On Average Gradient of Negative Photographic Materials.

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Abstract

The best transmission of image tone in the black-and-white print is obtained while the negative is developed up to the average gradient value of $\overline{g}_{neg} = 0{,}85$. *When this value is* $\overline{g}_{neg} = 0{,}62$ *the values of gradients of tone reproduction curve are* $g_{lin} = 0{,}96$, *and* $g_{tot} = 0{,}85$ *leading to reduction of contrast and loss of details of the image in shadows and lights. When* $\overline{g}_{neg} = 0{,}95$ *, the increasing of print contrast and losing of details in shadows of the image are observed.*

Introduction

The nature of reproduction of the brightness of the object being shot in the final photographic image during the negative and positive photo process is estimated by the Goldberg's graphic scheme of tone reproduction. It is known that the dispersion of light caused by camera lens, aperture, shutter, camera backs and emulsive layer in the process of film exposure having the object contrast K=100, leads to decrease of image contrast up to K=33 and promotes the decreasing of optical densities in shadows of the image. Characteristic curve of photo material having S-shape form, the losses of image details in shadows and lights in object with large intervals of brightness are observed.

While in cinematography the Rule of Goldberg ($\overline{g}_{neg}\overline{g}_{pos}$ = 1,0) is widely used for positive films with the interval of exposures of 1:1000, in photography printing from negative on photographic paper the interval of exposure used is no more than 1:50, that corresponds to the interval of densities Δ D=1,7, that is photopaper is not able to reproduce completely the given interval of illumination of the object (the maximum optical density of the photography paper is 1,95-2,0), that results in the distortion of operation factors of tone-reproduction.

In photography for the correct reproduction of image tones of real object and conditions of shooting according to Levenberg T.M., the equation of Goldberg is $\overline{g}_{neg}\overline{g}_{pos}$ = 1,6 - 1,8. In compliance with this, it is better for the white-and-black negative printing to use the special contrast photographic paper having $\overline{g}_{pos} = 2{,}6$ ($\overline{g}_{neg}\overline{g}_{pos}$ = 0,62 x 2,6 = 1,6). At the same time very little interval of the exposure of this photography paper (l_g^{pos} =0,6) leads to losses of details in lights and shadows.

To get photocopies of good quality (more thorough development of details in lights and shadows) it is necessary for the interval of densities of the negative $\Delta D_{neg} = D_{\max} - D_{\min}$ and the interval of the exposure on the photopaper with the given interval of densities (contrast of negative) to correspond to the useful interval of the exposure of photopaper l_g^{pos}, that is $\Delta D_{neg} = \Delta \lg H_{pos} = l_g^{pos}$. But in this case this correlation will not hold true. Printing on the photographic paper having normal degree of contrast ($\overline{g}_{pos} = 1{,}9$), results in the loss of details of the image as $\overline{g}_{neg}\overline{g}_{pos}$ = 0,62 x 1,9 = 1,17 < 1,6.

The increasing of the average gradient in the process of the development of negative film before 0,85 up to and next printing on the photography normal paper with good contrast ($\overline{g}_{pos}$=1,9 when l_g = 1,3-1,5) lead to less losses of details in lights and shadows (in terms of can tone reproduction) or could exclude them entirely as in this case $\overline{g}_{neg}\overline{g}_{pos}$ = 0,85 x 1,9 = 1,6 that is the Rule of Goldberg's met. The further increasing of the degree of negative film development up to $\overline{g}_{neg} = 0{,}95$ to the high contrast of the photocopy and loss of image details in shadows of the object.

The best transmission of half-tones of the image is observed with the gradient of straight-line (g_{lin}) portion of curve of tone reproduction is $g_{lin} = 1{,}2$ and the total gradient (g_{tot}) of the curve approaching $g_{tot} = 1{,}0$. According to Fig.l these conditions are met when developing a white-and-black film with the value of average gradient as high as $\overline{g}_{neg} = 0{,}85$.

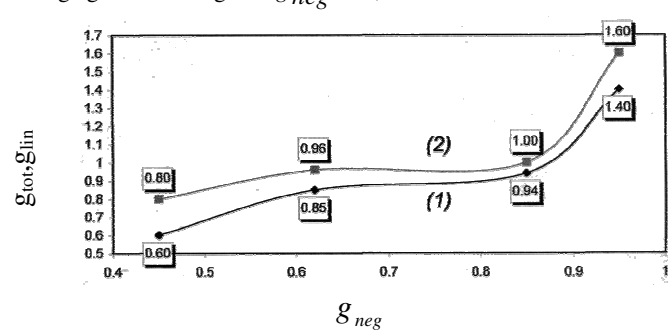

Figure 1. *The influence of average gradient of the negative film «Luckypan 100» on the value of the total gradient (1) and the gradient of straight-line (2) portion of the curve of tone-reproduction. Photo camera «Yashica» lens aperture 1:11*

When the average gradient of negative photo material is $\overline{g}_{neg} = 0{,}62$, (recommended by all-Union State Standard (GOST 10691.2-84)), the values of gradients of the curve of the tone

reproduction are $g_{lin} = 0{,}96$, and $g_{tot} = 0{,}85$ that leads to the decreasing of contrast and loss of image details in shadows and lights. When white-and-black film is developed $\overline{g}_{neg} = 0{,}95$ the increasing of contrast and loss of details in shadows of the image are observed an.

Thus our research on the white-and-black film «Luckypan 100» and other films mean that the best transmission of tones on the photocopy is observed when the photographic film is developed before the value of the average gradient $\overline{g}_{neg} = 0{,}85$ (Figure 2) but 0,62 is recommended by all-Union State Standard and the firm "Lucky".

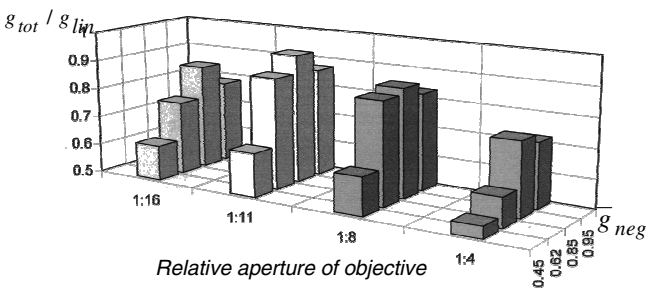

***Figure 2**. The influence of the lens aperture of the photo camera «Yashica» on the ratio of the average gradient to the gradient of straight-line portion of the curve of tone-reproduction.*

Date given in the article confirm that the white-and-black negative film has to be developed up to $\overline{g}_{neg} = 0{,}85$. This is evidenced by the latest recommendations of Kodak suggesting that professionals should develop new negative films «Kodak Tri-X PRO Film» and «Kodak Plus-X PRO Film» to develop up to $\overline{g}_{neg} = 0{,}80$. The same point of view about this issue was advanced by Dr. V.V.Andrejanov in the beginning of the 90-s of the last century.

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Author Biography

Red'ko Anatoly Vladimirovitch - honoured scientist of the Russian Federation (2002), Doctor of Engineering (1982), Professor (1983) is a well-known scientist and teacher, bright representative of St.-Petersburg school of photography science, leading expert in the field of photography science and applied photography. During his long scientific and pedagogical activity Prof. Red'ko wrote 11 monographers and manuals. Prof. Red'ko is the author of 20 patents for inventions and more than 227 scientific works published in the leading Russian and foreign photographic magazines.

Recrystallization of AgBr Particles in The Presence of Complex Ions

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Abstract

The process of ripening of AgBr low-size particles obtained under various conditions in the presence of $[Ag_nBr_m]^{-(m-n)}$ complex ions was investigated. The amount of twin AgBr crystals during recrystallization under these conditions was found out to increase.

The formation of AgBr small particles took place during destruction of complex ions $[Ag_nBr_m]^{-(m-n)}$. It was shown that these AgBr particles observed with the electronic microscopy technique were disk shaped. The AgBr particles aggregated and formed perfect spatial structures in the presence of abundant bromide ions. As a result of secondary aggregation, growth and recrystallization processes, spatial structures were transformed into crystals. The physical configuration of resulting crystals corresponded to etching structures for AgBr tabular crystals.

