JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 43, Number 1, January/February 1999

Investigation of Photographic Phenomena Connected with Change of Silver Dispersity

Serge F. Chernov and Valery N. Zakharov*[,†]
Research Centre of Molecular Diagnostics, Moscow, Russia
**Moscow State University "M. V. Lomonosov", Moscow, Russia*

Phenomena essential for practical photography were investigated by means of electron microscopy with the emphasis on the transformation of the size of colloidal silver particles and change of their spectral properties. Ways to change this size during photographic processing of the layers were studied and their mechanisms were worked out in detail in order to optimize them. It was established that in the process of spectrozonal intensification massive image silver with particle size of 0.1 to 0.2 μm was transformed into colloidal particles with the size of 3 to 6 nm. This process was accompanied by increase of spectral absorption intensity with its peak at 450 nm. Roles of formation of soluble silver complexes, influence of halogen ion, and multicyclicity of the process were investigated. Study of oxidizing dispersion properties of silver in a chromium halide bleacher with successive intensification of the silver image showed that effective dispersion of silver halide microcrystals could be achieved for the case of oxidation in chromium(6+) chloride or chromium(6+) bromide bleachs with high chromium(6+): chloride (bromide) molar ratio, as well as in the case of strong repeated reduction in the stannous chloride or borohydride salt solutions. It was noted that the chromium compounds played only a small part in the processes connected with silver particle transformation, and the intensification ratio depended on factors influencing morphology of silver halides (formed in the process of bleaching of initial colloidal silver particles) as well as the morphology of secondary silver obtained after redeposition of AgCl.

Journal of Imaging Science and Technology 43: 79–84 (1999)

Introduction

Many photographic phenomena, such as processes of intensification, toning, photographic reduction and redeposition, are connected with the change of composition and dispersity of silver and its salts. Processes taking place during spectrozonal redeposition (intensification) of silver in tin containing reducing agents as well as in chromium intensifiers are considered in this report. These processes are of relevance to the lowering of silver content in photographic emulsions as well as to the increase of optical densities and contrast (especially for x-ray photographic materials).

Experimental

The experiments on spectrozonal intensification of visible images and the study of chromium halide bleachers were carried out on AGFA D-7 Structurix radiographic film with high-optical density homogeneity of optical wedge silver images. After exposure in the x-ray camera the film was conventionally developed (Chibisov's developer No. 1, 1 min. , 20°C) and fixed in acid fixing bath ($Na_2S_2O_3 \cdot 5H_2O$—250 g/L, Na_2SO_3 – 25 g/L, H_2SO_4 (10% solution) – 50 mL/L, 7 min., 20°C). Then it was bleached by ferric trichloride (10 g/L $FeCl_3 \cdot H_2O$ with 6 mL/L HCl conc., up to full bleaching) and bleached samples were used for further processing as described below. For the electron microscope observations 4 × 4 mm areas, equal in number with optical wedge fields, were cut from the film wedge, the photographic layer was separated from the base by 1 to 2 min soaking in a mixture of cyclohexanol and water (1:1) and transferred to glass, with subsequent processing according to standard procedure for ultramicroscopy, as follows:

1. The layer was soaked in water for 10 min at 25°C and separated from the glass. This separation is not necessary, it can be done after polymerization, but with re-embedding of the sample into resin after separation.
2. Hardening in 3 to 5% solution of Serva glutaric aldehyde for 1 h.
3. Washing in distilled water, 2 times for 5 min, to eliminate glutaric aldehyde excess.
4. Dehydration in ethyl alcohol solution with increasing concentration: 20%—for 10 min, 40%—for 10 min, 60%—for 10 min, 80%—for 20 min, 96%—2 times for 20 min.
5. Dehydration in absolute acetone, 2 times for 30 min.
6. Preparation of Epon-812 epoxide resin mixture[1] and layer saturation in the mixture EPON: acetone = 1:4 for 6 to 8 h and in the mixture EPON: acetone = 1:1 for 12 h.
7. Embedding the layer in resin and with evacuation to 40- to 50-mm Hg for 2 to 3 h to remove residual acetone.
8. Polymerization of the resin for 6 h at 37°C and for 12 h at 65°C.

Sharpening of the block for the area needed was done after polymerization by microtome or by hand, with the use of an MBS-2 microscope (enlargement 56x). The sec-

---

Original manuscript received November 24, 1997

[†] IS&T Member

tions were obtained using LKB 5 and Sorvall MT-5000 ultramicrotomes with glass knives. The 6-mm-thick knives were made by the LKB Knife Marker 7800 B, cutting speed was 2 mm/s. The section thickness was determined by interference coloring and was generally equal to 50 to 90 nm. The sections were moved with the help of a cut collector to the middle of the tray, and removed to the net with Formvar film base. The thicker sections were stabilized by the evaporation of 10-nm carbon film onto them in a JEOL JEE-4X vacuum evaporating camera. Then the sections were inspected and photographed using JEOL JEM-100CX, Philips EM-12, or Hitachi H-500H electron microscopes with 100-kV accelerating voltage.

