The Preparation of Quaternary Ammonium Silver Halide and Its Thermal Decomposition Property

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Abstract

Novel white precipitates A, B, C and D were prepared by adding the aqueous solution of silver nitrate into the aqueous solution of quaternary ammonium halide salt such as cetyltrimethylammonium bromide (CTAB) or cetyltrimethylammonium iodide (CTAI). The element composition and property of the material were characterized by using elemental analyzer, XRD, TG-DTA and IR. It was proved that the precipitates are new materials that are different from the well-known silver halide, which are named as quaternary ammonium silver halide as cetyltrimethylammonium silver bromide and cetyltrimethylammonium silver iodide temporarily. The molecules are A: C₁₉H₄₂NAg₂Br₃; B: C₁₉H₄₂NAgBr₂; C: C₁₉H₄₂NAg₂I₃ and D: C₁₉H₄₂NAgI₂. We presume those quaternary ammonium silver halide are compounds which quaternary ammonium positive ion substitutes part of the silver ion of silver halide molecules.

Introduction

Quaternary ammonium salt is a kind of positive ion surface-active agent. It is used normally as softer and antibiotic of textiles. It can be dissolved into water usually. If the negative ion of the quaternary ammonium salt is halogen, after dissolved into the aqueous solution, the quaternary ammonium positive ion and the halogen negative ion are dissolved. While the aqueous solution of silver nitrate is added into the aqueous solution of the quaternary ammonium salt, a silver halide precipitate is obtained according to the theory of double decomposition reaction, the quaternary ammonium positive ion and the nitrate negative ion are left in the solution, that is:

$$R_4N^+X^- + AgNO_3 \longrightarrow R_4N^+ NO_3^- + AgX \neq$$

Quaternary ammonium salt is a kind of strong acid strong alkali salt. It can't react with base and form quaternary ammonium alkali. If the aqueous solution of the quaternary ammonium salt reacts with AgOH, silver halide and quaternary ammonium alkali will be formed ^[1] as follow:

$$R_4N^+X^- + AgOH \longrightarrow R_4N^+ OH^- + AgX \neq$$

CTAB is one of the quaternary ammonium salts. Its molecular formula is $C_{19}H_{42}NBr$. Its chemical structure is



CTAB can be used as micellar template in the preparation of silver nanoparticle, silver nanorods and nanowires^[2] by chemical reduction of AgNO₃ by NaBH₄ in the presence of trisodium citrate to stabilize the nanoparticles. To prepare nanorods and wires of varying aspect ratio, AgNO₃ was reduced by ascorbic acid in the presence of seed, the micellar template CTAB and NaOH. CTAB is also necessary to produce a high yield of rods.

Long chain quaternary ammonium salt can be used as modifier to change the structure of montmorillonite through cations exchange reaction and to enlarge the interlaminar distance^[3]. This progress is called as organization of montmorillonite^[4]. The reaction is:

 $CH_3(CH_2)_nR_3NX+M-Mont \longrightarrow CH_3(CH_2)_nR_3N-Mont +MX$

(R: —H, —CH₃; X : —Cl, —Br, —I; M: Na⁺, Ca²⁺, Mg²⁺) CTAB is used as modifier and the organized montmorillonite is called CTAB- montmorillonite^[5,6].

CTAI is another quaternary ammonium salts. Its molecular formula is $C_{19}H_{42}NI$. Its chemical structure is



The important characteristic of silver halide is light sensitive. It is the base of modern silver halide photography materials and photographic industry. Silver bromide and silver iodide are powders or crystal with yellow color.

However, in our work, after the reaction of quaternary ammonium salt such as CTAB or CTAI with AgNO₃, the precipitates are not silver halide, but novel materials. First, the precipitates are white color, not like the color of silver halide; Secondly, after washed with water and dried, the precipitates contains C, H, N, Ag and halogen by analyzing its element composition.

The new materials can be used as high effective antibiotics of textiles. The products are very especially suitable to be antibiotics for textile.

Detailed Descriptions

Preparation of quaternary ammonium silver halide. Precipitate A: 19.7mL of 0.9268M aqueous solution of silver nitrate was added into 100mL of 0.2744M aqueous solution of CTAB under stirring at 25 $^{\circ}$ C, a white precipitate different from silver bromide was obtained. The precipitate was separated from the solution and was thoroughly washed with water and dried, then a white powder was obtained.

Precipitate B: 14.8mL of 0.9268M aqueous solution of silver nitrate was added into 100mL of 0.2744M aqueous solution of CTAB under stirring at 25 $^{\circ}$ C, a white precipitate different from silver bromide was obtained. The precipitate was separated from the solution and was thoroughly washed with water and dried, then a white powder was obtained.

Precipitate C: 10.0mL of 0.9268M aqueous solution of silver nitrate was added into 100mL of 0.1390M aqueous solution of CTAI under stirring at 70 $^{\circ}$ C, a white precipitate different from silver iodide was obtained. The precipitate was separated from the solution and was thoroughly washed with water and dried, then a white powder was obtained.

Precipitate D: 7.50mL of 0.9268M aqueous solution of silver nitrate was added into 100mL of 0.1390M aqueous solution of CTAI under stirring at 70 $^{\circ}$ C, a white precipitate different from silver iodide was obtained. The precipitate was separated from the solution and was thoroughly washed with water and dried, then a white powder was obtained.

Materials Characterization. Elemental analyses were carried out by means of Heraeus CHN-O-RAPID (Germany) Analyzer. SEM investigation of precipitate B was carried out using SEM-5400 (JEOL) microscope. XRD were determined using a Rigaku D/Max 2500 diffractometer acquired with a Cu k (1.5406Å) radiation at 40kv and 200mA for a 2 angle of from 5° to 50°. Infrared spectra were measured using a Bruker Vector 22 spectrometer. Pure KBr was used as the background. Thermo Gravimetry (TG)-Differential Thermal Analysis (DTA) was performed on Pyris Diamond (PerkinElmer) and conducted in nitrogen atmosphere (100ml / min) between 25°C and 600°C. Sample of 10 mg was put in a Pt cell and heated at a constant rate of 10 °C / min.

Results

SEM Photo of precipitate B. It is shown in Figure 1.



