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Fogging Treatment in Preparing Direct Positive Emulsions†

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This study focuses on behavior of light-induced electrons, and electrons provided by fogging agents, and the effects of silver halide solvent and gold deposition on fog centers of direct positive emulsions. When an emulsion is photofogged, fog centers form preferably in the interior of the grain, indicating that light-induced electrons can be transferred to the conduction band of the silver halide crystal directly. Whereas, when a fogging agent is used, the internal fog centers form only where a sufficient amount of fogging agent exists and only after formation of the surface fog centers. In the above two cases, the ways electrons enter the conduction band are different. The results suggest that when emulsions are fogged, the addition of gold salt might reduce the dispersity of the fog centers. Plating of gold is the main reaction when enough fogging agent exists in the emulsion, and the replacement of silver atoms by gold atoms becomes important when the fogging agent is insufficient. When a direct positive emulsion is fogged, the plating of gold atoms on the fog centers is the main reaction, because of the large quantity of fogging agent.

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Introduction

In recent years, direct positive silver halide photographic emulsions have been developed for duplicating processes. A positive image can be obtained directly with these emulsions without previously forming a negative silver image. Two types of direct positive emulsions have gained importance in practice. In the first type, the grain surfaces are chemically fogged. When the emulsion is exposed, the fog centers on the surface of the exposed grain are destroyed by photo-oxidation. Surface or conventional development gives a positive image. In the second type, the silver halide grains are not subjected to fogging treatment before the exposure. During the exposure, the latent images are preferably formed in the interior of the crystal. After imagewise exposure if the emulsion layer is given a second uniform exposure while kept in a surface development solution or the emulsion is developed in a fogging surface developer, and a positive image is also produced.[1]

In preparing a direct positive emulsion of the first type, the silver halide grains, either with physical lattice imperfection or with internal chemical structure imperfection, must be fogged with a fogging agent alone or with a combination of a fogging agent and a gold compound. The fogging agent, such as thiourea dioxide or stannous chloride, provides electrons to reduce silver ions forming silver atom clusters. Can these electrons be transferred directly to the conduction band of the silver halide crystal? James,[2] considering the fact that certain developers could intensify the internal latent image, suggested that the electrons of these developers could be injected into the conduction band of the silver halide crystal. Fu and colleagues[3] showed that the electrons provided by a fogging agent, as well as photoinduced electrons, could enter the conduction band and be trapped internally forming internal fog centers, essentially the same as those formed by trapping photoelectrons. Saunders and West,[4] from an energy viewpoint, proposed that no effective direct electron injection from photographic developer into the conduction band of silver halide could occur at room temperature.

Gold plays important roles in chemical sensitization, latensification, and fogging treatment of the direct positive emulsion. In preparing a direct positive emulsion the combination of a fogging agent with a gold salt increases sensitivity significantly. The gold salt greatly increases the resistance of the fog centers to oxidation by air and, hence, increases the stability of the fog center during storage.[5,6] Vanassche[7] concluded that during the fogging treatment, gold ions could replace silver atoms in the fog center, forming gold–silver nuclei. Spencer, DeCann, and McCleary,[8] studied the function of gold in latensification of negative emulsions and indicated that the gold atoms deposited did not replace silver atoms contained in the latent image and sublatent image centers and also did not replace silver atoms contained in reduction-sensitization centers. James[9] suggested that the initial reaction was a replacement of silver by gold, but later stages of development of visible image by gold solution must involve gold plating onto the developing centers.

This work considers (1) the behavior of electrons, both induced by light and provided by a fogging agent, during fogging treatment, (2) the effect of the silver halide solvent on the fog center, and (3) the deposition of gold atoms on the fog center.

Experimental

Emulsion. A primitive core–shell emulsion doped with Rh^{+3} was prepared by a conventional double-jet method. The core was silver iodobromide with iodide content of 1.5 mol%

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TABLE I. Amounts of Fogging Agents

Emulsion number	Amount of fogging agents	$10^3 \times$ mg/mol AgX
	Thiourea dioxide	$NaAuCl_4$
F1-1	18	—
F1-2	25	—
F1-3	35	—
F2-1	3.5	3.5
F2-2	5	5
F2-3	7	7

TABLE II. Effect of Silver Halide Solvent on Fog Density

TAI	KSCN	pBr	Increment of fog density	
g/mol AgX	g/mol AgX		Emulsion F1-2*	Emulsion F2-2†
5	0	4.6	0	0
5	80	4.6	0.5	0.2
5	0	1.2	1.7	0.9
5	80	1.2	2.5	1.4