Introduction

The problem of the influence of complex ions $[Ag_nBr_m]^{-(m-n)}$ on the formation of tabular microcrystal (C) was discussed at large earlier [1, 2, 3]. However much remains unclear so far. It is common knowledge that tabular crystals nuclei are formed in the excess of bromide ions. The present authors assume [4] that Ostwald ripening (OR) of tabular C (with average equivalent diameter ~ 1 mcm) at pBr~0,75-0,5 results in their pronounced transformation into large tabular crystals (with average equivalent diameter ~ 10 mcm). These two processes, important for the formation and growth of tabular C, occur in the presence of complex ions $[Ag_nBr_m]^{-(m-n)}$. However, they cannot be explained by the effect of complex ions or by changing the solubility of silver halide. That is why we continued to investigate the influence of complex ions [AgnBrm]-(m-n) on the formation of tabular AgB crystals due to recrystallization of fine C synthesized at different pBr values. We have simulated and examined the processes occurring in emulsions during the formation and destruction of silver complex ions to find out the mechanism enabling the influence of complex ions $[Ag_nBr_m]^{-(m-n)}$ on crystallization of AgBr tabular C.

Experiments and Results

The influence of the solution containing silver complex ions $[Ag_nBr_m]^{-(m-n)}$ on OR of fine emulsions

Two fine emulsions were synthesized at different pBr values. Emulsion 1 was synthesized by a standard technique at pBr = 3,4 when C with cubic faces are formed. Emulsion 2 was synthesized at pBr = 1,6 when C with octahedral faces are formed. Then the two emulsions were subjected to OR at pBr = 0,75.

It is known that OR of fine C formed at different pBr values results in the formation of tabular crystals of different sizes because the amount of nuclei of tabular crystals depends on pBr values [5]. According to [5], the less is the amount of nuclei, the more is the size of tabular crystals. Larger tabular crystals are formed by means of recrystallization of fine C synthesized at greater p r values.

The pBr values in emulsions were adjusted by adding 2M KBr solution rich in silver complex ions. The use of this solution makes the recrystallization process smooth without the dissolution of a part or C sites in the excess of the Br- ions.

Electronic microphotographs of crystals (Emulsions 1 and 2) formed by OR are submitted In Fig. 1.

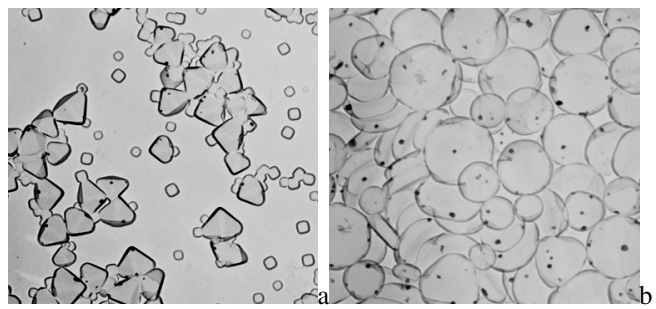


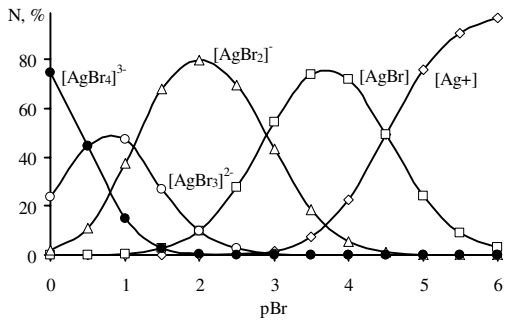
Figure 1. *The electronic microphotographs of coal replica of AgBr crystals formed during OR of emulsions: a- 1 (pBr = 3, 4); b- 2 (pBr = 1,6) (x 16000).*

It is seen that OR of Emulsion 1 (pBr = 3,4) in the presence of silver complex ions does not result in tabular crystals, but promotes the formation of twin C. OR of Emulsion 1 under ordinary conditions results in large tabular crystals. Tabular AgBr crystals can be formed in Emulsion 2 both under ordinary conditions of OR and in the presence of complex ions. The resulting tabular crystals are uniform as to their thickness and their habit.

These results show that the presence of complex ions affects the growth of AgBr crystals.

Preparation and examination of stability of the solution containing $[AgBr_m]^{-(m-1)}$ complex ions.

Since Ag+ ions are able of forming soluble complex compounds with halide-ions, solubility of AgHal deposit can be significantly increased by adding Hal- ions. Total dissolution of AgHal can occur in the presence of a sufficient amount of the complexing agent (Hal-). Relative concentrations of complex ions in solution depending on pHal value can be calculated based on standard instability constant values. Graphic dependences of relative concentration of complex [AgBrm]-(m-1) ions from pBr value at T = 25 are submitted in Fig. 2.



The instability constant values

K_{11}	K_{12}	K_{13}	K_{14}
$3{,}2\times10^{-05}$	$4{,}0\times10^{-08}$	$3{,}2\times10^{-09}$	$1{,}0\times10^{-09}$

Figure. 2. *Relative concentration of complex $[AgBr_m]^{-(m-1)}$ ions vs. pBr value at T = 25°C*

KBr solution rich in silver complex ions used in our experiment was prepared in the following way:

$KBr_{excess} + AgNO_3 \quad KNO_3 + AgBr\downarrow$

$[AgBr_2]^-$

$[AgBr_3]^{2-}$

$[AgBr_4]^{3-}$

The 0,005M $AgNO_3$ solution was added slowly to 50 ml of the 2M KBr solution by small portions (0,04 ml) and agitated at T = 25^0C. When introducing $AgNO_3$ the AgBr phase precipitated, then the AgBr precipitate was dissolved in the excess of KBr to form complex ions, thereby, the solution became transparent. During the process of saturation of the solution by complex ions the rate of dissolution slowed down. For the experiments we used an absolutely transparent r solution rich in silver complex ions. Proceeding from calculated dependences it is $[AgBr_4]^{-3}$ and $[AgBr_3]^{-2}$ complexes in solution that prevail in our experiments.

The resulting solution rich in silver complex ions $[AgBr_4]^{-3}$, $[AgBr_3]^{-2}$ was investigated as to its stability, i.e., the ability of the solution to remain transparent when affected by reagents solutions. Distilled water, the 2 KBr solution and the 0,005M $AgNO_3$ solution were used as reagents. The results are summarized in Table.

Table

Time of storing the solution rich in complex ions, (hour)	reagent		
	H_2O	2M solution KBr	0,005M solution $AgNO_3$
0	AgBr↓	AgBr↓	AgBr↓
24	AgBr↓	-	AgBr↓

The stability of a fresh solution of silver complex ions appeared to be less, since AgBr precipitate is formed when affected by any of the reagents. The solution stored within 24 hrs can be diluted by the 2M KBr solution without the formation of the AgBr precipitate.

The investigation of model formation of AgBr particles from the solution rich in silver complex ions

AgBr phase formation in the excess of the bromine ions when the KBr solution rich in silver complex ions was diluted by distilled water was observed with an optical microscope. The experiment was carried out in the gelatin-free medium. Individual AgBr particles (the size of particles ~ 0,5-0,8 mcm), formed at the first stage, were disk-shaped and moved under the action of Brownian motion and interacted among themselves with the help of forces of attraction. It is necessary to note that such a behavior of particles is inherent to the substances precipitated in a colloidal form. The interaction of AgBr particles resulted in structures of a regular form. Most of structures were tabular and had three beams. The optical microphotograph of beam structures from gBr particles is submitted in Fig. 3. It is seen that the length of the beams is different and is defined by the amount of aggregated particles.

