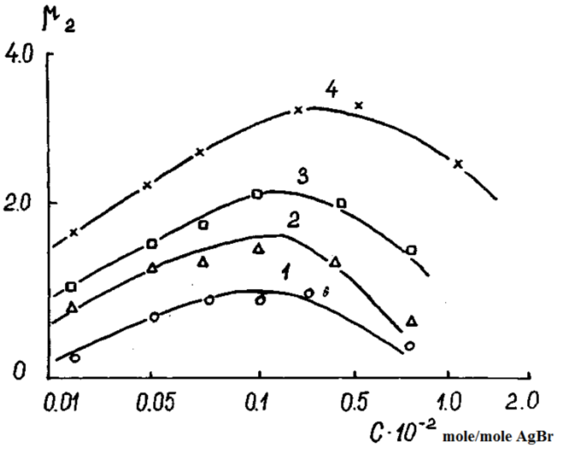


Fig. 28. Dependence of size μ_2 for luminescence of the dye adsorbed on emulsion microcrystals from concentration of the nitron entered into emulsion. Curves 1-4 belong to various (I, II, III, V) nitron: 1-I; 2-II; 3-III; 4-V.

Comparative luminescent and sensitometric researches have shown that at concentration of the nitron corresponding to maximum of dependences $\mu_1 = f(C)$ and $\mu_2 = f(C)$ (Fig. 27, 28), the greatest gain of own photosensitivity of AgBr – emulsions and the greatest efficiency of spectral sensitization of carbocyanine is observed. Reduction of sizes μ_1 and μ_2 at $C > 3 \cdot 10^{-3}$ mol/mol AgBr, obviously, are caused by desorption gelatin and dye from surface of microcrystals hydrophobic compounds. Really, it is known that the ospectrum luminescence of microcrystals of silver bromide appears at presence of gelatin [147]. Follows from the dependences presented on Fig. 27 and 28 also that the nature of influence of nitron on luminescence of silver halides and the adsorbed dyes is not identical. It is connected with various water repellency of the specified compounds which is characterized by coefficient of distribution (*K*) of nitron in two-phase system octanol – water

$$K = \frac{Coct}{C_{H_2O}} \qquad (4.7)$$

where C_{oct} – concentration of the relevant nitron in octanol, C_{H2O} – the same, but in water. The water repellency (*K*) was determined by the technique described in work (6). It has turned out that the distribution coefficient monotonously grows among nitron from I to V (Fig. 29) and increase of *K* correlates with influence of nitron on luminescent and photographic properties of AgBr.

In work [144] it has been established that efficiency of supersensitization by nitron of infrachromatic materials above, than ortho-and panchromatic. In this regard it is important to emphasize that increase in the presence of nitron of intensity of fluorescence of the thiapolycarbocyanine adsorbed on emulsion microcrystals is not identical to various dyes and is defined by length ofhypsochromicchain.

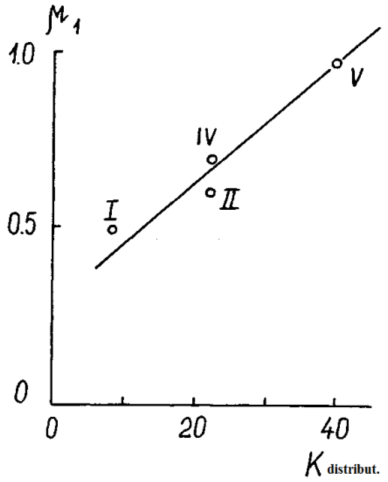


Fig. 29. Dependence of size μ_1, for ospectrum band ($\lambda_{max.}$ = 610 nm) AgBr emulsion luminescence from coefficient of distribution of various nitron. Figures at experimental points – numbers of the corresponding nitron.

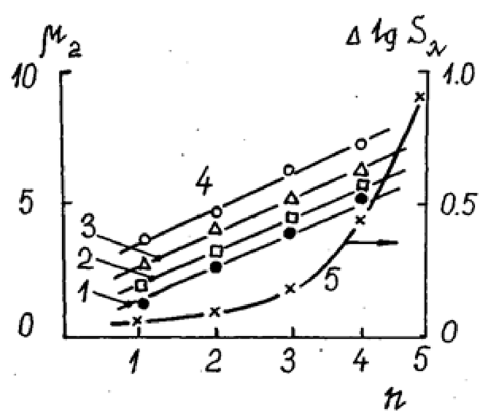


Fig. 30. Dependence of sizes μ_2 and $\Delta \lg S_\lambda$ for AgBr emulsion, sensitized by thiapolycarbocyanines at additional introduction of nitron, from length (*n*) ofhypsochromicchain of dyes. Concentration of Dyes $5 \cdot 10^{-5}$ mol/mol AgBr, nitron – $3\ 10^{-3}$ mol/mol AgBr.