It is not necessary to get rid of gelatin in this method. That is why the size of the smallest particles does not change due to the processes of coalescence, recrystallization, and dissolution. The method gives us the possibility to study the relative arrangement of the objects in the photographic layer as well as their conjunction in different planes.

Absorption spectra were recorded from 300 to 900 nm using a Hitachi 200-20 double-beam or a Beckman DU-8 single-beam spectrophotometer with an attachment for study of light-scattering samples. Precision of the measurement was 0.5 to 1.0 nm on the wavelength scale, and, 0.005 on the optical density scale.

Results and Discussion

Study of Visible Image Spectrozonal Intensification. ***Mechanism of Silver Halide Reduction in Photographic Layers.*** A transformation of initial large colloidal particles of developed silver (via oxidative conversion to AgHal) into extremely small silver particles (by AgHal reduction with stannite ions in the presence of ethylene diamine) takes place. The initial particles exhibit wide spectral absorption (neutral gray color), the latter has a narrow, very intense peak in their absorption spectrum (yellow color). The redeposited silver thus has spectral properties different from the initial properties,[2–4] i. e. , a narrow optical peak in absorption spectrum at 450 nm. Optical density for this peak is significantly greater than the optical density of the initial silver particles throughout the visible region of the spectrum. This peak, according to the literature,[5,6] may be due to absorption by Ag_2 centers, but at the same time this peak, according to Mie theory,[7] is caused by absorption by small colloidal particles. It follows from experimental works[8–10] that in the gelatin layers such an absorption band is due to 3 to 6-nm silver colloidal particles. The dependence of optical density on the size of colloidal silver particles is shown in Ref. 8. Moreover, acording to the theory of Mie and Refs. 11 throuh 16, the size of colloidal silver particles in gelatin is connected with the optical properties of photographic emulsions. A local increase of optical density in the sufficiently narrow spectral region (spectrozonal intensification) is a consequence of a decrease in silver particle size, and image contrast is defined by the silver particle size distribution (by the width of distribution peak and, as a consequence, by the width of the absorption spectrum peak). In the case of a narrow peak (close to monodisperse distribution), the value of optical contrast increases significantly. It was suggested that the particles of such a small size were created during silver chloride reduction by stannite ions in the presence of ethylene diamine (EA) in two successive reactions:

$$AgCl + 2EA = Ag(EA)_2^+ + Cl^-, \qquad (1)$$

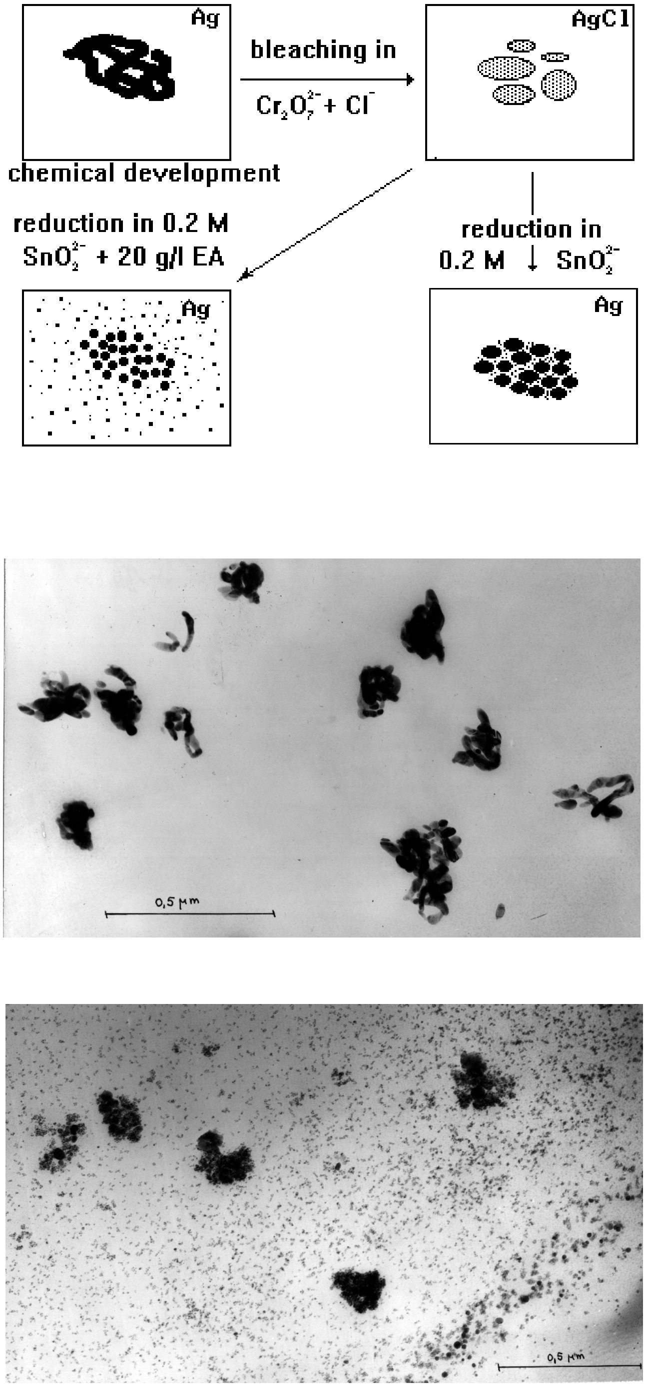

Figure 1. (a) The scheme of experiment on spectrozonal intensification of silver. (b) Electron microscopic photo of ultrafine section of initial photographic film. (c) Electron microscopic photo of ultrafine section of redeposited silver after spectrozonal intensification.

$$\begin{aligned} &2Ag(EA)_2^+ + SnO_2^{2-} + 4OH^- = \\ &2Ag + 4EA + SnO_4^{4-} + 2H_2O. \end{aligned} \qquad (2)$$

According to Eqs. 1 and 2, the silver particles are created by homogeneous reduction of silver ammine complexes. This scheme is based on work,[17] where it is shown that oxide, hydrate, nitrate, sulfate, carbonate, and halides of silver on interaction with the ligands (Add) such as ammonia, ethylene diamine, pyridine, bipyridine, tholuidine, and thiourea create water soluble in complexes of either the $[AgAdd]^+$ type or, with large ligand excess, $[AgAdd_2]^+$. This suggestion was verified by an electron microscopic investigation of this process by the ultrafine sections method. The scheme of this process is presented in Fig. 1.

We can see from the micrographs obtained that developed microcrystals (Chibisov developer, 1 min., 20°C) have thus formed thread balls with average size of 100 to 300 nm and characteristic filamentary structure [Fig. 1(b)]. After their transformation into silver chloride the threadlike structure disappears and the form of the particles becomes close to spherical and their sizes increases. A visible change of morphology is then observed during development of silver chloride microcrystals in the aqueous solution containing 0.2 M $SnCl_2$ with 0.8 M NaOH and 0.3 M ethylenediamine (EA). Two types of particles can be seen clearly: quite friable aggregates with the central part diameter of 100 to 200 nm and many more small particles [Fig. 1(c)]. From pictures at high magnification we estimate their diameter as 3 to 6 nm, in correspondence with the spectral characteristics of the redeposited silver mentioned above.

Therefore the main reason for the optical density intensification observed is because the particles of "smallest" silver which arise during redeposition in these conditions and fill the space in between considerably larger aggregates. Due to their small size, they efficiently attenuate the incident light in the blue region of the spectrum. During silver chloride reduction in the same tin salt solution not containing ethylenediamine we obtain silver aggregates close in size and form to the ones obtained in the solution with ethylenediamine, but the "smallest" particles are practically nonpresent. Under these redeposition conditions silver is probably formed as a result of silver chloride heterogeneous reduction by stannite ions:

$$2AgCl + SnO_2^{2-} + 4OH^- = 2Ag + 2Cl^- + SnO_4^{4-} + 2H_2O. \quad (3)$$

The competition of these two modes of reduction (the consecutive Reactions 1 and 2 and Reaction 3) defines the relative amount of "smallest" silver and, correspondingly, the degree of optical density increase. When the EA concentration is higher the $Ag(EA)_2$ product does not have enough time to reduce where it is formed and diffuses from the layer. As a result the image is eroded. It was established that when the EA concentration is above 1.5 M the silver sediment can be visually observed in the reducing solution. This observation is one more confirmation of the suggested silver phase transformation mechanism during silver redeposition.