Figure 1 SEM photo of precipitate B

Element Composition of quaternary ammonium silver halide. By testing, the element composition of the precipitate A to D, the result dates are list in table 1 with the calculated value from the molecules. The molecules are determined by the element composition and the chemical reactant equations (1) and (2):

 $1.5R_4NX + AgNO_3 \longrightarrow 0.5R_4NAg_2X_3 + R_4NNO_3 \quad (1)$

$$2R_4NX + A_gNO_3 \longrightarrow R_4NA_gX_2 + R_4NNO_3$$
(2)

Table 1. The deviations between the calculating volume and the measurements of the element composition of quaternary ammonium silver halide

The element composition of precipitate A to D (%)								
	С	Н	Ν	Ag	Х	Total		
А	31.098	5.795	2.058	29.320	31.729	100		
Ac	30.839	5.721	1.893	29.154	32.394	100		
В	41.611	7.430	2.849	19.625	28.485	100		
Bc	41.325	7.666	2.536	19.533	28.939	100		
С	26.016	4.862	1.725	23.520	43.877	100		
Cc	25.903	4.805	1.590	24.488	43.214	100		
D	31.461	5.759	2.317	16.272	44.191	100		
Dc	35.314	6.551	2.167	16.692	39.275	100		

In table 1, A, B, C, D are the measured values of precipitates A to D; Ac, Bc, Cc, Dc are the calculated values of precipitates A to D from the molecular A: $C_{19}H_{42}NAg_2Br_3$; B: $C_{19}H_{42}NAgBr_2$; C: $C_{19}H_{42}NAg_2I_3$; D: $C_{19}H_{42}NAgI_2$.

Light-stability of quaternary ammonium silver halide. The precipitate solutions and the white powders have high light-stability, no color change can be observed under light irradiating. It is well known that the color of silver bromide or silver iodide is changed easily from yellow to brown color under light irradiating.

IR Result of quaternary ammonium silver halide and CTAB, CTAI. The IR spectra of the quaternary ammonium silver halide and CTAB, CTAI are presented in figure 2 and figure 3.



Figure 2 IR spectra of quaternary ammonium silver bromide and CTAB



Figure 3 IR spectra of quaternary ammonium silver iodide and CTAI

XRD Patterns of quaternary ammonium silver halide and CTAB, CTAI. XRD of quaternary ammonium silver halide and CTAB, CTAI are presented in figure 4 and figure 5.



Figure 4 The XRD of quaternary ammonium silver bromide and CTAB



Figure 5 The XRD of quaternary ammonium silver iodide and CTAI

TG-DTA curves of CTAB and cetyltrimethylammonium silver bromide. TG-DTA curves (a) pure CTAB and cetyltrimethylammonium silver bromide, respectively under the protection by nitrogen is presented in figure6.



Figure 6 TG-DTA curves (*a*) *pure CTAB and cetyltrimethylammonium silver bromide.*

Discussion

According to the above results, we think that quaternary ammonium silver halide is not a mixture but a compound. First, it is appropriate for a compound and too high for a mixture even as the precipitate contains quaternary ammonium halide and silver halide which nearly 50%(mole percent), second, the shell of the mixture can be washed off by water during the washing process; thirdly, the color of the mixture will be changed under light irradiation even it has a transparent shell.

In addition, quaternary ammonium silver halide is not a complex compound. First, silver ion can become more

complex compounds with ammonia and amine^[7], but no report shows that it can become complex compounds with quaternary ammonium positive ion; Secondly, all the complex compounds are dissolvable in the solvent such as water easily^[7], for example, excessive Br⁻ can react with silver ion and dissolve the silver bromide precipitate; Thirdly, one silver ion of the silver complex compound needs two or more complex ion (mono-valence)/molecular, but the quaternary ammonium positive ion of this compound is less or equal than silver ion.

Quaternary ammonium silver halide is more hard dissolving in water than silver bromide at the temperature below 60°C. If the stirring is not full, yellow precipitate will appear during the preparation process; even this yellow precipitate disappears during a short time. In addition, even if potassium iodide is added into the aqueous solution of quaternary ammonium silver bromide, no silver iodide (yellow precipitate) present.

On the above grounds, we presume that quaternary ammonium silver halide is a compound which cetyltrimethylammonium positive ion substitutes part of the silver ion of silver bromide molecular. If the substituted silver ion is located in (111) of the silver halide crystal, the rate of substitution is 0.5, the precipitate is R_4NAgX_2 , if the substituted silver ion is located in (100) of the silver halide crystal, the precipitate is R₄NAg₂X₃ or $(R_4N)_2AgX_3$, the rate of substitution is 1/3 or 2/3. We think that the rate must be less than 1/2. If the rate is large than 1/2, the compound is more like CTAX and not like silver halide, quaternary ammonium silver halide may be dissolving easily, so the precipitate is only R₄NAg₂X₃, not (R₄N)₂AgX₃. Of course, more experiments are required to support this thought. In addition, the crystal compound of quaternary ammonium silver halide has a layer structure inferring from the SEM photo and the XRD result.

Usually, quaternary ammonium silver halide can't be dissolved in water, methanol, ethanol, glycol, glycerine, isopropyl alcohol, butanol, chloroform, benzol, xylene, dimethylketone, and ethyl acetate at room temperature. In our work, if the substitutive groups and halogen of quaternary ammonium salt are different, the similar precipitates can be prepared when they react with silver nitrate.

The TG–DTA curve of pure CTAB has two endothermic peaks at 110°C and 276°C in Fig.6 (a). The corresponding TG curve, however, exhibits only one weight loss process of ca. 100% around 276°C, reflecting the thermal decomposition of CTAB molecules. The plot for cetyltrimethylammonium silver bromide displays four endothermic peaks at 93°C, 114°C, 308°C and 426°C in Fig.6 (b). It is noted that the peaks for CTAB at 110°C and for cetyltrimethylammonium silver bromide at 93°C are not accompanied by any weight loss. These changes correspond to the melting of hydrocarbon chains in free CTAB and cetyltrimethylammonium silver bromide. For the peak at 114 °C in Fig.6 (b), it is believed to be desorption of moisture absorbed on the surface of cetyltrimethylammonium silver bromide. In the range from 200 °C to 400 °C, which is centered at 308 °C, can be assigned be the decomposition to of cetyltrimethylammonium silver bromide and formed the crystal structure of silver bromide in the process. Corresponding weight loss is ca. 57.5%. In addition, the DTA endothermic peak at 426 °C in Fig.6(b) is not accompanied by any weight loss on TG curve. This change corresponds to the melting of silver bromide.

Furthermore, we have done the experiments of antibiotic according to the Japanese standard JIS L1902. Quaternary ammonium silver bromide is very especially suitable to be an antibiotic for textile and it is very especially suitable for natural fiber.

Conclusion

We have prepared a white precipitate named as quaternary ammonium silver halide by adding the aqueous solution of silver nitrate into the aqueous solution of quaternary ammonium halide. Quaternary ammonium silver bromide is different from quaternary ammonium halide and silver halide.

Quaternary ammonium silver halide is not a mixture; it is a compound containing CTAX and silver halide compositions, and not a complex compound.

Quaternary ammonium silver halide is harder dissolving in water than silver bromide at the temperature less then $60^{\circ}C$.

The thermal decomposition property of quaternary ammonium silver bromide is different from cetyltrimethylammonium bromide and AgBr obviously.

We presume that quaternary ammonium silver halide is a compound which cetyltrimethylammonium positive ion substitutes part of the silver ion of silver halide molecular. The crystal compound of quaternary ammonium silver halide has a layer structure.