Curves belong to various 1-5 (II-V) nitron: 1 - II; 2 - III; 3 - IV; 4, 5 - V.

$$\Delta \lg S_{\lambda} = \lg\left(\frac{S_{\lambda}}{S_{\lambda}^{0}}\right) \qquad (4.8)$$

The specified results presented in Fig. 30 in the form of dependences $\mu_1 = f\,(C)$ and $\mu_2 = f\,(C)$ well confirm the "insulating" mechanism of supersensitization. In formula (4.8) S_{λ}^{0} – spectral response of AgBr-emulsion, sensitized by one of cyanine dyes with certain length of polymetine chain, a S_{λ} –spectral response of the specified emulsion at additional introduction of solution of supersensitizer V. Really, with increase in number (CH=CH) - groups among cyanine dyes of the same building there is deepening of their lowest vacant level under AgBr conduction band [1, page 282]. Thus, electronoacceptive function grows and time of life of the electrons taken according to the scheme increases

$$\mathrm{Kr} + \mathrm{e}^{-} \rightarrow \mathrm{Kr}^{-} \qquad (4.9)$$

Therefore the efficiency of action of the "insulating" laying interfering electron transition from radical anion of dye (Kr-) to oxygen molecule will increase among dyes with *n* from 1 to 5 that will well be coordinated with experimentally established facts.

As additional confirmation of the inhibiting action of hydrophobic compounds concerning loss of photoelectron on reactions (4.1) – (4.3) the following result can serve. In Fig. 31 the dependence of intensity of eletroinduced luminescence of AgBr-emulsion from voltage of pulse electric field with C,N-diphenylnitrone is shown. As follows from Fig. 31, threshold of the electroinduced luminescence of the specified emulsion

$$\Delta \lg S_{\lambda} = \lg\left(\frac{S_{\lambda}}{S_{\lambda}^{0}}\right) \qquad (4.8)$$

and $\mu_2 = f(n)$, well confirm the "insulating" mechanism of supersensitization. In formula (4.8) S_{λ}^{0} – spectral response of AgBr-emulsion, sensitized one of cyanine dyes with certain length of polymethyne chain, S_{λ} – spectral response of the specified emulsion at additional introduction of solution of supersensitizer V. Really, with increase in number (CH=CH) – groups among cyanine dyes of the same structure there is deepening of their lowest vacant level under AgBr conduction band [1 page 282]. Thus, electronoacceptive function grows and lifetime of the electrons taken according to the scheme increases

$$\mathrm{Kr} + \mathrm{e}- \rightarrow \mathrm{Kr}- \qquad (4.9)$$

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As additional confirmation of the inhibiting action of hydrophobic compounds concerning loss of photoelectron on reactions (4.1) – (4.3) the following result can serve. In Fig. 31 the dependence of intensity of electroinduced luminescence of AgBr-emulsion with C, N-diphenylnitrone from voltage of pulse electric field was shown. As follows from Fig. 31, threshold of the electroinduced luminescence of the provided emulsion it is considerable below, than for emulsion without nitron (compare to Fig. 4, curve 1) that is connected, apparently, with preservation of the electrons multiplied by the field in volume of microcrystals by means of hydrophobic compound.

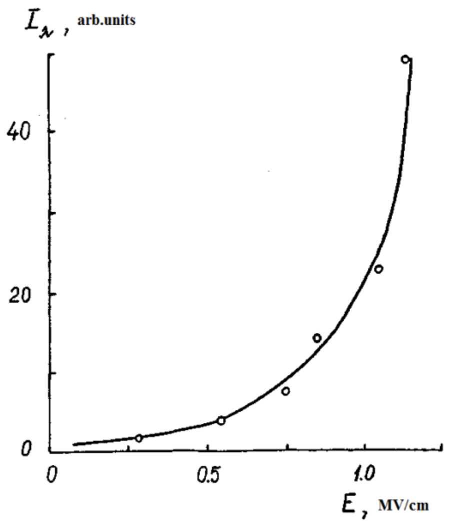

Fig. 31. Dependence of intensity (I_λ) the electroinduced luminescence of the AgBrI-emulsion containing C,N-diphenylnitron ($3 \cdot 10^{-3}$ mol/mol AgBrI) from electric field intensity (E), λ_{lum}= 570 nm.

Comparison of results of luminescent and photographic researches confirms conclusion about volume [143-145] that the "insulating" mechanism of supersensitization is connected by hydrophobic compounds with slowing down of reactions of desensitization and self-desensitization in which electronoacceptive dye, oxygen and moisture participate.

CONCLUSION

1. Features of the low-temperature luminescence of microcrystals of photographic emulsions and monocrystals of silver halides arising at action pulse ($\tau \approx 300$ nanoseconds) electric field with voltage $E > 10^6$ V/cm are studied (the so-called electroinduced luminescence – EIL). It is established that in area $E \geq 10^6$ V/cm increase in field gradient is followed by sharp increase of intensity of luminescence. The received result demonstrates that EIL is defined by process of multiplication of charge carriers in external electric field.

2. Spectrums of the photo and electroinduced luminescence of silver halides are studied. Coincidence of the specified spectrums at AgBr and AgBrI-microcrystals and monocrystals is revealed. It is established that in low-temperature spectrum (T = 77 J) EIL of monocrystal AgClI is observed band 2.45ev (luminescence of the autolocalized exciton, $Ag^{2+}e$) which is not excited by laser radiation. Emergence of luminescence of $Ag^{2+}e$ is caused by process of ionization of lattice cations of AgClI the charge carriers accelerated in electric field.