In the terms of homogeneous and heterogeneous reduction it means the following: with ethylenediamine concentrations larger than 1.5 M we have a practically pure homogeneous process, but with lower concentrations, reduction includes both homogeneous and heterogeneous components. To separate these processes is a very complicated problem. Accordingly, choice of optimum ethylenediamine concentration and duration of processing is determined by the desirable photographic effect, because a gain in image intensification may be accompanied by a loss of its resolving power (blurred image). We further note that at a given concentration of stannite ions (0.2 M), the intensity of the band with maximum at 450 nm, and correspondingly, the degree of intensification increase with EA concentration (from 0 to 1.5 M) reaching some saturation value. With EA concentrations exceeding 1.5 to 2.0 M densities begin to decrease and silver appears in the reducing solution. We suggest that EA reacts with AgCl forming soluble silver complexes which are reduced afterwards by the stannite ions, reduction being not heterogeneous, as in conventional development, but homogeneous. Such reduction leads to the formation of silver particles with a size not exceeding 7 nm, and with characteristic absorption in the 400 to 500-nm region. Without EA, the density scale intensification ratio (K_y) is 1.2 to 1.3; when EA concentration is 10 to 20 g/L, it reaches a value of 1.5 to 1.6, and does not increase if amine concentration increases further. Comparing the results of these sensitometric measurements with the electron microscopy we derive the conclusion: optical density increase after redeposition is a consequence of silver dispersity increase. These small silver particles get away from the maternal AgCl crystal by a distance of 0.2 to 2-μm.

Influence of Halogen Ions on Redeposited Silver Morphology. Figure 2(a) presents the scheme of the experiment to determine the influence of halogen ions on the kind of redeposited silver. The greatest change in the morphologic picture in comparison with the initial one is observed for redeposition via AgCl, the slightest for redeposition via AgI. In this last case the silver has a form of accumulations with the size of 0.2 to 0.5 μm, consisting of especially small formations (less than 0.01 μm), partly aggregated and partly separated in

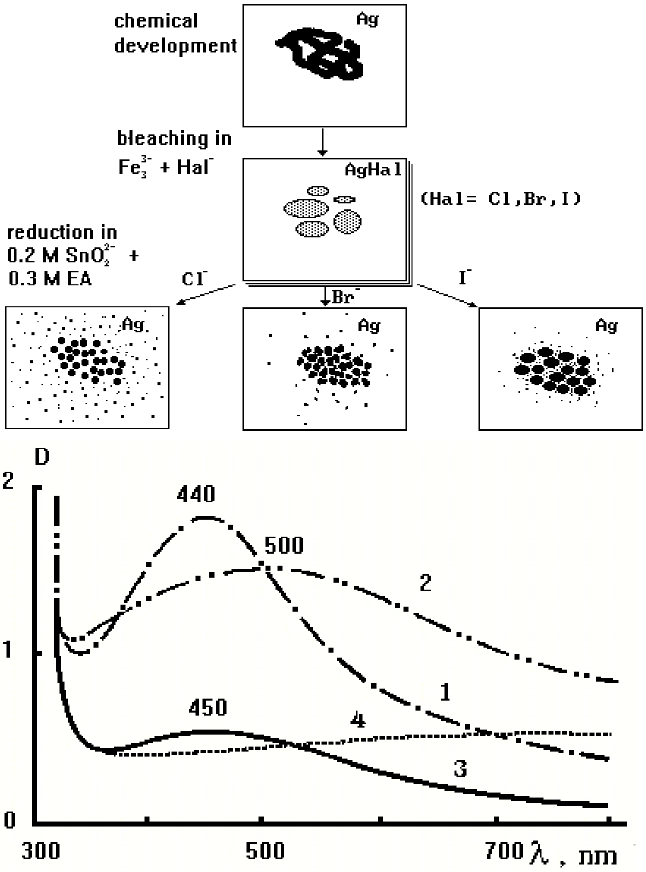

Figure 2. (a) The scheme of experimental study of the halogen ion influence on redeposited silver morphology. (b) Absorption spectra of photographic layers after spectrozonal intensification (deposition) obtained via different AgHal layers: 1 – via AgCl layer, 2 – via AgBr layer, 3 – via AgI layer [see Fig. 2(a)], 4 – initial silver layer [see "chemical development Ag" Fig. 2(a)].

space. There are smaller particles inside the accumulations, but their number is relatively small. Silver aggregates obtained from AgCl are slightly smaller in size than the ones obtained from AgI and are more compact. The space between them is filled by particles of 3 to 6 nm diam. This combination of particles of mainly two groups with about a hundred-fold size difference gives rise to the absorption spectrum with a distinct peak at 450 nm. A peculiar picture is given by the secondary silver formed by AgBr reduction. In this case large enough accumulations with the size of 0.2 to 0.4 μm and the smallest 3 to 6 nm particles at a considerable distance from the accumulations remain in the layer. The smallest particles are not so numerous as in the case of the AgCl–Ag transformation, but there are grains with the size of 0.01 to 0.03 μm at some distance from the large aggregates as well. These morphologic differences reveal themseves in the absorption spectrum [Fig. 2(b)]: the peak is shifted from 450 to 500 nm and is less distinct. Absorption by the smallest particles decreased while absorption in the longer wavelength regime increased. On the whole, however, in the case of AgCl–Ag and AgBr–Ag transformations a distinct increase in optical densities at 350 to 380 nm is observed. The AgI–Ag transformation does not give such an increase. Micrographs show quite convincingly that the absorption increase is connected to the appearance of small silver particles isolated spatially from the initial aggregates. It was shown by additional experiments that AgI was not dissolved in the ethylenediamine aqueous solution.