If the substitutive groups and halogen of quaternary ammonium salt are different, the similar materials can be prepared.

The discovery of quaternary ammonium silver halide not only supplies new type materials with special characteristics but also will broaden our knowledge about silver halide. There is many questions to be needed the chemistries to explain: Why is quaternary ammonium silver halide different from silver halide in color? Why is quaternary ammonium silver halide harder dissolving than silver bromide? Why has quaternary ammonium silver halide high light-stability, no change can be observed on the color after long time light irradiating? What is the crystal structure of quaternary ammonium silver halide? What is the thermal decomposition property of quaternary ammonium silver halide? What's the difference of molecular structure between quaternary ammonium silver halide and silver halide, CTAX? Is there any special function of quaternary ammonium silver halide? And so on. These works are waiting for the exploration.

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Ultra-fast Reduction Process in AgBr Nanocrystals Under External Influence

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Abstract

The induction period of chemical reduction process in emulsions based on AgBr nanocrystals could be substantially shorter than 1 ms [1]. The time of electrolytic reduction for both exposed and non-exposed AgBr microcrystals did not exceed 1.5 ms [2]. As was noted earlier [3] the speed of electron injection into the grain during electrolytic reduction could reach 10^{11} - $3x10^{12}$ electrons per second. This does not correspond to the traditional mechanisms of nucleation of silver particles including ionic stage of the process. The speed of electron injection according to these schemes does not exceed 10^6 electrons per second.

In this paper we continue to develop the percolation model of silver cluster aggregation in AgBr nanocrystals under powerful light beams. The mechanism of silver cluster appearance in the systems of this kind is based on the principle of structural correspondence of AgBr cation sub-lattice to the lattice of metallic silver [4]. According to this correspondence the motion of silver ions is not necessary for silver cluster formation in AgBr microcrystals. The percolation mechanism does not contradict the high speed of electron absorption by AgBr nanocrystals under external influence. The obtained results can be useful for development of photochromic materials.

The Problem

Particles in the nanometer-size range in recent years have received an enormous amount of attention, as their properties are substantially different from those of the bulk material. One of examples of such system is AgBr nanocrystals. They are used as dispersion in transparent polymeric films. Such materials are promising for displays, optical filters and other optoelectronic devices. One of significant problems intensely investigated are the main features of fast formation of these particles under external influence. Up to this moment there exists a lot of experimental data which indicate the possibility of high speed electron injection into the grain based on both inorganic and organic salts of silver. These phenomena can not be described by the use of traditional schemes of silver nucleation containing ionic steps of the process, since the experimentally observed speeds of electron injection into the grain are six orders of magnitude higher than the ones necessary for ionic processes. We can cite the following examples: 1) electrolytic reduction of emulsion grains [3], where fast speed of reduction disagrees with the relatively slow rate of ionic process; 2) laser flash photolysis of a silver bromide nanoparticle dispersion [5, 6], where absorption change equal to 0.8 was obtained in 5 ns and the transient absorptions was assigned to formation of Ag⁰ clusters; 3) chemical reduction of ultra-fine grained AgBr crystals under the action of flash [1, 7], where minimum injection rate of electrons was equal to 10^8 - 10^9 electrons per second and presence of compact silver specks was observed.

In this paper we will continue consideration of the most important aspects of ultra-fast reduction of AgBr nanocrystals, placed into redox solution, under the action of intensive actinic flash. The preliminary results were published in [8].

Main features of silver cluster formation under the action of intensive flash

As follows from the thermodynamic consideration by Moisar, Granzer et al. [9], the main events leading to silver phase formation take place in the electronic subsystem of AgBr.

Structure correspondence principle of AgBr cation sublattice to the lattice of metallic silver by Dankov [4] states that AgBr space lattice can be transformed to the lattice of metallic silver without change of silver atom positions, {100} cube planes in $[Ag^+ - Br^-]$ lattice corresponding to {110} octahedron planes and {001} cube planes in [Ag] lattice. In accordance with this principle the distances between silver atoms in {001} cube planes do not change after bromine atom withdrawal from the AgBr lattice and silver ion (e.g, from the interstial) taking its place. This atom "leaves the electron to the possession not only of one of his neighbors, but to the possession of complex of them" [9].

Statistic thermodynamic analysis for nanocrystals [10] showed that all usually considered electron traps in these crystals were two shallow to trap photoelectrons that made conventional step by step process questionable as well.

From the other hand, electronic mechanism of silver cluster formation in AgBr (and AgI) was proposed in [11], where the first principles molecular orbital calculations on an interstitial Ag for the microcrystals of AgBr and AgI were carried using the discrete variational (DV)- X_{α} method. In the presence of interstitial Ag (Ag_i), an interstitial level appears within the band gap. The interstitial orbital in AgBr is found to be delocalized and, as a result, the interstitial level reinforces the Ag_i - Ag covalent bond. The Ag_i - Ag covalent bond in AgBr is stronger than any other covalent bond around Ag_i. This bond is essential for the agglomeration of Ag atoms.

We suggest to use the same approach for the case of Ag_i located near the surface of AgBr nanocrystal (let us underline the well-known fact that the role of the surface in nanocrystals is much more essential than in microcrystals). The computational procedure is not finished yet, but preliminary results show, that the situation is quite similar to Ag_i in the volume of microcrystal. So, the building block of the percolation mechanism [12] consists of Ag_i and 4 neighboring Ag^+ ions.

We propose that after excitation of electron by photon it is possessed by this complex. If the time of ionic step is sufficiently small ($\leq 10^{-6}$ c), so this step essential for the overall process,

Mitchell's trap [10] situated on the surface is a good candidate for this complex and we have Ag₂ cluster as a result. If ionic step is long and ionic step should not be taken into account another agglomerations are possible, for example the proposed complex. Absorption of each photon leads to creation of these complexes. Their positions on the surface are random, the higher the concentration of photons the higher is the concentration of these complexes. The neighboring complexes (we consider the complexes as neighbors if they have the common edge) create bigger complexes filling the surface of microcrystal. This picture corresponds to the percolation scheme proposed in [12]. For some critical concentration of photons (and correspondingly electrons and complexes) the percolation threshold is exceeded and we have a metallic grid covering the whole surface of the microcrystal. The concrete form of this percolation greed will be random and depends on the position of bromine ions that absorb the photons (and therefore on the positions of the created complexes).

Conclusion

We elucidate the electronic mechanism of silver cluster appearance in AgBr nanocrystals. Our consideration is based on the principle of structural correspondence of AgBr cation sub-lattice to the lattice of metallic silver. According to our approach the motion of silver ions is not necessary for silver cluster formation in AgBr microcrystals. Therefore, percolation mechanism under investigation is in agreement with the high speed of electron absorption by AgBr nanocrystals under external influence.

The results obtained give the possibility to analyze the processes taking place in such system and can be useful for development of different sensors, optical filters, thin layer indicators, photonic devices, the materials with variable light transmission in the ultraviolet and visible spectrum intervals.