3. For photoemulsion layers the identical nature of change of density of blackening when exposure in external electric field and intensity of the low-temperature electroinduced luminescence at increase is established E in area $E \geq 10^6$ V/cm. It proves the identical mechanism of the observed phenomena which is connected with reproduction of charge carriers in external electric field.

4. The impact of the electronic and ionic polarization of silver halides arising in external electric field, on effect of the electroinduced luminescence is studied.

5. Influence of electric field on photoluminescence of silver halides is investigated. The dependence of effect of impact of external electric field on photoluminescence on concentration of the charge carriers created by light is shown.

6. It is established that introduction of hydrophobic organic compounds to silver halide photographic emulsions is followed by increase in intensity of recombinational luminescence of emulsion microcrystals and the dyes sensitizers adsorbed on surface of solid phase. The intensity of luminescence increases with growth of degree of water repellency of the used substance. The interfaced change of the sizes characterizing gain of photosensitivity (T = 300 K) and intensity of low-temperature luminescence of photoemulsion layers depending on concentration of the hydrophobic compounds is revealed. On the basis of the

received results the "insulating" mechanism of supersensitization of infrachromatic photographic materials is reasonable.

7. By means of uniform luminescent technique, mechanisms of two diverse processes – influences of external electric field on photosensitivity of photoemulsion layers and the supersensitization hydrophobic organic compounds promoting increase in efficiency of formation of the photographic image are found out.

THE LIST OF THE USED SOURCES

1. T. James. Theory of photographic process. L.: Chemistry, 1960, 672 pages.
2. P.V. Meyklyar. Physical processes at formation of the latent photographic image. M.: Science, 1972, 399 pages.
3. Bloch O., Renwick F.F. Oremayn as the Sensitizer, - Photogr. J., 1920. v. 60, N 14, p.145-147.
4. Dietz F. Zum Stand der Theorie der spectralen Sensibilisierung. Teil 1-2. – J. Signal AM, 1978, BD.6, Half 4, S.245-266.
5. B.I. Shapiro. Current state of the theory of supersensitization of negative silver halide photographic materials. – Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1980, t.25, No. 1, page 64-75.
6. B.I. Shapiro. Problems of supersensitization of photographic materials. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1986, t.31, No. 1, page 68-79.
7. W. West, Carroll B.H. Photo-Conductivity in Photographic Systems. – J. Chem. Physics, 1947, v.15, N8, p.529-536.
8. W. West, Carroll of B.H. Energy Transfer in the Photo-sensitization, Supersensitization and Antisensitization. - J. Chem. Physics, 1951, v.19, N4, p.417-427.
9. A.N. Terenin. Photochemistry of dyes. M.-L.: Prod. Academy of Sciences of the USSR, 1947, 353 pages.
10. Rosenoff A.E., Norland K.S., Ames A.E., Walworth V.K., Bird G.R. The Resolved Spectra of Small Cyanine Dye Aggregates and Mechanism of Supersensitization. - Photogr. Sci.Eng., 1968, v.12, N4. p.185-195.
11. V.L. Yermolaev, E.N. Bodunov, E.B. Sveshnikova, T.A. Shakhverdov. Nonradiative transfer of energy of electronic excitation. L.: Science, 1977, 311 pages.
12. Förster J. 10-th Spier's Memorial Lecture. Transfer Mechanisms of Electronic Excitation. - Disc. Faraday Soc., 1959, N27, p.7-17.
13. Dexter D. A Theory of Sensitized Luminescence in Solids. -J. Chem. Phys., 1953, v.21, N5, p.836-850.

14. Zuckerman B., Mingace H. Spectral Sensitization, Supersensitization and the Mechanisms of Dye-Sensitized Photoconductivity in AgBr Single Crystals. - J. Chem. Phys., 1969, v.5O, N8, p.3432-3444.

15. Zuckerman B. The Mechanism of Spectral Supersensitization of Silver Bromide. - Photogr. Sci. Eng., 197O, v.14, N5, p.336-341.

16. Bird G.R., Zuckerman B., Ames A.E. Structure of Dye Aggregates and the Mechanism of Photosensitization of AgBr. - Photochem. Photobiol., 1968, v.8, N5, p.393-410.

17. Gilman P.B. Review of the Mechanisms of Supersensitization. - Photogr. Sci. Eng., 1974. v.18, N4, p.418-430.

18. Gilman P.B., Koszelak J.D. Luminescent Evidence for the Hole-Trapping Mechanism of Supersensitization of J-Aggregates. - J. Photogr. Sci., 1973, v.21, N2, p.53-70.

19. Penner J.L., Gilman P.B. Spectral Shifts and Physical Layering of Sensitizing Dye Combinations in Silver Halide Emulsions. - Photogr. Sci. Eng., 1976, v.20, N3, p.97-106.

20. Riester 0. Supersensitizers. - Photogr. Sci. Eng., 1969, v.13, N1, p.13-17.

21. Brünner R., Oberth A.E., Pick G., Sheibe G. Zum Mechanismus der Übersensibilisierung photographischer Emulsionen - ein Beitrag zum Problem der Energieübertragung. - Z. Electrochem., 1958, B.62, H.2, S.132-145.

22. Brünner R., Graf A., Sheibe G. Über einige Klassen von neuartigen Übersensibilisatoren fur Pseudoisocyanine. -Z. wiss. Photogr. Photophys. Photochem., 1959, B.53, H.3, S.214-221.