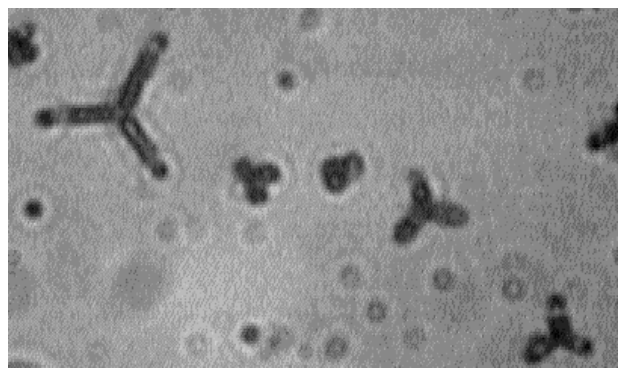


Figure 3. *AgBr beam structures.*

It should be noted that after AgBr particles are formed, the process of aggregate formation proceeds and lasts for a short period of time, and the particles that do not take part in this process, remain individual. Storage of beam structures in solution results in the formation of faces (see Fig. 4).

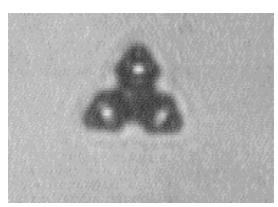


Figure 4. *AgBr crystal formed from the particle having a beam structure.*

To observe changes in beam structures during their growth, additional portions of water and the solution rich in complex ions were added into the system. Newly formed AgBr particles reacted with already available beam structures. A series of microphotographs showing changes of the shape of beam structures is submitted in Fig. 5.

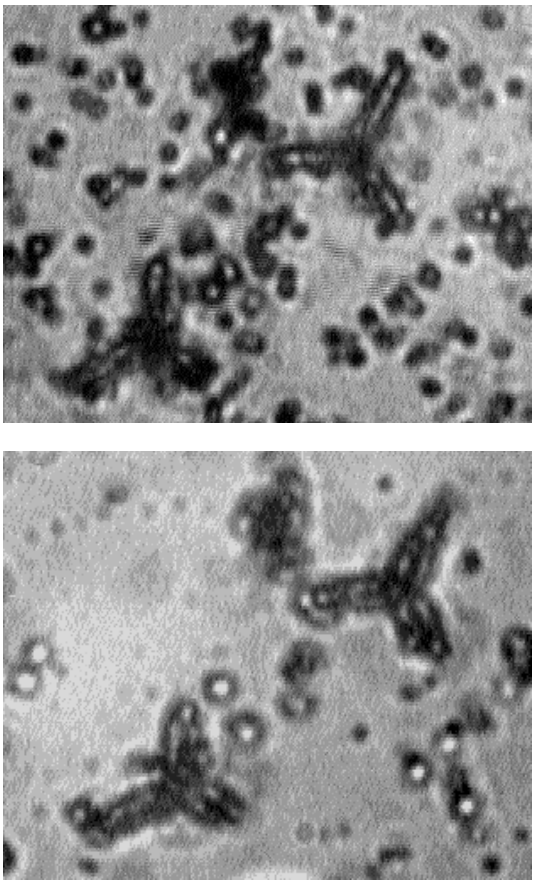


Figure 5. *Transformation of AgBr beam structures as a result of the interaction with AgBr particles.*

From optical microphotographs it is seen that there was no further linear growth of beam structures because of non-aggregation of newly formed gBr particles. With time there was observed a widening of beams in the center of the structure. Further changes in the shape of beam structures could be observed because of the difficulty to preserve a sample. However, examination of etch patterns of the tabular crystals showed that they are geometrically similar to the beam structures formed in our experiments. Etch patterns of the tabular crystals formed by recrystallization method of fine gBr particles under the conditions of prolonged ripening at T = 38^0 , pBr = 0,75 are given in Fig. 6.

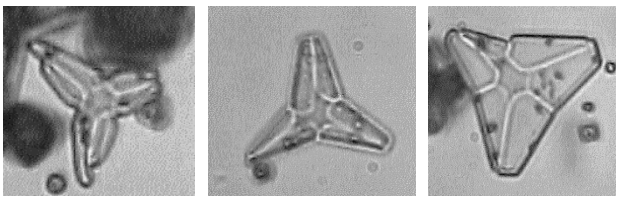


Figure 6. *Etch patterns of tabular AgBr crystals.*

Based on the experimental data, it can be assumed that the process of the transformation of AgBr particles into a beam structure can occur during the synthesis of tabular crystals and result in the appearance and growth of individual large AgBr crystals [4]. It can also be assumed that two consecutive processes take place in the system during the process of adjusting pBr value (up to 0,75). A certain amount of AgBr crystals dissolve in the excess of the bromine ions to form the silver complex ions. There appear local sites of the system with different concentrations of the silver complex ions. Mixing the sites results in liberation of AgBr particles which interact by attraction forces and form beam structures. This process is more effective at weak stirring. Beam structures are used as the frame of a tabular crystal. Then the beams widen and the crystalline mass coats the surface of the structure hiding the borders of blocks grown independently and, thereby, making the surface of a tabular crystal smooth.

A great number of twin MC when using KBr solution for OR of Emulsion 1 can be accounted for by the formation of AgBr particles. However, because of a high concentration of fine C, AgBr particles do not interact but serve as nuclei of isometric twin C. In the case of the recrystallization of Emulsion 2 nuclei of tabular crystals are already present in the system before the solution rich in the silver complex ions is added. Probably, nuclei of tabular crystals and AgBr particles are similar as to their chemical nature since the synthesis of fine C in the excess of the bromine ions should be accompanied by liberation of a certain amount of AgBr particles. That is why, the newly formed particles react with nuclei of tabular crystals resulting in more homogeneous tabular crystals.

Conclusion

It is experimentally shown that the presence of silver complex ions influences the recrystallization process of fine C. Cubic MC recrystallize with the formation of isometric twin C. AgBr particles easily precipitate from the solution rich in the complex ions during the decomposition of these ions. The resulting particles behave as colloidal particles. They interact with the formation of the spatial structures similar to etch patterns of tabular crystals.

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Autor Biography

Larisa V. Sotnikova was born in Kemerovo (Russia) on October 26, 1966. In 1989 graduated from the State University of Kemerovo, Chemistry Faculty. Since 1989 she worked on Inorganic Chemistry and, later, General Physics departments of Kemerovo State University as a Scientific Researcher. Doctor of Science since 1998. Fields of research: silver halide photographic emulsion crystallization and chemical sensitization processes. The author of more than 75 scientific publications.

The Influence of I^- on Photographic Characteristics of Complex Photographic Systems on the Basis of $AgBr/AgBr_xI_y$ Tabular Microcrystals

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Abstract

The process of chemical sensitization of complex photographic systems at various concentrations of sodium thiosulfate and potassium thiocyanate was studied. The emulsion, containing microcrystals of the core-shell *type, can include microcrystals whose structure and halogenide composition are various, e.g.: AgBr tabular microcrystals with the $AgBr_xI_y$ lateral shell, AgBr tabular microcrystals, $AgBr_xI_y$ tabular microcrystals and AgBr tabular microcrystals with the $AgBr_xI_y$ unbroken shell. These silver halide photographic systems can be referred to as* complex photographic systems *because of their multicomponent composition. Based on the photographic characteristics of the complex systems it was established their composition could be determined in an indirect manner. It was shown that AgBr tabular microcrystals prevailed when building-up the $AgBr_{0.96}I_{0.04}$ fine grain emulsions on AgBr tabular microcrystals synthesized at pBr=1.8,* core-shell *microcrystals - at pBr=1,9 and $AgBr_{0.96}I_{0.04}$ tabular microcrystals - at pBr=2.*

Introduce

Now in photographic chemistry much attention is given to the "core - shell" systems, AgBr microcrystals with the AgBrxIy lateral shell in particular. But to synthesize the system which would contain only tabular microcrystals with the lateral shell is technologically difficult. Therefore, this emulsion can actually include the microcrystals differing in the halide composition and structure, e.g. AgBr tabular microcrystals with the AgBrxIy lateral shell, AgBr tabular microcrystals, AgBrxIy tabular microcrystals and AgBr microcrystals with the anisotropic AgBrxIy shell. As the given systems are multicomponent they can be called complex photographic systems on the basis of silver halide. They must be investigated to determine the influence of each component on the characteristics of the photolayers prepared on the basis of these systems. The given paper presents the results of the investigation of chemical sensitization of complex photographic systems formed on the basis of AgBr/AgBrxIy tabular microcrystals.