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Bacteriorhodopsin Absorbed on Silver Halide Nanocrystals

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Abstract

It is well known that light absorption triggers transformation chain of bacteriophodopsin (bR) [1]. Protein goes through intermediate states which usually are denoted in alphabetic order: K,L,M,N and O. These transformations and electric potential changes correlated with them occur in ten picoseconds. The value of electric potential photoinduced by bR molecules on single membrane is 100 mV. The energy is stored electrostatically in accordance with the mechanisms of molecular condenser appearing under flash action. To obtain high photopotentials (up to 10-12 V) it is necessary to use packs of oriented membranes or bR molecules.

We propose to use the molecules of bacteriorhodopsin adsorbed on silver halide crystals to overcome the threshold of spontaneous nucleation from small silver specks to colloidal ones in very short time interval. The kinetic curves of the chemical development process of ultra fine-grained emulsion were demonstrated in [2]. Appearing of colloidal dispersion of silver particles leads to effective scattering and absorption of actinic light. Such systems can be considered in the framework of integrated chemical systems [3].

Introduction

The theoretical analysis of optical trigger based on molecules of bacteriorhodopsin adsorbed on ultra fine-grained silver halide crystals was carried out. The principal possibility for overcoming the electric potential threshold of non-selective reduction of the ultra fine-grained silver halide crystals during actinic flash action was noted [4]. We have shown experimentally [5] that lifetime of free electric carriers for optoacoustic effect in photoemulsions is in nanosecond time scale. It means that latent image centers (LICs) in silver halide crystals are formed in nanoseconds under certain conditions. In order to transform LICs to development centers in a very short time interval we propose to use the molecules of bacteriorhodopsin adsorbed on silver halide crystals. The main electric peculiarity of organized assemblies of bacteriorhodopsin molecules is tremendous change of their electric potential up to 10-12 V during actinic flash action due to spectral transformations. Taking into account this effect the process of non-selective reduction of small silver clusters (LIC) to big silver particles of colloidal dispersion can be effectively switched on in 10 picoseconds after flash action. It was demonstrated that optical density for the system based on ultra fine-grained crystals exceeds value D=1 in 5 milliseconds under experimental conditions [2]. Rising of electrical potential of bacteriorhodopsin molecules can significantly decrease time of appearing of silver colloidal particles in this system. Such systems could be useful as effective photochromic inorganic materials or photochromic sensors [6].

Results and discussion

Organic polymer systems doped with strong nonlinear optical functional molecules have emerged as a new class of electrooptical materials and have received considerable interest for integrated optical device applications. Macroscopic optical properties of these materials, such as photovoltaic effects, electrooptical effects, harmonic generation, and photorefractive effects, are always associated with microscopic polarizabilities through the molecular orientational distribution. Many measurement techniques have been employed to determine the orientational time response rates of molecules and the contribution of molecular orientation to nonlinear optical susceptibility. Bacteriorhodopsin is the light transducing protein found in nature in a crystalline biological membrane. It is known to exhibit strong photovoltaic behavior and large optical nonlinearities. However, there is significant difficulty in forming uniform, transparent, stable, and robust bR films. Recently it was shown [8] that bR films with photovoltaic and electro-optical properties can be achieved by embedding bR molecules in a poly(vinyl alcohol) (PVA) polymer matrix. In these films, the PVA polymer host is doped with a small concentration Of bR. When an AC rectangular or sinusoidal external electric field is applied across the resulting material, a modulated photocurrent is observed when a laser beam illuminates the sample. We propose to modify this material adding ultra finegrained silver halide crystals (20 nm in diameter) into polymer film. In this case molecules of bR could be used as electro-optical trigger generating the process of silver nucleation in silver halide matrix under powerful flash action.

Let us consider in details properties of small silver particles in framework of so called new phase nucleation and growth theory. Thermodynamic approach is viable in the case of systems consisting of a large number of atoms, molecules or ions, e.g. in the case of macroscopic systems. A photographic layer is the macroscopic system, since it consists of a great number of AgHal microcrystals. We treat the system of these microcrystals as a statistical ensemble.

The peculiarities in electrolytic reduction of AgBr grains were observed in [9-11]. The amount of electrons necessary for reduction of AgBr crystals corresponds completely to the number of silver ions in the grain. A grain of 0,01 mm³ volume was reduced by 2,1 * 10^{10} electrons injected from external source, these amount of electrons corresponds to the number of initial silver ions [9]. The time of full reduction of grains of 1,4 µm average diameter and a potential of 1 V of platinum electrode equals 10 ms, which corresponds to an injection rate of $3*10^{12}$ electrons per second [10]. But such extraordinary high rate (10^{11} –

 $3*10^{12}$ electrons per second [10]. But such extraordinary high rate (10 – $3*10^{12}$ electrons per second) of electrolytic reduction of AgBr grains precludes the possibility of a staged development of the process according to conventional schemes [12].

For further refinement of the general picture experiments on electrolytic reduction for whole emulsion layers and not for separate grains in comparison with chemical reduction (ultra fast chemical developing) of the same layers may be of considerable interest. In the electrolytic reduction process there is no direct injection of electrons from the cathode into the emulsion grains. The role of a "reduction atmosphere" forming in the vicinity of the cathode is specially stressed in [11]. The nature of this "atmosphere" as well as the nature of electron carriers has not been clarified. However, even if there is no direct electron transfer, all the dependences and conclusions remain completely valid from point of view of thermodynamics. The reduction process may develop according to two different schemes:

- 1. direct injection
 - e (cathode) + Ag_{Ag}^{+} (emulsion grain) $\Rightarrow Ag_{Ag}^{x}$
- 2. with the aid of a donor-acceptor impurity

e (cathode) + A \Rightarrow A⁻ A⁻ (donor) + Ag_{Ag}⁺ \Rightarrow A + Ag_{Ag}^x

The results of thermodynamic analysis of these two cases coincide. For electrolytic reduction Faraday's law is valid, i.g. reduction of each silver grain requires the transition of one electron from the cathode. This condition holds sufficiently strictly at small cathode displacement rates, i.e. conditions close to equilibrium

Values of electric potentials of emulsion grains

State of the system	<i>Relative values of electric potential</i> [mV]			
1. Equilibrium system Ag _∞ AgBr/Ag ⁺	0			
2. Specks of full latent image	-20: -170			
3. Specks of latent subimage	-170 : -270			
4. Increase in light sensitivity	-100 : -300			
5. Onset of spontaneous fogging	-300 : -400			
6. Disappearance of discrepancy betwee	een			
kinetics of unexposed grains and the	at of			
grains with latent image specks	-800			
7. Oxidation processes (desensitization	n, >0			
oxidation of latent image and visible	e			

blackening) Conclusions

It can be easily seen that the photo-induced jump of bR molecule potential is much higher than all the values in the table. So, the value of this jump is sufficient to initiate the ultra-fast silver nucleation process. Taking into account very small time of this jump the process of non-selective reduction of small silver clusters (LICs) to big silver particles of colloidal dispersion can be effectively switched on in 10 picoseconds after flash action. Such electro-optical trigger could be useful to create new photonic devices.