23. A.S. Davydov. Theory of solid state. M.: Science, 1976, 558 pages.

24. E.B. Lifshits, S.V. Natanson, I.I. Influence of color indiffusible component on process of optical sensitization of silver halide emulsions. - Progress nauchn. fotogr., 1962. t.8, page 44-54.

25. S.V. Natanson. About possibility of increase in effect of optical sensitization. - Zhurn. nauchn, and prikl. fotogr. and kinematogr., 1963. t.8, No. 5, page 362-369.

26. S.V. Natanson. On the Possibility of Increase in Effect of Sensitization. - J. Fotogr. Science, 1962. v.10. N 1. p.9-14.

27. S.V. Natanson, E.B. Lifshits. About the main phenomena causing spectral sensitization of silver halide emulsions. - Progress nauchn. fotogr., 1976, t.17, page 23-42.

28. Riester O. Spectral Sensitization by Desensitizers. - Photogr. Scientific Engineer, 1974. v. 18, N 3, p.295-301.

29. Gilman P.B. The Luminescent Properties of 1,1'-diethyl-2,2'-cyanine Alone and Adsorbed to Silver Halides. -Photogr. Sci. Eng., 1967. v.ll. N 4, p.222-232.

30. Gilman P.B. Effects of Aggregation, Temperature and Supersensitization on the Luminescence of 1,1'-diethyl-2.2'-cyanine Adsorbed to Silver Chloride. - Photogr. Sci. Eng., 1968, v.12. N 5, p.230-243.

31. Jones J.E., Gilman P.B. Study of the Mechanism of Supersensitization of l,l'-diethyl-2,2'-cyanine. - Photogr. Sci. Eng., 1973. v.17. N 4, p.367-372.

32. Gilman P.B. A Review of the Electrochemical Boundaries for the Photochemistry of Spectrally Sensitized Silver Halide Emulsions. - Pure Appl. Chem., 1977. v.49. p.357-377.

33. Carroll B.H. The Vogel Centennial: Dye Sensitization, Past and Future. Closing Summary of Conference. - Photogr. Sci. Eng., 1974, v.18. N 4. p.454-456.

34. Collier S.S. Study of the Mechanism of Self-Supersensitization of an Efficient J-Aggregate. - Photogr. Sci. Eng., 1974. v.18. N 4. P.43O-44O.

35. Nelson R.C. A Mechanism for the Supersensitization of Pseudocyanine. - J. Photogr. Sci., 1974, v.22. N1. p.56-59.

36. Tributsch H., Gerischer H. The Use of Semiconductor Electrodes in the Study of Photochemical Reactions. - Ber. Bunsenges. Phys. Chem., 1969, B.73, H.8, S.850-854.

37. Gerischer H., Tributsch H. Electrochemische Untersuchungen zur Spectralen Sensibilisierung von ZnO-Einkristalen. - Ber. Bunsenges. Phys. Chem., 1968. B.72, H.3, S.437-445.

38. Tributsch H., Gerischer H. Electrochemische Untersuchungen über den Mechanismus das Sensibilisierung und Übersensibilisierung an Einkristalen. - Ber. Bunsenges. Phys. Chem.. 1969. B.73, H.3, S.251-260.

39. Tributsch H. Electrochemische Untersuchungen über die Sensibilisierungeigenschaften und das Photochemische Verhalten von Pseudoisocyanine-Farbstoffaggregaten an ZnO-Electroden. - Ber. Bunsenges. Phys. Chem., 1969, B.73, H.6, S.582-590.

40. Watanabe J., Fujishima A., Honda K. Effect of Hydroquinone on the Electrochemical Spectral Sensitization of CdS Single Crystal Electrode. - Ber. Bunsenges. Phys. Chem., 1975. B.79, H.12, S.1213-1217.

41. Fujishima A., Iwase J., Watanabe J., Honda K. Evidence for the Oxidation of Supersensitizers at the CdS-Electrode. J. Amer. Chem. Soc., 1975, v.97, N 14, p.4134-4135.

42. Dietz F. Zum Stand der Theorie der spectralen Supersensibllisierung. Teil 2. – J. Signal AM. 1978, B.6, H.5, S.341-361.

43. Cert.of authorship No. 154474 (USSR). Way of sensitization of silver halide photographic emulsions (A.F. Vompe, G.F. Kurepina, Levkoyev. I.I., N.N. Sveshnikov, A.V. Borin, N.S. Vulfson, A.V. Kazymov, Doncha L.K., G.E. Vasilenko, L.V. Ivanova, N.V. Monich, S.I. Ryskina, N.V. Siletskaya). - Printed in B.I., 1963, No. 9.

44. Cert.of authorship No. 184613 (USSR). Way of increase in photosensitivity of silver halide photographic materials (A.V. Borin, M.V. Mishakova, L.R. Shaymardanova, Ya.A. Levin, N.A. Shvink.).-Printed in B.I., 1966, No. 15.

45. Cert.of authorship No. 142524 (USSR). Way of receiving silver halide infrachromatic layers, sensitized tricarbocyanine dyes (M.A. Akhmedzyanov, V.A. Kukhtin, V.I. Slesareva, A.V. Borin, K.M. Khaykin, K.M. Kirillova).-Printed in B.I., 1961, No. 21.