Results and Discussion

The conditions for the synthesis and chemical sensitization of AgBr tabular microcrystals and AgBr/AgBr0,96I0,04 tabular microcrystals are presented in Table 1. The photographic emulsions formed during the synthesis of tabular microcrystals underwent chemical sensitization. Then, based on the results of sensitometric tests, the kinetic dependences of sensitivity and fog density were plotted.

Table 1. Conditions for the synthesis and chemical sensitization of AgBr tabular microcrystals and AgBr/AgBr0,96I0,04 tabular microcrystals

№	T-microcrystals AgBr		№	T-microcrystals AgBr/AgBr0,96I0,04		
	pBr for the synthesis of AgBr fine grain emulsions	$C(Na_2S_2O_3)$ $*10^{-5}$, mol/molAg		pBr for the synthesis of AgBr fine grain emulsions	$C(Na_2S_2O_3)$ $*10^{-5}$, mol/molAg	C_{KSCN}, ml/gAg
1		1,0	10		2,0	0,4
2	2,0	2,0	11	2,0	0,5	0,6
3		0,5	12		2,0	0
4		1,0	13		2,0	0,4
5	1,9	2,0	14	1,9	0,5	0,6
6		0,5	15		2,0	0
7		1,0	16		2,0	0,4
8	1,8	2,0	17	1,8	0,5	0,6
9		0,5	18		2,0	0

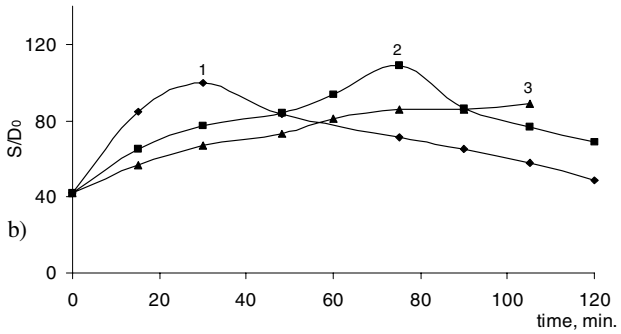
On the basis of these dependences we determined the optimum conditions for chemical sensitization under which the maximum level of sensitivity is observed at the minimum level of fog density. The kinetic dependences of sensitivity are always considered together with the kinetic dependences of fog density. Hence, it is common practice to interpret the results of chemical (or spectral) sensitization by plotting the two types of the above mentioned kinetic dependences. But the same results can be presented as one dependence if Svs.D0 (relative sensitivity) is calculated. The kinetic S/D0 dependences are submitted in Fig. 1 and Fig. 2.

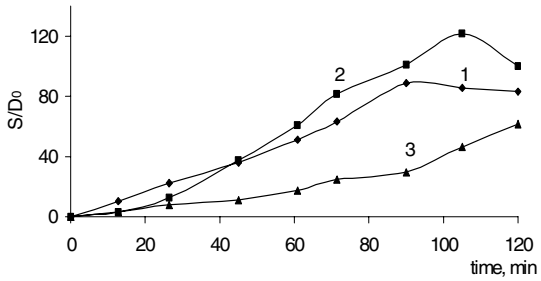
For each determined dependence presented in Fig. 1. and Fig. 2. we defined the maximum S/D0 values. The given values, the conditions for the synthesis and chemical sensitization are submitted in Table 2.

Having defined the maximum S/D0 values for all the emulsions and the conditions for chemical sensitization, the conditions enabling maximum sensitivity at minimum fog density were selected. The histograms (Fig. 3 and Fig. 4) were plotted on the basis of the experimental data. The histogram for AgBr tabular microcrystals, synthesized at various pBr values for the synthesis of AgBr fine grain emulsions is presented in Fig. 3. The histogram for AgBr/AgBr0,96I0,04 tabular microcrystals, synthesized at various pBr values for the synthesis of AgBr fine grain emulsions is presented in Fig. 4.

Table 2. Maximum S/D_0values

Fig.	pBr for the synthesis of AgBr fine grain emulsions	$C(Na_2S_2O_3)*10^{-5}$, mol/molAg	C_{KSCN}, ml/gAg	time, min	S/D_0
1.a.	2,0	1,0	-	30	100
		2,0	-	75	108
		0,5	-	105	89
1.b.	1,9	1,0	-	30	112
		2,0	-	15	62
		0,5	-	75	117
1.c.	1,8	1,0	-	90	89
		2,0	-	105	122
		0,5	-	120	62
2.a.	2,0	0,5	0,6	105	77
		2,0	0,4	90	71
		2,0	0	45	39
2.b.	1,9	0,5	0,6	45	172
		2,0	0,4	60	96
		2,0	0	0	59
2.c. a)	1,8	0,5	0,6	75	79
		2,0	0,4	75	66
		2,0	0	105	98





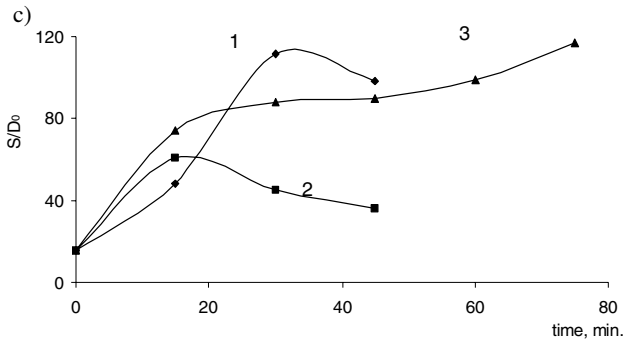


Figure 1. *The kinetic S/D0 dependences for AgBr tabular microcrystals (curve 1 – $C(Na_2S_2O_3)=1*10^{-5}$, curve 2 - $C(Na_2S_2O_3)=2*10^{-5}$, curve 1 – $C(Na_2S_2O_3)=5*10^{-6}$: a) pBr for the synthesis of AgBr fine grain emulsions is equal to 2, b) pBr for the synthesis of AgBr fine grain emulsions is equal to 1.9, c) pBr for the synthesis of AgBr fine grain emulsions is equal to 1.8*

Fig. 3. it is seen that the S/D0 values increase for the emulsion synthesized at pBr=2 with increase in sodium thiosulfate concentration (TS), this is also true for the emulsion synthesized at pBr=1.8. While with increase in TS concentration the maximum S/D0 value for the emulsion synthesized at pBr=1.9 decreases. From this histogram it can also be seen that the S/D0 values first increase, then decrease at the TS concentrations 0.5*10-5 and 1*10-5 when pBr values for the synthesis of AgBr fine grain emulsions increase. While at the TS concentration 2*10-5 S/D0 values first decrease, then increase. Hence, it can be concluded that AgBr tabular microcrystals synthesized at pBr=1.9 are most sensitive to light exposure as they achieve their maximum S/D0 value at the lowest TS concentration. Further increase in TS concentration results in fog optical density increase and S/D0 value decrease. Whereas the emulsions synthesized at pBr=1.8 and 2 do not achieve their maximum within the same period of time because of the low TS concentration. In comparison with the emulsion synthesized at pBr=1.9, their maximum values achieve approximately the same level when the TS concentration is increased four times as much.

From the histogram (Fig. 4.) it is evident that at pBr=2, the S/D0 values, in comparison with silver bromide tabular microcrystals, appreciably decrease due to the appearance of the phase of fine silver bromoiodide grain microcrystals in the system, possessing low sensitivity. At pBr=1.8 the S/D0 values also decrease though not so appreciably due to fog optical density increase compared to silver bromide tabular microcrystals. At pBr=1.9 the S/D0 values become the highest in our experiments, and in comparison with silver bromide microcrystals the maximum is achieved at a higher TS concentration. It can be accounted for by the fact that silver bromoiodide microcrystals need a stronger sensitizing effect to achieve maximum sensitivity.