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The Effect of the Size of AgBr (111) and AgBrI (111) Microcrystals on Silver Center Formation

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Abstract

The monocrystal and amorphous solid surface attract attention of many scientists in view of the fundamental significant research of the processes in science of materials. The problem of active surface is of great interest, as many processes such as crystal growth, absorption, new phase formation, catalysis and so on proceed with surface participation and are determined with the degree of the surface activity. The monocrystal surface is investigated by numerous methods. This enables get extended information about the correlation of processes proceeded on it with the physicochemical properties of materials. However, the electron-microscope method for comparative research of the AgBr microcrystals surface structure at all synthesis stages and photoemulsion optimization has not been applied earlier. Generally it is connected with a difficult preparation of microcrystals. This paper shows the results of the surface research of AgBr microcrystals with different size and composition by the electron-microscope method and demonstrates the formation properties of silver centers on the microcrystal surface by various decoration methods.

Introduction

One of the major defects of crystal lattice structure is a surface of a crystal. Break of crystal lattice results in alteration in coordination sphere of ions on the bond length surface. Frenkel [1] showed possibility of space-charge region in ionic crystals. Kliver [2] deduced that because of the difference between internodal silver ion energy and holes in AgBr crystals electric field appeared near the surface. It directed from a near-surface layer to the surface. That means the near-surface layer is enriched with internodal silver ions. Poppel and Blakely [3] developed this idea and offered to consider the surface as a source of additional charged defects. The reason of double electric layer in AgHal microcrystal can be redistribution of defects between and the surface. Because of higher mobility.

The value and mark of the surface charge depend on adsorption of different photoactive admixtures, such as gelatin, Ag⁺ ions, Br⁻ ions etc on the surface. Depending on the surface charge mark photoelectrons generated in the microcrystal will drift either to the surface of to the depth of the crystal. The state of the surface depends also on different admixtures in microcrystals. For instance, iodine admixture results in conductivity growth. Nowadays the causes of this event are vague. However, it is revealed that getting highly sensitive photomaterials requires decrease of ionic conductivity of microcrystals. So, to understand processes occurring on the microcrystal surface under microcrystal photolysis it is necessary to have information about the state of microcrystal surface at all stages of preparation and optimization of photomaterials.

One of the methods to investigate the surface is the decoration method (the surface is precipitated with different metals in vacuum). The display of active zones (sensitivity centers) on the AgBr microcrystal surface was applied and developed by H. Haefke, V. Plarikanova and K. Starbova [4, 5, and 6]. Those scientists used two decoration methods – common (precipitation of different metals in vacuum) and photographic (exposure with a light and post-development). They showed that the use of the decoration methods enables study the processes of chemical sensitizing of photolysis and post-processing of photomaterials under development.

V. Cheremisina [7] carried out experiments with the help of the listed decoration methods of emulsive AgBr microcrystals of various habitus. She indicated that the number of silver particles on the surface of AgBr microcrystals depends on microcrystal cut. The number of particles is more on the microcrystal (111) surface than on the microcrystal (100) surface and doesn't depend on the decoration method. She considered defects on the surface of kink site type connected with Br⁻ as concentration centers.

This paper shows the results of the effect of AgBr (111) microcrystal size and iodine admixtures on the surface state and peculiar features of silver cluster formation. The obtained data are discussed with help of ionic conductivity data and sociometric data.

Experimental Technique

To solve experimental problems we synthesized AgBr emulsive microcrystals of octahedral habitus of 0.4 and 0.7 µm by the controlled double jet crystallization method. The obtained emulsion was processed in KI solution (converting) under iodide concentration 1 mol. % during 15 min. under 52°C. To make the electron-microscope analysis we released microcrystals from gelatine by the way of enzyme split in protease aqueous solution under pH = 10. The residue obtained under hydrolyzation was centrifuged, deposited on the object-plate and dried. We divided the samples into some groups and examined: 1) the surface of AgBr and AgBrI microcrystals of different size; 2) distribution of concentration centers by the delayed development method; 3) distribution of concentration centers by two methods (photographic decoration and silver decoration by precipitation in vacuum). Further we dissolved AgBrI microcrystals in 15 % sodium thiosulfate solution. We caught and deposited the washed out replica on the object - net. We viewed the replicas with the help of the electron microscope.

The Obtained Results and Discussion

The investigation of the surface state of AgBr microcrystals of octahedral cut in emulsive medium under pBr = 3 and temperature $t = 52^{\circ}C$ enabled us conclude the following:

- We could observe the change in AgBr (111) microcrystal cut. In that case we could observe round peaks and edges of AgBr microcrystals of 0.7 μm. AgBr microcrystals of 0.4 μm were modified in form (they acquired a cubic form). At the same time crystal cubes were peakless.
- 2. AgBr (111) microcrystals of 0.4 and 0.7 μ m didn't change their cut form after 1 mol. % KI emulsion (pBr = 3).

We can explain the obtained results. We made synthesis of microcrystals of octahedral cut under pBr = 1.6. After the microcrystals had been washed and redispersed the value of pBr increased to up to 3. When pBr = 3, one usually should provide chemical maturation of AgBr microcrystals of any habitus and storage of primitive photoemulsions. It is well known that under pBr = 3, microcrystals of cubic cut are subjected to crystallization, that's why in this case we may expect changes in their cut. All this information is confirmed by our data obtained. We also may deduce that the rate of microcrystal form modification depends on their size and KI admixture concentration other things equal. As pBr increases from 1.3 to 3.0 as supersaturation occurs in the emulsion owing to the difference of chemical potentials $\Delta \mu$ = $\mu(111)$ - $\mu(100)$ for appropriate edges of microcrystals. At the same time the formation of centers of sensitivity (of Ag_n type) can take place under such conditions. Evidently this process is common, i.e. in all cases when pBr changes in the emulsion, Ag_n centers are formed during microcrystal modification. These centers can show themselves as both sensitivity centers and fog centers. Supersaturation in emulsion reaches the definite layer because of some factors: 1) putting solutions into a reactor; 2) different size of the microcrystals; 3) different chemical potential of silver in solution and on the surface of microcrystal faces (111) and (100). Depending on the saturation creation method it can be homogeneous and of local character (it determines by gelatine concentration, temperature, pBr value and mix rate). One can suggest the supersaturation emerging from $\Delta \mu$ (Ag⁺) difference is of local character. As a result recrystallization of microcrystals (111) occurs, they change their form into spherical or cuboctahedronical form. The fact of putting KI into the emulsion may slow recrystallization process (111) and it can be connected with selective adsorption of iodide ions at the definite microcrystal faces and with face completion (111).