Transformations of the "Smallest" Silver Particles. It can be inferred from the silver reduction mechanism derived above that the intensification degree will grow on repetition of oxidation–reduction stages. However, our experiments have shown that optical density increases efficiently (2 to 3 times) after the first cycle only. On repetition the additional optical density increase was only 10 to 20%.

An explanation for this was obtained by studying the electron microscopic pictures of secondary (redeposited) silver during subsequent oxidation–reduction transformations. The scheme of the experiment is presented in Fig. 3. Morphology of secondary silver obtained by oxidation of silver particles to AgCl and reduction in the solution of stannite with ethylenediamine gave evidence of simultaneous homogeneous and heterogeneous silver chloride reduction. After oxidation of secondary silver in the presence of Cl⁻, the smallest silver particles (with 3 to 6 nm diam) disappeared and the picture became morphologically similar to the AgCl image formed from developed silver. During chemical development this AgCl gave the same thread balls as initial developed silver. If secondary silver reduction was carried out without EA the bunches of aggregates with the size of 0.1 to 0.3 μm were obtained instead of the threads. They contained a large number of particles in the 10 to 12 nm size range, linked together. The presence of ethylenediamine in the reduction stage leads only to the repetition of the initial process: both aggregates and 3 to 6 nm particles again appeared. It is necessary to note that after the first as well as after the second oxidation–reduction cycles, these particles are at some distance from the central part of the large silver aggregates. That means that during their formation contact with a silver halide crystalline phase is absent.

Thus, the processes of silver transformation by oxidation into AgCl and reduction by stannite ions can undergo many cycles without significant changes, morphology of redeposited silver being determined mainly by the chemical nature of reducing solution. Silver particles with 3 to 6 nm diam and an absorption peak at 450 nm formed in the photographic layer under the conditions described above apparently are the smallest metallic silver particles stable in the gelatin matrix. If some atoms are separated, they convert immediately into molecular aggregates which are mobile in the gelatin matrix. Therefore oxidation of the smallest silver particles to AgCl can be accompanied by formation of relatively large silver halide crystals in the size range of up to 0.05 to 0.2 μm. At this stage a noticeable increase in the photometric equivalent occurs.

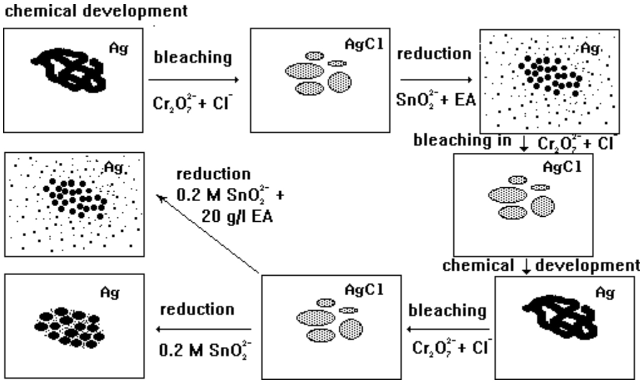

Figure 3. The scheme of experimental study of repeated silver redeposition.

Oxidative Dispersion of Silver in Chrome Halide Bleachers. It is well known[18] that it is possible to intensify a silver image by halidization of reduced silver and subsequent reduction of the halides. In our opinion, the intensifying system which uses bleach, comprising potassium bichromate and hydrochloric acid, produces silver halide as bulky loose aggregates transforming during reduction into silver with increased covering power. The reaction of silver oxidation in chromium(6+) halide bleachers is:

$$Cr_2O_7^{2-} + 6Ag + 14H^+ + 6Cl^- = 6AgCl + 2Cr^{3+} + 7H_20. \quad (4)$$

It is also known that bichromate ions oxidize silver to Ag^+ even without halogen ions:

$$Cr_2O_7^{2-} + 6Ag + 14H^+ = 6Ag^+ + 2Cr^{3+} + 7H_20. \quad (5)$$

Therefore, during processing in chromium(6+) halide bleach, the possibility of Ag oxidation according to Reaction 5 under conditions of a relative shortage of halogen ions near silver particles is not excluded. In this case a rapid transformation of Ag^+ into AgCl can follow Reaction 5. A change of the AgCl formation mechanism can in turn, influence its morphology and the morphology of secondary reduced Ag. The scheme of our experiment is presented in Fig. 4. Silver chloride obtained by oxidation of reduced silver particles in the solution with 0.1 M CrO_3 and 0.2 M NaCl (pH 1.0) was mainly observed as elongated aggregates with the size of 0.2 to 0.3 μm. Now, after oxidation in the solution having the same pH and an equal amount of CrO_3, but containing only 0.02 M NaCl, it looks a bit different. In addition to the same AgCl aggregates, a large number of particles with the diameter of 3 to 8 nm also appear in the layer. The morphologic picture transforms differently during subsequent reduction. After reduction by stannous chlo-