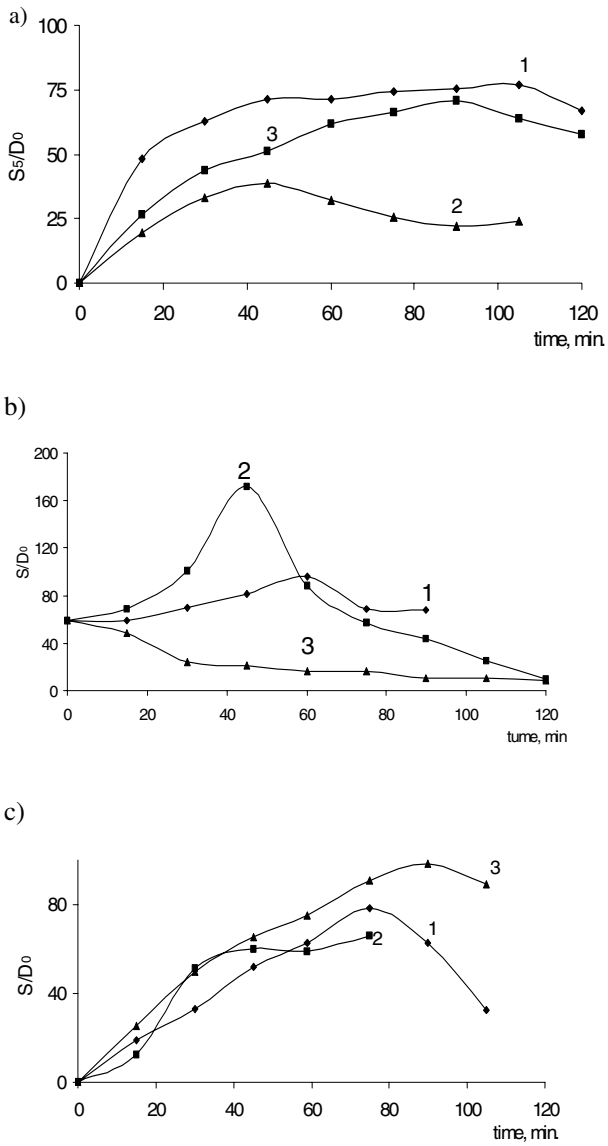


Figure 2. *The kinetic S/D0 dependences for AgBr/AgBr$_{0,96}$I$_{0.04}$ tabular microcrystals (curve 1 – C(Na$_2$S$_2$O$_3$)=5*10^{-6}, C(KSCN)=0.6ml/gAg, curve 2 - C(Na$_2$S$_2$O$_3$)=2*10^{-5}, C(KSCN)=0.4ml/gAg ,curve 3 - C(Na$_2$S$_2$O$_3$)=2*10^{-5}, C(KSCN)=0ml/gAg: a) pBr for the synthesis of AgBr fine grain emulsions is equal to 2, b) pBr for the synthesis of AgBr fine grain emulsions is equal to 1.9, c) pBr for the synthesis of AgBr fine grain emulsions is equal to 1.8*

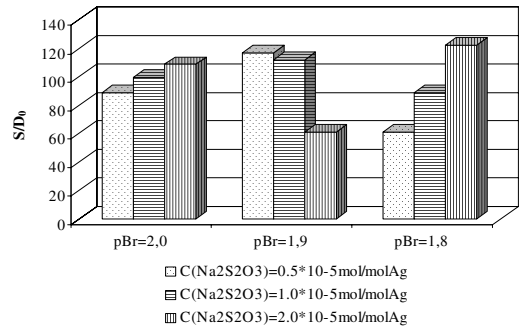


Fig. 3. Optimum S/D0 values for AgBr tabular microcrystals, synthesized at various pBr values for the synthesis of AgBr fine grain emulsions

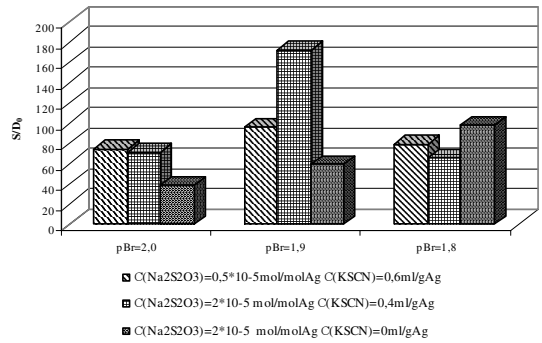


Fig. 4. Optimum S/D0 values for AgBr/AgBr0,96I0,04 tabular microcrystals, synthesized at various pBr values for the synthesis of AgBr fine grain emulsions

Conclusions

It can be concluded that there exists certain dependence between photographic characteristics of complex systems and their structural composition.

The AgBr tabular microcrystals prevail after growing the AgBr0.96I0.04 fine grain emulsion on AgBr tabular microcrystals synthesized at pBr=1.8, the "core - shell" microcrystals – at pBr=1.9, the AgBr/AgBr0.96I0.04 tabular microcrystals - at pBr=2.

Biography

Anton P. Prostenko was born in Blagoveschenck (Russia) on January 20, 1980. In 2001 he graduated from Kemerovo State University, the Chemistry faculty. Now he working in State University of Kemerovo. His field of research is mass crystallization processes of silver halides, the author of 26 scientific publications..

The Research of the Process of AgBrI Microcrystals Crystallization and Sensitization with Varied Iodide Concentration

Nadejda S. Zvidentsova, Natalya V. Gerasimchuk, Irina L. Shvaiko, Tatiana V. Morozova, Lev V. Kolesnikov; Kemerovo State University; Kemerovo, Russia

Abstract

Iodide addition plays an essential role in synthesis of AgBr emulsions actively influencing both on the process of crystallization (nucleus functions, solubility at re-crystallization), and on photographic properties (sensitivity, efficiency of the chemical and spectral sensitization, development mechanism etc.). The process of crystallization of mixed AgBrI (111) microcrystals of the different size (0.4 – 1.5 μm) with varied iodide concentration (0.5 – 2 mol. %) was investigated. The results of iodide amount influence the critical size of nucleus and a supersaturation are presented. Effective and critical growth rates of microcrystals are calculated. Dependence of microcrystals average size on iodide concentration is shown. The process of the spontaneous and chemical sensitization of mixed AgBrI (111) microcrystals is researched. For emulsions received in modes of converting optimum iodide concentration is 1.5 mol. %. It is shown that the efficiency of chemical ripening process of emulsions on the basis of AgBrI microcrystals depends on the iodide concentration, the microcrystals size and the way of chemical ripening.

Introduction

It is known that action of iodide ions in mixed AgBrI emulsions is complex and ambiguous. In literature the role of iodide ions on the formation and properties of emulsion grains and on the chemical and spectral sensitization is widely discussed [1-4]. Summarizing results of the carried out researches, it is possible to draw a conclusion that action of iodide ions is reduced basically to the following:

- the width of the forbidden band of the mixed microcrystals depends on content AgI, which results in the change of spectral distribution of emulsions own sensitivity;
- the increase of the iodide concentration results in the increasing of the interstitial ions concentration, and accordingly, in the increasing of ionic conductivity;
- the iodide ions influence the sensitivity centers formation and their evolution during the production of emulsion;
- the presence of the iodide ions promote processes of the temporary capture of the interstitial silver ions. Thus occurrence of the octahedral face strengthens linkage, that, possibly, and determines the increased concentration of the extrinsic centers on the face (111).

The authors of works [5-7] have found out the effect of the spontaneous sensitization consisting in the formation of sensitivity in the process of octahedral AgBr microcrystals ripening without the participation of photographically active admixtures. The Ag_n sensitivity centers are formed during habit microcrystals modification at supersaturation in the system owing to the difference of chemical potentials of silver on the crystal surface μ(111) - μ(100). The influence of the crystallization conditions and precipitation, microcrystals sizes and the cadmium concentration, on the efficiency of the spontaneous ripening is shown. The purpose of the present work is the research of the iodide influence on the effect of the spontaneous sensitization depending on the way of its introduction in silver bromide microcrystals.