46. M.A. Akhmedzyanov, Lerner S.A., I.P. Sotnikova, A.S. Fakhrutdinov, S.G. Fatanyants. Research of some arylphosphine as activators of optical sensitization. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1969, t.14, No. 2, page 148-149.

47. Large R.F. The Use of Electrochemical Potential Data in Studies of Spectral Sensitization: Photographic Sensitivity/ Ed. Cox R.J. London-N.Y.: Acad. Press. 1973. p.241-263.

48. B.I. Shapiro. Current state of the theory of spectral sensitization and desensitization of silver halides organic dyes. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1977, t.22, No. 2, page 143-156.

49. V.M. Belous, Zhukov S.A., Orlovskaya N.A., E.F. Klimzo, B.I. Shapiro. To question of the mechanism of supersensitization of photographic materials. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1983, t.28, No. 5, page 370-373.

50. K.V. Chibisov. Nature of photographic sensitivity. M.: Science, 1980, 403 pages.

51. Klein E., Mateec R. Studies of the Effects of the Constant Fields on the Latent Image Formation. - Z. Electrochem., 1959, B.63, H.9, S.833-838.

52. A.L. Kartuzhansky. Elementary photographic processes in electric field. - Physical progress. sciences, 1961, t.73, No. 3, page 471.

53. Haynes J.R ., Shokley W.S. Radiative Recombination of Electrons and Holes in Silicon. Phys.Rev., 1951, v.82, p.935-941.

54. Hamilton J.F., Brady L.E. Enhancement of Formation of Latent Image in Emulsion Grains by Electric Field. -J. Appl. Phys., 1959. v.30, N6, p.1893-1899.

55. Rothstein J.F. Enhancement of Photographic Speed and Sensitivity by Electric Fields. – Photogr. Sci. Eng., 1960, v.4, N1, p.5-11.

56. V.I. Kalashnikova, D.M. Samoylovich, Yu.F. Pevchev, K.G. Finogenov. About influence of electric field on density of blackening of photographic emulsions. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1964, t.9, No. 6, page 464-466.

57. Yu.F. Pevchev, V.I. Kalashnikova, L.P. Konovalova. About the mechanism of influence of pulse electric field on photographic process. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1970, t.15, No. 4, page 250-256.

58. Yu.P. Smirnov, P.V. Meyklyar, A.N. Musina. Influence of pulse electric field on topography of the centers of the latent image of model emulsion microcrystals. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1983, t.28, No. 1, page 50-54.

59. Yu.F. Pevchev, L.P. Konovalova. About influence of pulse electric field on topography of the latent photographic image. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1970, t.15, No. 2, page 145-147.

60. V.I. Kalashnikova, Yu.F. Pevchev, K.G. Finogenov. About influence of electric fields on sensitivity of photographic emulsions. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1967, t.12, No. 1, page 42-45.

61. D.M. Samoylovich, I.V. Ardashev. About the mechanism of influence of pulse electric field on formation of the latent photographic image. - Dokl. Academy of Sciences of the USSR, 1969, t.184, No. 2, page 327-330.

62. A.A. Kolyubin, E.V. Kozhanov. About orientation of the centers of manifestation in microcrystals of the photographic layers exhibited with application of electric field. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1972, t. 17, No. 4, page 250-253.

63. A.A. Kolyubin. About possibility of management of sensitivity of nuclear photographic emulsion by means of electric field. Diss. physical. - mat. sciences, Moscow, 1972, 172 pages.

64. G.B. Gorlin, L.G. Paritsky, A.A. Bagdanavichyus. Features of impact of electric field on sensitivity of photographic emulsion at low temperature. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1972, t.17, No. 4, page 300-301.

65. G.B. Gorlin, L.G. Paritsky, T.V. Puzanova. Conversion of Gershel effect in electric field. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1972, t.17, No. 5, page 387-389.

66. I.V. Ardashev, D.M. Samoylovich. Features of formation of the latent image in crystals of silver halides taking into account role of near-surface layer of charges. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1973, t.18, No. 1, page 28-31.

67. Yu.P. Smirnov. Research of topography of the centers of manifestation and ionic conduction of emulsion crystals. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1973, t.18, No. 4, page 247-251.

68. V.I. Kalashnikova, A.A. Kolyubin, B.D. Lemeshko, Yu.F. Pevchev. Nuclear emulsions with the managed sensitivity. - Izv. Academy of Sciences of the USSR, it is gray. physical., 1973, t.37, No. 7, page 1514-1517.

69. Yu.P. Smirnov. Influence of gelatin on topography of the centers of manifestation and ionic conduction of emulsion microcrystals. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1974, t.19, No. 3, page 224-225.

70. N.N. Korotayev, P.V. Meyklyar. The photo-electric phenomena in photographic layers. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1974, t.19, No. 3, page 204-210.

71. G.B. Gorlin, L.G. Paritsky, S.M. Ryvkin, V.T. Tulanov. Influence of constant electric field on Rotstein's effect. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1976, t.21, No. 1, page 59-61.

72. G.B. Gorlin. Research of action of electric field on forming of the image in silver halides and development of semiconductor photographic system with the managed sensitivity. Autoref. Diss. physical. - mat. sciences, Odessa, 1977, 16 pages.