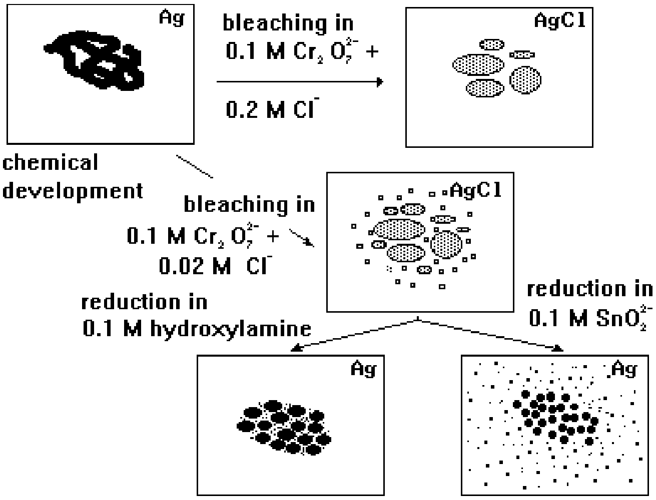

Figure 4. The scheme of experimental study of silver oxidizing dispersion in chromium halide bleaches.

ride (pH 12.2) highly loose aggregates with the size about 0.1 μm, along with closely situated 3 to 15 nm particles with close to spherical form remain in the layer as well. On reduction with hydroxylamine with the same pH as for stannous chloride solution, the silver aggregates have a more compact structure and approximately the same size. In the same time the silver phase with high dispersity is absent near these aggregates. These morphologic distinctions affect the absorption spectra of reduced silver. In the first case the picture is toned brown, characteristic for silver particles of colloidal size, in the second one the hue is close to neutral gray. The situation analogous to the stannous chloride reduction case takes place with other "strong" reducing agents (dimethylamine borane, hydrazine borane, and sodium borohydride) whose solutions at pH 12 have redox potential ranging between -900 and -1050 mV (with reference to silver–silver chloride electrode). Meanwhile, using photographic developers (metol, hydroquinone) with the same pH, we obtain the same picture as in the hydroxylamine case. These reducing systems are less active and have a more positive potential (not less than -500 mV). It seems that at such potentials, oligoatomic silver clusters, formed at the initial stage of reduction of high-dispersity silver halide particles, oxidize to Ag^+ again. Thus, we can obtain effective dispersion of silver microcrystals by their oxidation to silver chloride or bromide, respectively, and further reduction if on the oxidation stage we use chromium(6+)-chloride or chromium(6+)-bromide bleachs with high molar ratio chromium(6+): chloride (bromide) and on the reduction stage we use strong reducing agents (stannous chloride and borohydride derivatives). If we use less strong reducing agents (hydroxylamine, metol, and hydroquinone), it is impossible to observe a highly disperse silver phase, probably owing to silver solution.

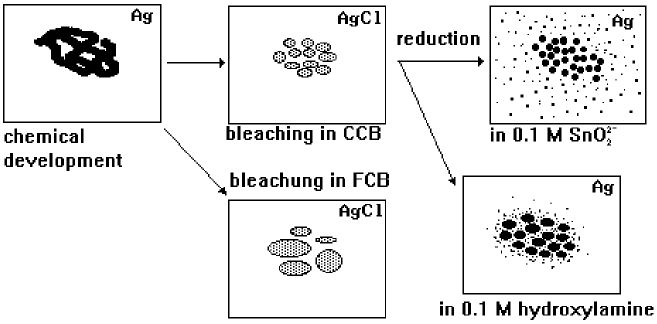

Figure 5. The scheme of experimental study of the influence of chromium chloride (0. 03M $K_2Cr_2O_7$ + 0. 006M HCl) and iron chloride (0. 03M $Fe_2(SO_4)_3$ + 0. 25M NaCl + 0. 06M H_2SO_4) bleaches.

Morphologic Transformations of Silver in Chromium Intensifiers. Chromium intensifier is well known in photographic practice[18]: the developed and fixed image is bleached in a hydrochloric acid solution of potassium bichromate, cleared by potassium metabisulphite, and reduced in the light using a photographic developer. Intensification is not more than 40%, however if we change developing agent to stannous chloride alkaline solution, 2.5× intensification can be achieved. Insoluble chromium compounds are considered to contribute to the intensification observed.[19]

In our opinion, the contribution of chromium compounds to intensification efficiency is in reality, not large, and the intensification ratio in this system depends on some factors influencing morphology of both silver halide (formed during bleaching of initial silver particles) and secondary silver (obtained during AgCl reduction). To estimate the contribution to optical density due to colored chromium compounds, a bleached stop wedge image was processed in sodium thiosulphate solution to remove silver halide. It was thus shown experimentally that residual absorption in the intensified image was minor. The scheme of our experiment is presented in Fig. 5.