In this connection the following tasks have been set:

1. To research crystallization process features of the mixed AgBrI microcrystals (MC) at the variation of iodide concentration within the limits of 0.5 ÷ 2.0 mol. %.
2. To investigate the chemical and spontaneous sensitization of AgBrI-MC with the various size (0.4 ÷ 1.5 μm) at varied concentration of iodide.
3. To investigate the properties AgBrI crystals, obtained in modes co-crystallization and conversion of AgBr-MC in KI solutions.

Experimental

To solve the given tasks experiments on synthesis of photographic emulsions with AgBrI microcrystals of the various sizes (from 0.4 up to 1.5 μm) is carried out at the variation of iodide concentration (from 0.5 up to 2.0 mol. %) by the controlled double-jet crystallization technique.

The following parameters were constant during synthesis: crystallization temperature was equal to 45°C, the ammonia concentration was 0.44 mole/l, the introduction speed of solutions was $4.2 \cdot 10^{-3}$ mole/min, the pBr-value is 1.6. The chemical ripening of emulsions was carried out at T=52°C, pBr = 3.0 and pH = 6.3 for 3 - 4 h. The emulsions were coated at about 5 g of silver per square meter. Grains sizes and form were controlled by the electron-microscopic method.

The crystallization kinetics of AgBrI grains was investigated. It is shown that without iodide addition microcrystals have a little bit greater average size (d = 0.7 μm), than at the iodide concentration 0.5 mol. % (d = 0.53 μm), and 1 mol. % (d = 0.47 μm). Change of grains sizes is possibly connected with iodide ions building into the crystal lattice, and this result in the slowing down of microcrystals growth. However grains number thus increases, as the number of crystal lattice defects increases. Another reason of crystal growth retardation is the reduction of the nuclear critical size (r^*) at the iodide addition (from r^* = 10 nm up to r^* = 1 nm), therefore, conditions for formations of greater crystal number (supersaturation increases), but smaller on the sizes, are created.

It is shown that the crystals number (N) sharply increases on the initial synthesis stage owing to high value of supersaturation (S

= 1.26), it achieves the maximum value and then decreases, and the number of particles practically does not vary at the end of synthesis. After the achievement of maximum value N, supersaturation in the system decreases, conditions of ionic crystal growth emerge.

The dependence of crystals growth rate during synthesis is also obtained. Maximum crystals growth rate (G ~110 Å/s) is achieved at the nucleation stage, then growth rate value sharply decreases (G ~ 20-30 Å/s) and changes a little at the end of synthesis (G ~ 5 Å/s). Maximum growth rate is due to high values of supersaturation. There is a reason to assume that on the initial stage of synthesis inner part of grains represents disordered structure. At the final stage the crystallization conditions meet the requirements for the formation of more perfect monocrystal structure.

On the basis of the experimental data analysis, the nucleus critical size (r*) and the supersaturation in the solution (S) during crystallization are determined. The nucleus critical size depends on the degree of supersaturation in the system. The critical size is minimum (r^* ~ 1 nm) at the maximum supersaturation (S = 1.26) which is confirmed by literary data [8]. The nuclei critical size is less at greater iodide concentration in the system. The emulsion with the greater iodide contents (1 mol. %) has greater supersaturation than the emulsion with 0.5 mol. %.

Further emulsions were exposed to the chemical sensitization in different modes of ripening. The process of spontaneous (ripening of the emulsion without introduction of photographically active admixtures) and gold sensitizations with the addition of various gold compositions (chloroauric acid, aurum thiocyanat) were investigated.

Figure 1 shows that the emulsion speed increases approximately in 3.5 times at spontaneous ripening, in comparison with the primitive emulsion. When chloroauric acid ($HAuCl_4$) is used as chemical sensitizer the speed decreasing directly after gold introductions with simultaneous increase of the fog level during the subsequent ripening is observed (Figure 1, curve 2). The greatest speed incremental value ($S_{0.85}$ = 160) at spontaneous-gold sensitization is observed at the addition of aurum thiocyanat (Figure 2).

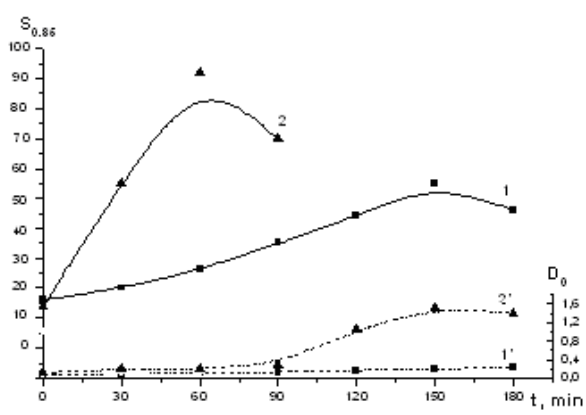


Figure 1. *Sensitivity ($S_{0.85}$) and fog level (D_0) vs. ripening time for AgBrI (1 mol. %) microcrystals, d = 1.37 µm, in the mode of spontaneous (1, 1') and spontaneous-gold (2, 2') sensitization.*

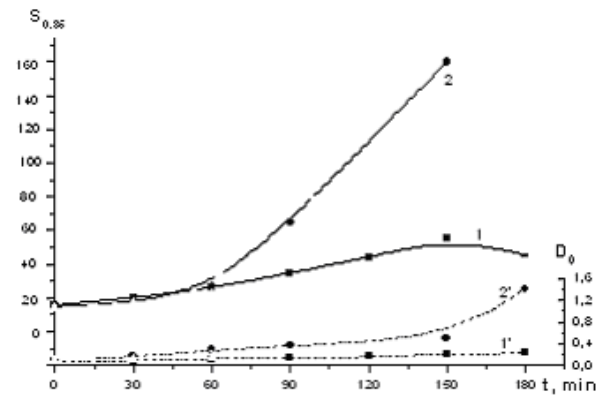


Figure 2. *Sensitivity ($S_{0.85}$) and fog level (D_0) vs. ripening time for AgBrI (1 mol. %) microcrystals, d = 1.37 µm, in the mode of spontaneous (1, 1') and spontaneous-gold (2, 2') sensitization.*

Iodide concentration influence on the effect of spontaneous sensitization of AgBrI-emulsions with the varied iodide contents were carried out. The optimal iodide contents in sensitized emulsions is 1 mol. %.

On the basis of the obtained results it is possible to conclude that iodide ions have essential influence on the occurrence of lattice imperfections. The addition of iodide increases interstitial silver ions concentration and as well as the ionic conductivity. It means that photoelectrons are trapped more easily and the sensitivity increases.

Figure 3 shows that at spontaneous ripening of the emulsions maximum speed grows with increasing of average grain size. Optimal average size is d = 1.37 µm. It is possible to assume, that at the further size increase sensitivity decrease will be observed as the processes of photoelectrons capture will occur not only on the surface, but also in grain.

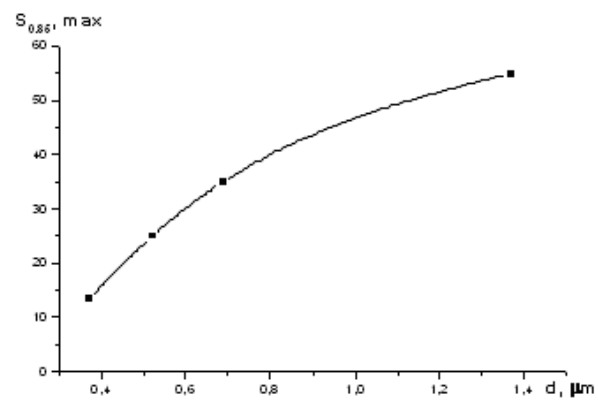


Figure 3. *Maximum sensitivity vs. average size of AgBrI (1 mol. %) microcrystals in the mode of spontaneous ripening.*

Besides, investigation of the pure AgBr-emulsions with

MCs (d = 0.7 μm) processed in solution KI (conversion) at varied iodide concentration (0.25 ÷ 3 mol. %) was carried out. Emulsions were maintained during 15 min. at T = 52°C (Figure 4, curve 1). The emulsion was exposed to chemical ripening in the mode of spontaneous sensitization within 3 hours (Figure 4, curve 2). Grains sizes and form were controlled by the electron-microscopic method.