73. E.A. Galashin. Thermodynamic theory of photographic sensitivity. Diss dokt. chemical sciences, Moscow, 1971, 452 pages.

74. A.E. Kravtsov, Pip V.A., M.V. Reznikov, M.V. Fok. Methods of visualization of images. - Tr. FIAN, 1981, t.129, page 13-65.

75. V.M. Ulanov. Management of sensitivity of photographic materials of electric field. - Zhurn. Nauchn., and prikl. fotogr. and kinematogr., 1986, t.31, No. 2, page 114-122.

76. Pat.37119824 (USA). A Method of Photographic Speed Enhancement by Strong Electric Field (McMaster R.C., Rhoten M.L.), 1973.

77. V.I. Kalashnikova, E.V. Kozhanov. About influence of electric field on sensitivity of microcrystals of plumbic chloride. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1979, t.24, No. 1, page 50-51.

78. G.K. Belyaev, A.D. Kovtun, Yu.M. Makarov, N.A. Nikonov. Change of photosensitivity of photographic layers in electric field. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1979, t.24, No. 4, page 241-245.

79. A.Ya. Didenko, V.I. Kalashnikova, A.V. Krylov. Multiplicational mechanism of management of sensitivity and dynamic memory of photographic emulsion. - Conf. on processes of strengthening in the photographic systems of registration of information. Minsk, 1981, page 106.

80. D.M. Samoylovich, Y.V. Ardashev. Behavior of Space Charge of Crystals Subjected to Electric fields of the Impulse. - Photogr. Scientific Engineer, 1973, v.17, N3, p.351-353.

81. Gushchin of E.M., V.V. Zhukov, A.N. Lebedev, S.V. Som. Increase in sensitivity of film in pulse electric field. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1984, t.29, No. 4, page 285-289.

82. E.V. Kozhanov, Lancers V.M.O of possibility of increase in absolute photosensitivity of photographic emulsion using electric field. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1979, t.24, No. 4, page 292-295.

83. A.L. Kartuzhansky, Lancers V.M. Features of formation of the latent image in the mode of avalanche reproduction of electrons. - In sb.: Chemistry of solid state, Kemerovo, State University, 1981, page 24-34.

84. A.L. Kartuzhansky, Lancers V.M. The effects in photoemulsion microcrystals caused by reproduction of carriers in strong electric fields. - Physical. and tekhn. poluprovodn., 1982, t.16, No. 2, page 337-339.

85. A.Ya. Didenko, B.D. Lemeshko, V.A. Ostrovsky. Research of action of electric field on sensitivity of silver halide photoemulsion when exposure by nanosecond light pulses. – Proc. of the conf. M., 1983, page 87.

86. V.M. Ulanov. Influence of strong electric field on characteristics of photographic materials. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1982, t.27, No. 3, page 223-225.

87. V.I. Tarasov, V.M. Ulanov. About temperature effect on effect of multiplication. - Zhurn. nauchn. and prikl. fotogr. and kinematogr. 1983, t.28, No. 1, page 61-63.

88. A.Ya. Didenko, B.D. Lemeshko, V.A. Ostrovsky. The electroinduced sensitization of silver halide emulsions. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1985, t.30, No. 5, page 376-379.

89. A.Ya. Didenko, B.D. Lemeshko, V.A. Ostrovsky. Action of repeated electric impulses on effect of increase in photosensitivity of photographic emulsions. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1986, t.31, No. 1, page 53-55.

90. Ulanov V.M. Electroabsorption in microcrystals. - Zhurn. tekhn. physics, 1982, t.52, No. 3, page 545-547.

91. Cert.of authorship No. 1200714 (USSR). Way of record of the latent image on silver halide photocarriers, mainly in the conditions of background influence (A.Ya. Didenko, V.A. Lemeshko B.D. Ostrovsky.). - Opubl. in B.I., 1985, No. 48.

92. V.M. Belous, A.Ya. Didenko, Zhukov S.A., B.D. Lemeshko, V.A. Ostrovsky, V.P. Churashov. The electroinduced luminescence of microcrystals of photographic emulsions. – Proc.conf. "Physical processes in photosensitive systems on the basis of silver salts", Kemerovo, 1986, page 28-29.

93. Henish G. Electroluminescence, M.: World, 1964, 455 pages.

94. I.K. Vereshchagin. Electroluminescence of crystals, M.: Science, 1974, 279 pages.

95. Hippel R. Electronic Breakdown of Solid and Liquid Insulators. - J. Appl. Phys., 1938, v.8, N12, p.815-832.

96. Frölich H. Electrical Breakdown in Some Crystals. -Proc. Roy. Soc., 1937, v.A-60, N2, p .230-241.

97. Shockley W. Hot Electrons in Germanium and Ohm's Law. -Bell Syst. Techn. J., 1951, v.30, p.990-999; Shockley W. Problems Related to p-n Junctions in Silicon. - Czechoslov. J. Phys., 1961, v.ll, N 2, p.88-121.

98. V.A. Chuyenkov. To behavior of valent semiconductors of type of germanium in stronger electric field. - Zhurn. tekhn. physics, 1958, t.28, No. 4, page 470-479.