For the bleaching stage chromium chloride bleacher (CCB), containing 10 g/L of $K_2Cr_2O_7$ and 6mL/L of HCl (conc.), and for the reduction stage P-2 X-ray developer were used.[5] Linear dependence, i.e., constant K_y, is valid over a wide interval of initial optical densities. The results also apply with other developers (hydroquinone, hydroxylamine sulphate, sodium boron hydride, etc.): intensification is close to linear with intensification ratio (K_y) equal to 1.5 to 1.7. This value decreases to 1.05 to 1.20 if we substitute the CCB with a chloride bleach containing Fe(3+) or Cu(2+) as the oxidizing agents. A special place among investigated reducing agents is occupied by Sn(2+): for this system K_y has a large value for any bleach and $K_y(Cr) > K_y(Fe)$ [or $K_y(Cu)$]. For full bleaching of images in a CCB or a ferric chloride bleach (FCB) at room temperature not more than 1 min is necessary. Retaining the film samples in the same solutions for 10 to 20 min does not affect intensification efficiency. At ten-fold increase of chloride ion content in the FCB (by adding HCl or KCl) K_y does not depend on bleaching time either. Meanwhile, adding an excess of chlorine ions to CCB decreases K_y, independent of the type of chemistry used for secondary reduction.

We assume that the observed decrease of K_y reflects increased solubility (in the presence of excess chloride ions) of AgCl during processing in CCB that leads to particular structural features. This assumption is confirmed by results of electron microscopic investigations: rather bulky and loose AgCl particles are formed in a CCB while in FCB they are more dense. Morphological distinctions appearing during rehalidization are "remembered" in the re-established layer. These data concerning the morphology of secondary silver, obtained by reduction in stannous chloride alkaline solution, show that the share of smallest particles and the looseness of aggregated silver, obtained on reduction after processing in a CCB, are higher than after processing in an FCB. Both these factors are reflected in the value of the intensification ratio.

A different picture is given by secondary silver reduced (after processing by CCB) not by stannite ions, but by hydroxylamine alkaline solution. While the loose structure of silver aggregates is conserved, the almost total disappearence of the smallest particles remote from the large aggregates is observed, and individual accumulations of silver in the aggregates are more monolithic. As stated above, we can obtain practicaly the same value of K_y both with hydroxylamine and other reducing agents. Apparently for all these reducing agents mainly a heterogeneous mechanism of AgCl reduction is realized. For Sn(2+) alkaline solutions the process of AgCl reduction through soluble complexes, leading to formation of especially high-dispersity silver, is more efficient. This silver is responsible for the increase of optical density in the blue region of the spectrum.

Thus, it is established that silver chloride, obtained in chromium(6+) chloride bleach, has a more loose structure compared to AgCl, formed in oxidizing systems based on Fe(3+) or Cu(2+). This leads to its more efficient dispersity during subsequent reduction. Additional dispersion during redeposition takes place with alkaline Sn(2+) reducing agent, which incorporates the homogeneous mechanism of reduction.

Conclusions

Investigation of photographic processes yielding a change of silver dispersity is of high importance for scientific photography. It is possibile to follow the evolution of silver particles during photographic processing of the layers and work out in detail the mechanisms of the reactions that form them, to optimize them.

We established that the properties of silver transformed by oxidation to AgHal and reduction by stannite ions can undergo a large number of cycles without significant change. Morphology of redeposited silver is determined mainly by the chemical nature of the reducing agent. Silver particles with a diameter of 3 to 6 nm and an absorption peak at 450 nm, are apparently the smallest possible particles of metallic silver stable in the gelatin matrix. On separation of only a few atoms, they are capable of disintegrating immediately into molecular aggregates. Study of the processes of silver oxidative dispersion in chromium halide bleachs with subsequent intensification of silver image has shown that it is possible to achieve effective dispersion of reduced silver microcrystals by their oxidation to silver chloride or bromide and subsequent reduction, if at the oxidation stage we use chromium(6+) chloride or chromium(6+) bromide bleachs with a high molar ratio chromium(6+): chloride (bromide) and at the reduction stage we use strong reducing agents (stannous chloride or borohydride derivatives). But in the case of less strong reducing agents (hydroxylamine, metol, and hydroquinone) it is not possible to achieve high-dispersity silver in the photographic layer.