Presented data show that the maximum speed is observed for the emulsion with pure AgBr-MCs in the mode of spontaneous sensitization. The dependence of the speed on iodide concentration (Figure 4) is complete. At the treatment of AgBr-MCs by KI solution at small concentration the maximum speed decreases. At the further increasing of KI concentration the speed increases again. The greatest speed is observed at iodide concentration 1.5 mol. %, but with the further increasing of iodide concentration the maximum speed decreases. It can be explained by etching of KI solution on AgBr-MCs. It is known that the etching process occurs on the surface defects, i.e., in the same places where the sensitivity centers are formed. Naturally, that it results in speed decreasing. It is necessary to note, that the speed curve of the primitive emulsion is of similar type.

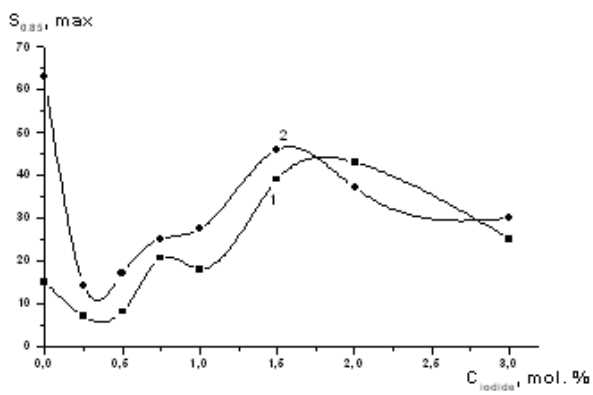


Figure 4. *Maximum sensitivity vs. iodide concentration for AgBr microcrystals (d = 0.7 μm) after treatment by KI solution.*

Results of the electron-microscopic analysis show that at the treatment of AgBr-MCs (d = 0.7 μm) by the KI solution 1 mol. % the octahedral shape of grains becomes more expressed.

Conclusion

Thus, obtained results allow drawing a conclusion:

1. Crystallization and chemical sensitization processes of AgBr (I) MCs with various sizes at the iodide concentration variation are investigated.
2. It is shown, that efficiency of chemical ripening depends on average grain size, iodide concentration and a way of the KI adding and type of chemical ripening.

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Author Biography

Nadejda S. Zvidentsova got Ph.D degree in Physical Chemistry in the Kemerovo State University, Russia in 1993, now she is an associate professor of the Kemerovo State University. She works at the department of experimental physics. Her major research field is silver halide photographic chemistry.

Investigation of the tabular silver halide crystals preparation by controlled Ostwald ripening method.

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Abstract

Recently, it has become possible to growth large tabular silver halide crystals from organic solvents or mixture of gelatin-water solution and polar aprotic organic solvent. In this study, the silver halide emulsion precipitated by controlled Ostwald ripening method was carried out. The size and the form of silver halide crystals getting in the presence of dimethyl sulfoxide, were studied. The concentration of dimethyl sulfoxide and halogen ion excess, and the ionic strength were constant during the emulsion synthesis.

Introduction

More traditional methods of preparing silver halide crystals populations at the defined grain size and grain distribution employed gelatin-water solutions [1]. Recently, it is proposed to employ non-water solutions using polar aprotic solvents [2-4] or gelatin-water solutions of protic solvents with dissociation constant smaller than that of water [5-7]. Silver halide crystals precipitated under such conditions are characterised by the presence of twin planes and a large number of lattice defects, therefore facilitating the formation of tabular crystals. One of the most important properties of tabular crystals is their large specific surface, which is favourable for the preparation of high sensitivity emulsions during spectrally sensitised process. Further, the ratio of the volume and the surface area of the tabular crystals are low compared to block shaped crystals, which means that less expensive silver halide is needed for the same specific surface area.

Until now, the high-molecular compounds like directors or modifying growth agents were used in traditional methods of preparing tabular silver halide crystals [e.g. 8-10]. Nowadays, it is easier to get large population of T-crystals employed gelatin-water solution of polar aprotic solvents. Although, the growth mechanism and twin formation for silver halide crystals grown from aprotic solvents was studied recently [11-23], not many researchers have precipitated silver halide emulsion under such conditions until now [3, 6, 24, 25].

The subject of prior study [24] was a comparison of the sensitometric properties of some silver halide emulsions precipitated by single-jet method in the presence of polar aprotic solvents and/or alcohols. All the solvents were mixed with water at the 50:50 volume ratio. The results are compiled in Table 1.

The highest value of relative contrast and relative speed were observed, when the dimethyl sulfoxide was used as solvent. In this connection the presented study aims to investigate the possibility of substitute ammonia with dimethyl sulfoxide (DMSO) in controlling Ostwald ripening method and examine influence of DMSO on the shape and size these silver halide crystals.

Table 1. Sensitometric properties of silver halide light-sensitive emulsions obtained from mixture of water and organic solvents relative to same emulsion obtained from pure water without ammonia [24].

Solvent	Fog	Relative contrast	Relative speed
Water (ref. emulsion)	0.00	1.00	1.00
Dimethyl sulphoxide	0.00	1.49	3.72
Dimethyl formamide	0.21	0.89	2.35
Tetrahydrofuran	0.02	1.04	3.00
Acetone	0.00	1.29	2.96
Dioxane	0.00	1.08	3.46
Isopropyl alcohol	0.05	0.91	1.07
Ethyl acetate	0.15	1.62	0.53

Controlled Ostwald ripening method was worked out by W. Romer and W. Markocki at Wroc³aw University of Technology in the year 1961 [26]. Delivering components, which are necessary to growth of this crystal, carries out the production of specified population of silver halide crystals at the slightly supersaturated solution.

The large solubility of silver halide colloidal suspension, so-called a Lippmann's emulsion (the size of silver halide crystals – 0.02-0.03 μm.), is used in this method. First, „nucleus" emulsion containing crystals 0.2 μm is prepared. Next, the Lippmann's emulsion, solution of ammonia and solution of potassium bromide are added successively at specified dose to the reaction vessel. Presence of ammonia and potassium bromide in colloidal suspension increase the solubility of silver halide. The crystals of Lippmann's emulsion dissolve and their mass is placed on the surface of larger growing crystal of „nucleus" emulsion. Silver halide crystals obtained by controlling Ostwald ripening method have properties similar to crystals growing by double-jet method.

Experimental

The investigated emulsion was prepared using controlled Ostwald ripening method in three stages. First, the Lippmann's emulsion precipitation was carried out using single-jet method at a temperature of 50°C. Figure 1 is a schematic diagram, which describes the synthesis in some detail, including the sequence and time of addition of given solutions to the reaction vessel.

The chemical composition of the solution used in the above synthesis was as follows:

Solution A: water, 120.0 cm^3; gelatin, 5.0 g.

Solution B: water, 40.0 cm^3; silver nitrate, 20.0 g; water to volume, 80 cm^3.

Solution C: water, 30.0 cm^3; potassium bromide, 14.0 g; solution A, 25.0 cm^3; water to volume, 80 cm^3.

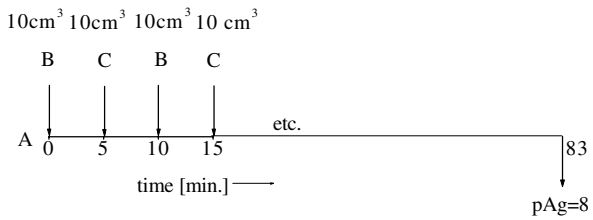

Figure 1. *Diagram of Lippmann's emulsion preparation.*

In the second stage, the „nucleus" emulsion was prepared by heating, strongly mixed Lippmann's emulsion, DMSO (to get 50 percentage by volume) and 1.19 g potassium bromide (to get the pBr=1).

In the third stage, the recrystalization process took place also. Concentration of bromide ion (0.1 mol/dm^3) and DMSO (50 percentage by volume) as well as the value of ionic strength (0.56) were constant during the second and third stage of process. Recrystalization process was ended when the silver halide crystals included at emulsion grew to the expected size. In this way, three emulsions were prepared by changing of recrystalization time 10, 15, 20 minutes respectively. Detailed pattern of emulsion preparation is compiled in Table 2.