99. L.V. Keldysh. To the theory of ionization by collision in semiconductors. - Zhurn. ex-lane and teor. physics, 1965, t.48, No. 12, page 1692-1707.

100. Wolff P.A. Theory of Electron Multiplication in Silicon and Germanium. - Phys. Rev., 1954, v.95, p.1415-1420.

101. Chynoweth A.G. Ionization by Electrons and Holes in Silicon. - Phys. Rev., 1958, v.109, p.1537-1543.

102. V.A. Chuyenkov. To the theory of ionization by collision in semiconductors. - Physical. TV. bodies, 1967, t.9, No. 1, page 48-58.

103. Photon multiplication in crystals. Works IF AN ESSR, 1976, No. 34.

104. E.R. Ilmas, G.G. Liydya, Ch.B. Lushchik. Photon multiplication in crystals. – Opt.and Spectr., 1965, t.18, No. 4, page 631-635.

105. S.N. Ivanov, E.R. Ilmas, Ch.B. Lushchik, V. Mihailing. In, Photon multiplication in crystals - Phys. Solid State, 1973, t.15, No. 5, page 1574-1578.

106. B.N. Meleshkin, V.V. Mihailing, V.E. Oranovsky, Orekhanov I. P.A Pasternyak, S. Pachesova, A.S. Salamatov, M.V. Fok, A.S. Yarov. Photon multiplication in alkaline and haloid crystals. - Works FIAN of Lebedev, 1975, t.80, page 140-148.

107. V.M. Belous, E.R. Ilmas. About effect of photon multiplication in silver chloride. - Zhurn. prikl. spectroscopy, 1968, t.9, No. 4, page 698-700.

108. V.M. Belous, E.R. Ilmas, N.S. Rooze. Role of reproduction of electronic excitation in luminescence and photographic process in silver halides. - Physical. TV. bodies, 1969, t.11, No. 3, page 606-612.

109. N.S. Rooze. Reproduction of electron-hole couples in photographic emulsion. - Physical. TV. bodies, 1974, t.16, No. 5, page 1557-1559.

110. V.M. Belous, Bard N.G., E.A. Dolbinova, I.L. Kuusmann, Ch.B. Lushchik, N.S. Rooze. Electronic excitation, luminescence and formation of the latent image in silver halides. - Zhurn. Nauchn. and prikl. fotogr. and kinematogr., 1978, t.23, No. 6, page 460-472.

111. A.Ya. Didenko, N.A. Dobrodeyev. Ionization by collision in silver bromide. In sb.: The kinetic phenomena in semiconductors and dielectrics. Energoatomizdat, 1985, page 90-94.

112. A.Ya. Didenko, N.A. Dobrodeyev, M.N. Mamonov. Calculation of coefficient of ionization by collision and function of distribution of electrons in photoemulsion microcrystals. – Proc.conf. "Physical processes in photosensitive systems on the basis of silver salts", Kemerovo, 1986, page 62.

113. V.L. Levshin. Photoluminescence of liquid and solid matters. M.-L.: GITTL, 1951, 456 with,

114. V.M. Belous, Orlovskaya N.A., V.I. Tolstobrov, K.V. Chibisov. Functions of the impurity centers arising at sulphurous sensitization of silver-halide photographic emulsions. Dokl. Academy of Sciences of the USSR, 1977, t.235, No. 6, page 1339-1342.

115. V.M. Belous. Some features of luminescence of silver and haloid crystalline phosphors. Diss. physical. - mat. sciences, Saratov, 1964, 250 pages.

116. Matossi F., Nudelman S. Electroluminescence Excited by Short Field Pulses. - Phys. Rev., 1955, v.99, N4; p.1100-1103.

117. Cert.of authorship No. 1173380 (USSR). Way of photography on the silver halide photocarrier (A.Ya. Didenko, V.A. Lemeshko B.D Ostrovsky.). - Opubl. in B.I., 1985, No. 30, page 194.

118. A.Yu. Akhmerov, V.M. Belous, A.Ya. Didenko, B.D. Lemeshko, V.A. Ostrovsky. The mechanism of the electroinduced luminescence of silver halide photographic materials. - Pre-print of MEPhI, M., 1988, 23 pages.

119. V.M. Belous, N.G. Dyachenko. About influence of infrared light on luminescence of silver chloride. News of Academy of Sciences of the USSR, 1961, T.XXV, No. 4, page 547-548.

120. V.M. Belous, N.G. Dyachenko. About influence of infrared light on luminescence of silver chloride, - Opt.and Spectr., 1961, t.10, No. 5, page 649-652.

121. V.M. Belous. Luminescent and electret properties of sensitive crystalline phosphors and photographic emulsions some photochemically. Diss. physical. - mat. sciences, Odessa, 1970, 398 pages.

122. V. Meydinger. Chemistry of photographic processes. Collection of articles, SILT, 1951, page 9.

123. M.A. Babalov, B.A. Dolgoshein, B Onions. And., F.R. Sosnin, Studying sensitivity of photoemulsions in big electric fields. - Prib. and tekhn. expery., 1962, No. 5, page 178-179.

124. M.Z. Peskov, P.V. Meyklyar. Influence of electric field on photographic properties of emulsion layers. – Zhurn.nauchn. and prikl. fotogr. and kinematogr., 1967, t.12, No. 5, page 352-357.