By studying processes connected with silver transformation under chromium intensification, we established that the contribution of chromium compounds to intensification efficiency is not significant. The intensification ratio in this system depends on the factors influencing the morphology of both silver halide, formed on bleaching of the initial silver particles, and secondary silver, obtained by secondary AgCl reduction. Silver chloride, obtained in a chromium(6+) chloride bleach, has a more loose structure in comparison to AgCl formed in an iron(3+) chloride bleach. This morphological difference leads to a more efficient dispersion of AgCl obtained with CCB after subsequent reduction.

Acknowledgments. This investigation was partly supported by the Russian Foundation for Basic Research (Grant N. 96-03-32263A) and the Henry Holmes Smith Foundation (Grant ZPV 000). We would like also to thank R. Heron (Indiana University) for useful discussion.

Editors Note. The reader is directed to the recent report[20] of similar morphological changes in colloidal silver produced by laser irradiation. In this work, Kamat and co-workers provide analogous correlation of spectroscopic and morphological changes to those presented in the present paper.

References

1. N. Reid, *Ultramicrotomy,* American Els. Publishing. Co., New York, 1975.
2. V. A. Kondratiev, A. A. Vitt, L. L. Antonova, and T. K. Barkova, Image intensification in phototechnical films by silver redeposition, *Poligrafija* (in Russian) **6,** 26 (1984).
3. V. A. Kondratiev and S. F. Chernov, About mechanism of development of silver halides in photographic emulsions, *Doklady AN SSSR* (in Russian) **283,** 664 (1985).
4. G. A. Branitsky, A. V. Kaparikha, V. V. Lapshina, L. P. Rogach, V. V. Sviridov, and D. V. Stashonok, Intensifying of photographic images by silver particles dispergation, *Vesti AN BSSR* (in Russian), *Seria Chem. Sci.* **6,** 37 (1985).
5. T. Tani and M. Murofushi, *J. Imaging Sci. Technol.* **38,** 1 (1994).
6. S. Guo and R. K. Hailstone, Spectroscopic and sensitometric studies of chemically produced silver clusters, *J. Imaging Sci. Technol.* **40,** 3 (1996).
7. G. Mie, Beitrage zur Optische Medien, Speziell kolloidaler Metallösungen, *Ann. Physik* **25B,** 377 (1908).
8. S. Chernov, E. Galashin and Y. Fedorov, The role of silver clusters in reduction of emulsion grains, *J. Inf. Rec. Mater.* **18,** 107 (1990).
9. S. Chernov and V. Zakharov, Light extinction by silver and gold colloidal particles, *J. Mod. Opt.* **36,** 1541 (1989).
10. S. Chernov and V. Zakharov, Optical and physical properties of silver color centers in microcrystals in silver bromide films, *J. Photogr. Sci.* **44,** 50 (1996).
11. K. S. Shifrin, The light scattering in turbid medium (in Russian), Gostechizdat, Moscow-Leningrad, 1951.
12. M. V. Savostianova and I. S. Radchenko, The modern questions stated about optical properties of silver in ultra-fine-grained distribution, *Zh. Nauchn. Prikl. Forogr. Kinematogr.* (in Russian) **25,** 303 (1980).
13. S. N. Latisheva, A. N. Latishev and L. L. Orekhova, About the structure of colloidal band in absorption light spectrum of silver colloidal particles, *Opt. Spectroscop.* (in Russian) **30,** 524 (1971).
14. D. C. Scillman and C. R. Berry, Spectral extinction of colloidal silver, *J. Opt. Soc. Amer.* **63,** 707 (1973).
15. A. N. Latishev, E. A. Galashin and K. V. Chibisov, Some peculiarities of absorption spectra of photochemically colored silver halide, *Zh. Nauchn. Prikl. Forogr. Kinematogr* (in Russian) **17,** 144 (1972).
16. V. D. Stashonok, O. V. Sergeeva, M. V. Artem’ev and V. I. Grigorenko, About the relationship between color and structure of silver image and absorption spectrum of forming its image, *Zh. Nauchn. Prikl. Forogr. Kinematogr* (in Russian) **35,** 280 (1990).
17. P. Ripan and I. Ceteanu, *Chim. Metal.* vol. 2, Editura Didactica si Pedagogica, Bucuresti, 1969.
18. V. Mikulin, Additional Treatment of Photographic Materials (in Russian), Goskinoizdat, Moscow, 1952.
19. L. Kartuzhansky and L. Krasni-Admony, Chemistry and Physics of Processes (in Russian), Chemistry, Leningrad, 1983, p. 91.
20. P. V. Kamat, M. Flumiana, and G. V. Hartland, Picosecond dynamics of silver nano-clusters, *J. Phys. Chem. B* **102,** 3123 (1998).