The experiments of the peculiarities of silver particle formation on primitive microcrystal (111) surface showed that this process, a number and localization of Ag_n centers after microcrystal development can depend on such factors as developer's composition and concentration, the time of development, a form and size of microcrystals. Therefore when the effect of AgBr and AgBrI sizes on peculiarities of Ag_n^- center formation had been investigated, we could choose the appropriate sample preparation regimes, which were similar to all of them. When using diluted 1:100 developer we could see silvers of spherical form and nearly similar size on the AgBr surface. The distribution of silver particles was not homogeneous on the microcrystal faces. The number of particles per microcrystal increased with rise of microcrystal size. At the same time we could see obvious spread of development centers per microcrystal. If the size of microcrystal decreased, this spread decreased too (Table 1).

When AgBrI microcrystals were developed without taking into consideration their size, we could see the formation of homogenous silver particles on the AgBrI surface. Silver particles started growing near the peaks and edges of the microcrystals. In this case we also could see the distribution of silver particles was not homogeneous on the microcrystal faces. Table 1 shows data about a number of silver particles revealed on AgBr and AgBrI surface of octahedral cut after development. We may conclude from these data that the number of silver particles depends on microcrystal size, i.e. it runs up to 10^{10} particles per microcrystal with the rise of microcrystal size.

 Table 1. The number of Ag particles 10¹⁰ cm⁻² revealed on the surface of AgBr and AgBrl microcrystals of octahedral cut after development

 δ°

 The group of samples

iol. %	Microcrystal size, µm	The group of samples						
lodide concentration, m		Developed microcrystals	Exposed and developed microcrystals	Surface decoration by Ag precipitation in vacuum				
1	0,7	1	2,5	2,7				
1	0,3	0,2	2,2	1,9				
0	0,7	1,4	1,9	-				
0	0,3	0,5	3,3	-				

Crystallization centers revealed under small light levels can be characterized as the most active centers on the microcrystal surface. The bigger microcrystal is the more silver centers are on the microcrystal surface. It is known that the microcrystal development rate depends on the nature of developed centers and reaches maximum more for latent-image centers than fog centers. However, under low light one may assert that all revealed centers have rather high activity to silver concentration process and can be both sensitivity centers and fog centers under appropriate condition. Under high light one may assert that high concentration of electron-hole pairs and low concentration of internodal silver ions result in fall of concentration centers which grow efficiently. It means that it is possible to reveal the deepest shallow traps as in the case of low light. High concentration of electron-hole pairs and sufficiently high ion conductivity will enable to reveal all most active silver concentration zones. In all type of light (high and low) it is necessary to take account of photoelectrons (holes) and internodal silver ions. As a result we may reveal also less active zones. The general number of such centers will characterize the limit number of centers on the surface of microcrystals which are able to form silver particles of any nature. To reveal limit number of concentration centers on the AgBr and AgBrI surface we exposed them with single high-intensive light pulse during 10^{-3} sec. Then the microcrystals were exposed with help of the delayed development method. Here are the peculiarities of silver particle formation on the surface of exposed microcrystals:

- 1. increase of silver particles on the surface of all microcrystals in comparison with preliminary exposure;
- 2. silver particles decorate boundaries and surface of microcrystal faces;
- 3. the number of increased centers is near limit number;
- 4. the shape of increasing silver particles is mainly round;
- Ag_n particles are arranged at some distance from each other without forming links and thin film. It means that growth of silver particles observed by us meets the requirement of free surface energy minimum of Ag_n.

We can see from the data of Table 1 that the number of particles forming on AgBr and AgBrI surface is within 10^{10} cm⁻². When we had precipitated gold on AgBr surface we could see formation of fine-dyspersated gold particles of nearly similar size, which were distributed uniformly on the face surface. However, at the same time gold particles distributed at some distance from microcrystal edges. We might observe formation of particles on AgBrI surface. Those particles distributed uniformly on the surface without setback from microcrystal edges. It should be noted that we could observe formation of almost similar number of gold particles for microcrystals of different size. Development center limit number coincides with the case of decoration with gold under photographic decoration way.



Figure 1. Maximum sensitivity vs. average size of AgBrl (1 mol. %) microcrystals in the mode of spontaneous ripening.

Our aim was also to examine mixed AgBrI (iodide concentration 1 mol. %) microcrystals of 0.7 and 1.37 μ m, obtained by means of cocrystallization. In this case if pBr increased from 1.6 to 3 we did not observe evident cut change. However, the character of particle development on AgBrI surface (after light-striking) at pBr = 1.6 could be compared to that we had

observed during photographic decoration of surface of AgBrI obtained by converting at pBr = 3. If pBr increased to 3 the character of particle development on AgBrI surface could be compared to that we had observed during decoration of surface of AgBrI obtained by converting at pBr = 3. It may be connected with the fact when iodide cocrystallizes with AgBr, the number of crystal defects increased in comparison with converting method. When middle size of AgBrI was increased, the number of developed particles increased too. This result is well matched with sensitometric investigations, i.e. if to increase middle size of AgBrI, emulsion speed increased too. Optimal size of AgBrI was 1.37 μ m in this case (Figure 1).

The Main Results and Conclusions

- 1. When pBr = 3, we can see modification of AgBr (111) surface and cut in emulsion. At the same time the smaller microcrystal size is, the faster modification occurs.
- 2. When one molar KI is put into emulsion, modification of AgBr (111) surface slows.
- 3. The number of concentration centers, which are more active, is greater on the surface of AgBr (111) and AgBrI (111) microcrystals of $0.7 \mu m$ than of $0.4 \mu m$.
- Limit concentration of silver particle centers is 10¹⁰-10¹¹cm⁻². It coincides with surface state density connected with Br_s ions on surface defects of kink site and does not depend on microcrystal size. It enables to examine Br_s defects as silver concentration centers.

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Integrated Chemical System Approach to Silver Halide Emulsions

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Abstract

We investigate the materials and techniques available for construction of integrated chemical system (ICS) [1] based on silver halides. A typical ICS consists of a number of components, each serving a different function. A list of these, with some examples, includes the following: supports, catalysts, charge carriers and mediators, linking and coupling agents, photosensitive centers, electro-active centers, chemically sensitive centers. Electrochemical indicator devices as well as electrolytic sensitization [2] and redox properties of photographic emulsion are analyzed. Photographic film on the base of ultra-fine grained AgBr crystals is another example of ICS. This ICS could be useful to protect eyes under powerful flash action. In some ICSs, electrons or ions are transferred between species or across membranes. This charge transfer can be facilitated by appropriate mediators. Model photosensitizers could be such mediators. Structural-dynamics characteristic of exited states of photosensitizers and perspectives of its application in modern ICSs are given.

Introduction

Large complex systems (macrosystems) generally have hierarchical structures, i.e. they are assembled from smaller units that are, in turn, built from smaller and simpler ones, finally down to units with atomic and molecular dimensions.