125. A.B. Akopova, B.A. Babakhanyan, G.M. Garibyan, N.V. Magradze, L.V. Melkumyan. About distribution of the latent image in nuclear emulsions under the influence of pulse electric field. - Dokl. Academy of Sciences of the USSR, 1971, t.200, No. 3, page 617-619.

126. A.Ya. Didenko, B.D. Lemeshko, V.A. Ostrovsky, M.V. Tuzhikov. Influence of duration of the front of high-voltage impulse on the size of effect of change of sensitivity of photographic emulsion. Zh.nauchn. and prikl. fotogr. and kinematogr., 1986, t.31. No. 4, page 291-294.

127. A.Ya. Didenko, B.D. Lemeshko, V.A. Ostrovsky, I.P. Moroz, Temperature effect on the electroinduced vualeobrazovaniye and photosensitivity of photographic emulsion in stronger electric field. – Zh.nauchn. and prikl. fotogr. and kinematogr., 1987, t.32, No. 4 of page 252-255.

128. Cert.of authorship No. 1105854 (USSR). Way of photography on the haloid and silver carrier (A.Ya. Didenko, B.D. Lemeshko, M.V. Tuzhikov, V.A. Ostrovsky.). - Opubl in B.I., 1984, No. 29.

129. E.M. Gushchin, A.N. Lebedev, S.V.Somov. Role of electronic polarization in Rotstein's effect. - Zhurn. tekhn. physical., 1986, t.56, No. 10, page 1973-1979.

130. A.Ya. Didenko, V.A. Ostrovsky, B.D. Lemeshko. Change of sensitivity of photographic materials at influence by high-voltage impulses of voltage. – Zh. nauchn. and prikl. fotogr. and kinematogr., 1987, t.32, No. 2, page 138-141.

131. Vacek V. Electroluminescence of AgCl Crystals Excited by Short Field Pulses. - Phys. Stat. Sol., 1967, v.23, N1, p.105-111.

132. V.M. Belous, V.I. Bugriyenko, V.K. Marinchik. Research of photoelectret condition of photographic emulsions. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1970, t.15, No. 1, page 61-63.

133. V.I. Marinchik V.K. Bugriyenko, V.M. Belous. Thermoelectret condition of photoemulsion layers. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1970, t.15, No. 2, page 151-153.

134. V.I. Mikhaylenko, B.I. Kucherenko. Determination of structure of the difficult spectral contour consisting of symmetric bands. – Opt.and Spectr., 1975, t.37, No. 5, page 115-119.

135. A.Yu. Akhmerov, V.M. Belous, A.Ya. Didenko, B.D. Lemeshko, the Luminescence of silver halides at pulse excitation by electric field and radiation of the laser. – Proc.conf.. "Luminescence of molecules and crystals", Tallinn, 1987, page 110.

136. Kanzaki H., Sakuragi S., Sakamoto H. Luminescence of Paired Iodine Centers.-Sol. St. Comm., 1971, v.9, p.2285.

137. V.M. Belous, K.V. Chibisov. Luminescent researches of chlorsilver photographic emulsions. - Dokl. Academy of Sciences of the USSR, 1969, t.187, No. 3, page 593-596.

138. James T.H. Some Effects of Environment on Latent Image Formation by Light. - Photogr. Sci. Eng., 1970, v.14, N1, p.84-96.

139. Games T.H. Modification of Spectral Sensitization by Alteration in Environment. - Photogr. Sci. Eng., 1974, v.18, N1, p.100-108.

140. Babcock T.A., Michrina B.P., McCue P.A., James T.H. Effect of Moisture on Photographic Sensitivity. -Photogr. Sci. Eng., 1973, v.17, N4. p.373-381.

141. A.L. Kartuzhansky, A.V. Borin, V.O. Ivanov. Processes of aging and storageability of photographic materials. M.: Chemistry, 1976, page 126.

142. A.N. Terenin. Photonics of molecules of dyes and related organic compounds. L.: Science, 1977, 190 pages.

143. A.Yu. Akhmerov, B.M. Belous, B.I. Shapiro. Influence of hydrophobic organic compounds on luminescence of spectrally sensitized microcrystals of AgBr. – Opt.and Spectr., I960, t.48, No. 1, page 178-180.

144. B.I. Shapiro, V.P. Mikhaylov, M.I. Demchuk, A.F. Chernyavsky, Waqar A.G., Mikheyeva of L.I. Investigation of infrachromatic photolayers for spectroscopy in wide interval of times of exposure. - Zhurn. prikl. spectroscopy, 1981, t.35, No. 1, page 79-84.

145. B.I. Shapiro. Oxidation reduction reactions in processes of spectral sensitization. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1981, t.26, No. 3, page 208-220.

146. V.M. Belous. About the mechanism of formation of the latent photographic image in brom- and iodine emulsions. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1967, t.12, No. 4, page 297-299.

147. S.P. Yefimov, V.I. Zakharov, A.L. Kartuzhansky, G.G. Martysh, L.I. Schur. Luminescence and photosensitivity of primitive photographic AgBr-emulsions with full or partial replacement gelatin on polyvinyl alcohol. - Zhurn. nauchn. and prikl. fotogr. and kinematogr., 1978, t.23, No. 5, page 351-357.