The form of crystals was observed using microscope with immersing lens.

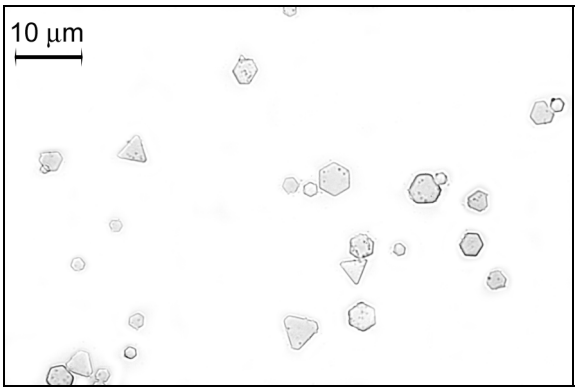

Figure 2. *Silver bromide crystals of „nucleus" emulsion C obtained by controlled Ostwald ripening method, 26 minute of growth.*

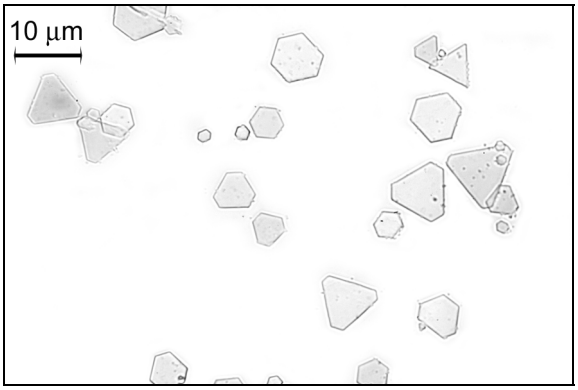

Figure 3. *Silver bromide crystals of emulsion C obtained by controlled Ostwald ripening method, 46 minute of growth.*

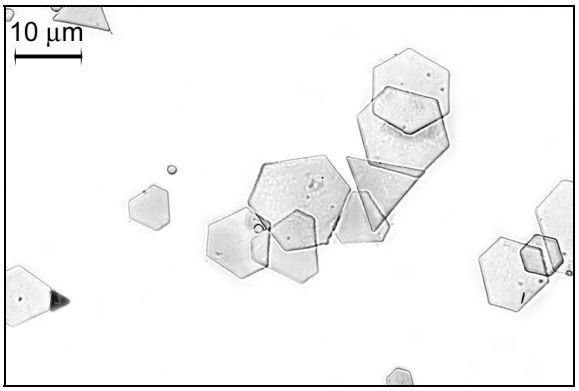

Figure 4. *Silver bromide crystals of emulsion C obtained after 86 minute of growth.*

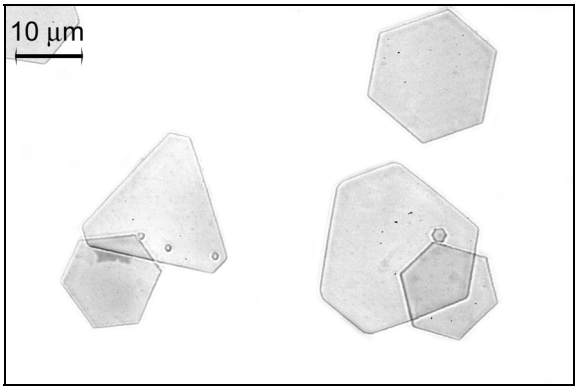

Figure 5. *Silver bromide crystals of emulsion C obtained after 126 minute of growth.*

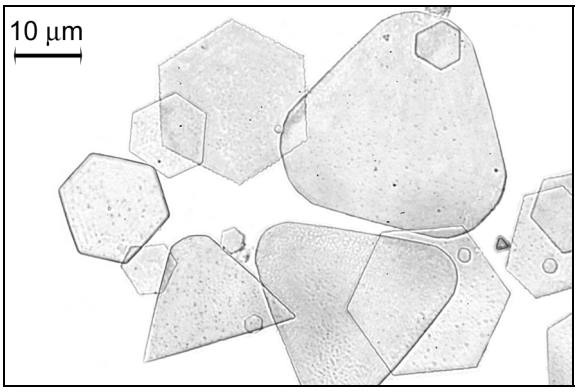

Figure 6. *Silver bromide crystals of emulsion C obtained after 166 minute of growth.*

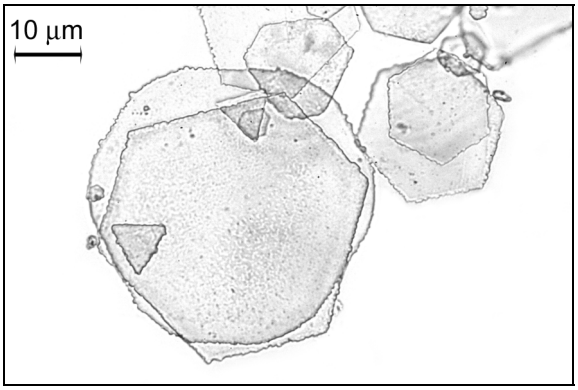

Figure 7. *Silver bromide crystals of emulsion obtained after 206 minute of growth.*

Table 2. Detailed pattern of emulsion preparation. L – Lippmann's emulsion [cm^3], DMSO – dimethyl sulfoxide [cm^3]. The concentration of the excess of bromide ions is 0.1 mol/cm^3 (pBr=1).

Stage	Action and composition of emulsion solution	Time of stage [min.]		
		Emuls. A	Emuls. B	Emuls. C
2	Recrystalization 50 L + 50 DMSO „nucleus" emulsion	20	26	36
3	Recrystalization 100 cm^3 obtained emulsion + 20 L + 20 DMSO	10 [1)]	15 [1)]	20 [1)]

[1)] This stage was repeated nine times

Results

As a result of research was affirmed that the „nucleus" emulsion included tabular silver halide crystals in triangular and hexagonal shapes (Figure 2 illustrates crystals of „nucleus" emulsion C). The average size of crystals was 4 µm.

The most short recrystalization time in second stage was conducive to form 65% of tabular silver halide crystals in emulsion A. Increase of recrystalization time led up to increse percentage fraction of tabular silver halide crystals in whole population (emulsions B – 80%) and decrease dispersion of crystal size. The 99% of tabular silver halide crystals in whole population were formed, when the recrystalization time was 20 minutes (emulsion C). Moreover, crystals include in emulsion C had lowest dispersion of crystal size. Microscopic image of silver halide crystals of emulsion C during the crystal growth was illustrated in the Figures 3-7. Samples for microscope analysis were taken in 46, 86, 126, 166 and 206 minute.

Photomicrographs show that the increase of recrystallization time led up to increase crystals size, increase aspect ratio and changed crystals shape. Initially, the crystals had triangular and hexagonal tabular shape. After 166 minutes of recrystallization, triangular and hexagonal tabular crystals with poorly rounded edges were formed and the mean size of crystals was 24 µm. (Figure 6). After 206 minutes of recrystallization, triangular and hexagonal tabular crystals with strongly rounded edges were formed. (Figure 7).

The results indicated that the presence of DMSO in the reaction vessel was conducive to form twin planes in the growing crystals, because the Lippmann's emulsion was precipitated in condition, which didn't form twin planes, so it hadn't included tabular crystals [27].

Forming of hexagonal tabular crystals and disappearance of the triangular tabular crystals were observed during the recrystalization [28]. G. Bögels, et al. found the same relation but in pure DMSO (0.1 and 0.2 M $AgBr_2$) [20].

Substitute of ammonia with dimethyl sulfoxide in controlling Ostwald ripening method makes possible forming triangular and hexagonal tabular crystals. The crystals morphology depends on the various variables like: the concentration of the excess of halide ions, concentration of organic solvents, concentration of neutral salts (ionic strength of the solution), concentration of gelatin and other physical and chemical parameters. In order to precipitation of monodispersive silver halide crystals, further investigation will be doing.

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