Level of the "integrated chemical system" (ICS), [1] (the term is coined in connection with systems designed to carry out photoelectrochemical reactions) \equiv nanostructure, microsystem, mesosystem level. At this level we are concerned with structures that contain a number of different components and several phases. The operation at this level frequently requires consideration of interfacial processes and mechanisms of mass and charge transport.

Definition [1]. *ICSs* are heterogeneous, multiphase systems involving several different components designed and arranged for specific functions or to carry out specific reactions or processes. Often the different components will be organized

structurally and will show synergistic effects. Usually it is the interaction of the components of the ICS that determines its properties.

Examples.

1) Biology. Different macromolecules and other components assembled in a unique way to form a particular structure or carry out a certain process, e.g. several different enzymes contained in a membrane in contact with a liquid phase with dissolved reactants.

2) Electronics. Transistors and integrated circuits, that require dopants, junctions, metal leads, contacts, and encapsulants.

AgBr nanocrystals in the transparent polymeric matrix placed into redox solution with high negative potential are another example of ICS.

Results and discussion

We developed electrochemical indicator device containing two supports coated by transparent conducting layers with electrolyte situated between them. This electrolyte contains Ag salt, coordination agent, solvent and oxidizer. Under voltage between electrodes equal to 2 - 5 V a process of electrochemical precipitation of metallic silver on the cathode as well as a formation of black film on the anode takes place. As a result of these processes optical density D = 2 and more appears. The indicator has an important advantage: it has a possibility to restore initial light transmission by several ways. This can be done by polarity change, short circuit of electrodes and switching of power supply [3].

It is well-known that reduction of silver is the main feature of the photographic process. The possibility of its electric control is one of the interesting problems that needs investigation. Let us note in this context that besides traditional ways of reduction sensitization (chemical sensitization, hydrogen hyper sensitization etc.) it is possible to use electrolytic treatment to increase the speed of photographic layers. This means that electrons are "injected" into the grains of fine-grain emulsion before exposure. As a rule the transfer of electrons is not direct and the reduction process may develop with the aid of a donor-acceptor impurity. During this process the absolute value of electric potential of emulsion grains is not essential, the main features of reduction are determined by relative values of electric potentials vs. equilibrium system Ag_{es}/AgBr/Ag⁺. Increase of light sensitivity occurs when these values lie in the interval between -100 and -300 mV [2].

Let us discuss now the way electrolytic sensitization can be realized. A light sensitive layer is placed directly on the anode, the cathode moving on the surface of this layer. This treatment takes place before exposure. In this case, in contrast to earlier approaches, emulsion laver serves as both near cathode and near anode space. Therefore, there exists a possibility not only to essentially decrease a length which ions pass and concentrate the substances, but to govern an electrochemical process of sensitization and development as well. The main feature of this method of sensitization is an injection of electrons into emulsion by the cathode and development of secondary processes possessing strong reducing character. The mechanism of reduction process is very complicated and still unknown in details. Hydrogen, appearing in active atomic state in the electrolytic process, plays probably the most decisive role in sensitization. A sort of reducing atmosphere is formed near cathode, this fact explaining the effect of electrolytic reduction of grains. So, this sensitization is a kind of reducing one.

Let us consider an example of electrolytic sensitization. Photographic paper was placed into electrolyte containing 0.1 M solution of KNO_3 . Then it was placed on the anode and under voltage switched on, the process of electrolytic sensitization was carried on. The cathode moved on the surface under 10 - 20 V voltage and the linear current density was up to 0.1 A/cm. A cathode velocity was equal to 1 cm/s. After electrolytic sensitization photographic paper was exposed, reduced and

sensitometric investigation was carried out. An effect of up to 10 times increase of photographic speed was obtained.

Electrolytic sensitization gives a possibility to reach the limit values of photographic speed and to control electrically the photographic process.

Model photosensitizers are another example of typical ICS constituent. Such systems have been under intensive investigation last years. The electrogenerated chemiluminescence processes of the Ru(bpy)_3^{2+} / tripropylamine system at glassy carbon, platinum, and gold electrodes were observed [4]. Solid-state organic light-emitting diodes based on tris(2,2'-bipyridine)ruthenium(II) complexes were studied as well [5]. In this case the maximum of emission spectrum of a single layer was at 660 nm under 3.1 V and - 114° C.

Similar low temperature emission spectra have been obtained for the same type photosensityzers in the 1.8 - 77 K temperature interval. Moreover, we determined structural-dynamic characteristics for complexes of metals with different electronic structure: transition metals (d-elements), non-transition metals with closed d-shell and lanthanides (f-elements) by low temperature phosphorescence and ODMR spectroscopy. 2,2'bipyridine and 1,10-phenontraline were used as ligands. Further investigations can contain another types of triplet states of coordination compounds including states of inter ligand, metal ligand and inter valence charge transfer.

From our point of view, these compounds could be used to construct solid-state organic light emission diodes.

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Complex Pd (II) Compounds as Chemical Sensitizers

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Abstract

The conditions for chemical sensitization of isometric AgBr grains in the presence of palladium ions were determined. The complex ions $[PdX_4]^{2^-}$ (where $X = C\Gamma$, Br^- , SCN, $SO_3^{2^-}$) were used as a sensitizer. It was established that the process of secondary dissociation of $[PdX_4]^{2^-}$ preceded the sensitization process itself. It was fond out that the electrolyte solution with the same ligand could be used for controlling the secondary dissociation process.

The chemical sensitization was shown to be most effective when using the $K_2[PdCl_4]$ complex as a sensitizer.

Introduction

Conventional methods of chemical sensitization of AgHal grains do not always provide for the required photographic characteristics. Selective localization of impurity centers on certain crystal sites is preferable when carrying out chemical sensitization. All the stages of the photoprocess can be affected by including catalytically active elements, e.g. palladium, into the composition of the latent image centers (LIC). Introduction of complex compounds, such as $[PdX_4]^{2-}$ (X = Br⁻, Cl⁻, NO²⁻, SO³⁻, SCN⁻) into AgHal grains is possible both at the stage of their synthesis, and chemical sensitization.

The aim the present paper is to determine the conditions for chemical sensitization enabling the inclusion of the palladium ions in the latent image centers (LIC) structure of isometric AgBr grains and the determination photographic properties of emulsion layers including these grains.

Experiment

At the first stage a photographic emulsion containing AgBr grains {100} with the average equivalent diameter $\Box_{\tau} = 0.5$ mcm and coefficient of variation $C_v = 10 - 15$ % was prepared. Then $[PdX_4]^{2-}$ ions (from 10^{-5} up to 10^{-3} mole/mole Ag) were added into the emulsion after the basic sensitizers (Na₂S₂O₃ and HAuCl₄) during sulfur-plus-gold sensitization. The volume of the added complex solution was equal to 0,1 ml, the time of sensitization was 60 min.

Result and Discussion

The sensitometric characteristics of the resulting layers with various ligandes are submitted in Table 1.

Photographic speed increase is observed when introducing complex compounds with the concentrations - 10^{-5} - 10^{-4} mole Pd/mole Ag - for all of them except for the complex with chloride ligands.

The greatest photographic speed increase is observed when using the complex with SCN⁻ ligands, however, fog optical density, thereby, considerably increases ($D_0 = 0.7$ and 0.4 for the concentrations 10^{-4} and 10^{-5} mole Pd/mole Ag, accordingly). Probably, in this case SCN⁻ ions liberated from the complex as a result of its secondary dissociation act as sensitizers. Desensitization in the case of introducing the complex ion with Br⁻ and Cl⁻ ligands is most likely to be caused by the liberation of an additional amount

of halide ions capable of acting as desensitizers [1]. Hence, if the processes of secondary dissociation of complex ions are excluded or limited in number, it is possible to use palladium complex compounds as chemical sensitizers.

characteristics of emulsion layers								
Chemical s	Sensitometric							
add	characteristics							
Complex	Complex Concentration mole/mole Ag		S _{0,85}	D _{max}	D ₀			
	_	2,8	11	3,5	0,04			
	10 ⁻³	2,1	10	3,7	0,04			
K ₂ [PdCl ₄]	10 ⁻⁴	2	7	2,8	0,02			
	10 ⁻⁵	1,5	4	2,5	0,03			
	10 ⁻³	1,5	9	3,5	0,03			
K_2PdBr_4	10 ⁻⁴	2,3	15	3,6	0,04			
	10 ⁻⁵	3	13	3,8	0,01			
	10 ⁻³	3	12	4,2	1,02			
	10 ⁻⁴	4	15	3,8	0,70			
K ₂ [Pd(SCN) ₄]	10 ⁻⁵	4	18	3,3	0,40			
	10 ⁻³	1,6	9	3,39	0,01			
	10 ⁻⁴	5	23	4,46	0,01			
	10 ⁻⁵	1,3	7	3,4	0,05			

 Table 1. Influence of various ligands on the sensitometric

 characteristics of emulsion layers

The $[PdX_4]^{2^2}$ complex ions are known to easily undergo secondary dissociation in water solution resulting in ion charge reduction [2]. To control the degree of secondary dissociation of complex ions is possible by adding the electrolyte containing ligand-ions into the solution. Therefore, to the complex compound solution used during chemical sensitization, the electrolyte with ligand-ions (the background electrolyte) was added. The results of the influence of the background electrolyte on sensitometric characteristics of emulsion layers are submitted in Table 2 as the values of optimum photosensitivity and maximum optical density.

For a complex compound with chloride-ligands photographic speed increase is observed at concentrations of the background electrolyte > 0,1 M. As stability of the complex to secondary dissociation is low, it can be assumed that at concentrations <0,1 M secondary dissociation does proceed. It can also be assumed that the impulse for a catalytic effect of Pd(II) ions in this compound is the process of replacement of chlorideligands by bromide-ligands proceeding on the surface of AgHal grains which increases the activity of incorporating the Pd(II) ions into the sensitivity center (SC).

The optimum concentration of the background electrolyte is 0,01 - 0,1 M for Br⁻ ligands. Greater concentrations result in desensitization, probably, because of the excess of Br⁻ ions and their negative influence on chemical sensitization.

Table 2. Influence of the concentration of the background	
electrolyte on sensitometric characteristics of emulsion laye	ers

Chemical sensitization additives		K ₂ PdCl ₄ + KCl		K ₂ PdBr ₄ + KBr		K₂[Pd(SCN)₄] + KSCN		Na ₆ [Pd(SO ₃)₄] + Na₂SO ₃	
Concentration of the complex mole/mole Ag	Concentration of background electrolyte, M	S _{0,85}	D _{max}	S _{0,85}	D _{max}	S _{0,85}	D _{max}	S _{0,85}	D _{max}
	-	10	3,7	9	3,5	12	4,2	6	2,7
10 ⁻³	0,01	9	3,6	14	4,8	14	4,3	9	3,2
10	0,1	12	4,0	15	4,1	10	4,5	8	3,2
	1	18	4,4	15	4,0	9	4,8	6	2,8
	-	7	2,8	15	3,6	15	3,8	13	3,6
10 ⁻⁴	0,01	9	4,5	20	3,8	12	4,0	15	3,7
10	0,1	17	4,6	18	3,6	22	5,0	14	3,5
	1	25	4,5	7	3,5	15	3,5	12	3,9
10 ⁻⁵	-	4	2,5	13	3,8	18	3,3	7	3,4
	0,01	17	3,5	15	3,9	17	3,7	10	3,3
	0,1	12	3,4	16	4,2	15	3,7	12	3,5
	1	7	3,0	10	4,0	20	3,9	11	3,5

Based on the experimental data it can be stated that it is most expedient to use palladium complex ions with Cl⁻ ligands during chemical sensitization and the complex ion solution must be added in the presence of the KCl background electrolyte whose concentration > 1 M.

The compound with SCN⁻ ligands, when changing the concentration of the background electrolyte, reduces photographic speed due to minimum optical density increase, while some photographic speed increase is probably caused by increase in the amount of SCN⁻ introduced into the system, which is known as a sensitizer for grains. In this connection a number of experiments consisting in the introduction of an equivalent amount of SCN⁻ ions into the emulsion during sensitization have been carried out. The results of the experiments are submitted in Table 3 as optimum sensitometric characteristics.

Analysis of sensitometric characteristics of the samples allows us to state that palladium complex ions with SCN⁻ ligands can act as sensitizers for AgBr emulsions.

Thus, it can be assumed that CS is complicated by secondary dissociation of $[PdX_4]^{2-}$, resulting in the reduction of the charge of the complex ion. To control the degree of secondary dissociation of complex ions is possible by adding the electrolyte containing ligand ions into the solution. It is shown that it is most expedient to use the complex compound K₂[PdCl₄] during CS which must be introduced in the presence of the KCl background electrolyte whose concentration > 1 M.

Table 3. Sensitometric characteristics of samples containing
AgBr grains sensitized by K ₂ [Pd(SCN ₄)] with various
concentrations of the background electrolyte and equivalent
amount of KSCN.

Chemical sen	Sensitometric				
auuitive	35		Chara	ciensii	5
	KSCN,				
$R_2[FU(3CN)_4],$	mole / mole	S _{0,2}	S _{0,85}	D _{max}	D ₀
mole/ mole Ag	Ag				
-	-	2,8	11	3,5	0,04
	-	4	18	3,3	0,03
10 ⁻⁵	5 10 ⁻⁶	4	17	3,7	0,03
	5 10 ⁻⁵	3	15	3,7	0,02
	5 10 ⁻⁴	4,5	20	3,9	0,03
	5·10 ⁻⁶	2	10	3,5	0,02
-	5 10 ⁻⁵	1,5	12	2	0,02
	5 10 ⁻⁴	1,5	10	1,8	0,02

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