* Tho fog density before adding solvent is 1.2

† The fog density before adding solvent is 1.5

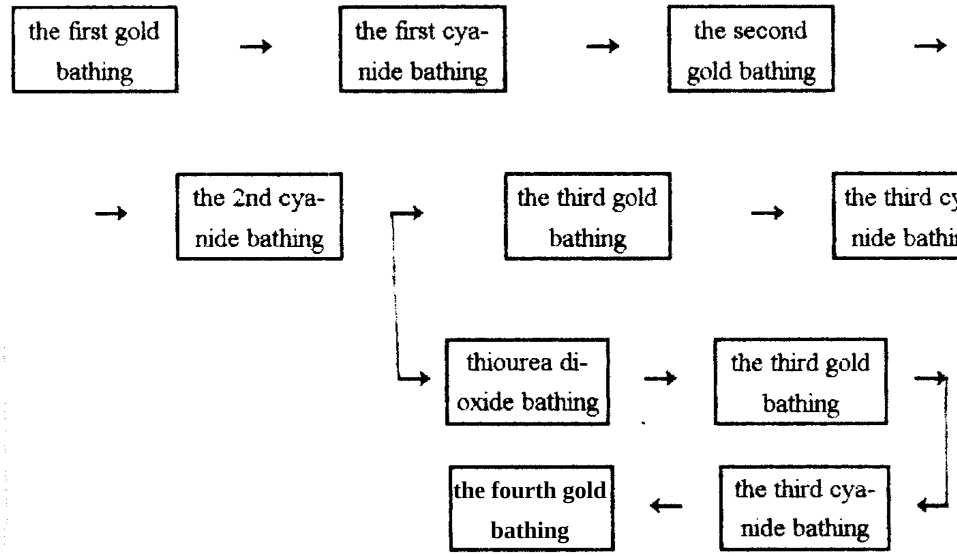


Figure 1. Bathing procedure for coated Emulsion F1-2.

and Rh^{+3} content of 20 mg per mole silver halide. The shell was silver bromochloride with bromide content of 18 mol% and Rh^{+3} content of 30 mg per mole silver halide. The mole ratio of the core to shell was 1:1.3. Observation by electron microscopy showed that the core–shell grains were monodisperse with cubic core and cubic shell. The average edge size of the shell was 0.3 µm.[10]

Emulsion Fogged by Exposure and Chemical Reduction. The coated primitive emulsion samples were exposed for varying times, then the samples were developed by surface and internal developers, respectively.

The primitive emulsion was chemically fogged by thiourea dioxide alone and thiourea dioxide plus gold salt, respectively. The amounts of the fogging agents are listed in Table I. For the first part of this study, each fogging treatment was carried out at 50°C with varied times. After fogging treatment, the coated emulsion samples were developed by surface and internal developers, respectively. For the other two parts of the study, the fogging treatment was continued at 50°C until a certain fog density was reached, then a small amount of 4-hydoxyl-6-methyl-1, 3,3a,7-tetraazaindene, TAI, was added to stop fogging.

The surface developer was D-72, the internal developer was D-72 plus KI (1 g per liter development solution), and all developments were performed at 20°C for 4 min.

Effect of Silver Halide Solvent on the Fog Center. To find the effect of a silver halide solvent on the fog center, potassium thiocyanate and potassium bromide were added to emulsions F1-2 and F2-2, respectively. The amounts of the two chemicals are shown in Table II. The fog densities were measured after surface development and normal fixing.

Deposition of Gold on the Fog Center. The coatings of both emulsions F1-2 and F2-2 were alternately immersed into sodium cyanide and gold salt solutions. Each bathing was 9 min. After each bathing, the samples were washed with a potassium bromide solution two times (30 s for the first and 4.5 min for the second). The flow charts of bathing procedures are shown in Figs. 1 and 2. The three solutions used in this study (sodium cyanide, gold salt, and potassium bromide), were slightly different from those used in Ref. 8.

The stock sodium cyanide solution was prepared by first mixing 9 ml of 2.5 mol/l sodium hydroxide, 2.5 ml of 1 mol/l acetic acid, and water to make 1 L. KCN (38 mg) was then dissolved in this solution. The working solution was obtained by diluting the stock solution before use. The concentration of the working solution was determined by experiments. The maximum concentration that did not decrease the density of the silver image without gold was used for bathing.

The composition of the stock gold-salt solution was chloroauric acid 30 mg, potassium thiocyanate 350 mg, potassium bromide 300 mg, and water to make 1 L. The work solution was prepared by a 1:10 ratio of diluting the stock solution.

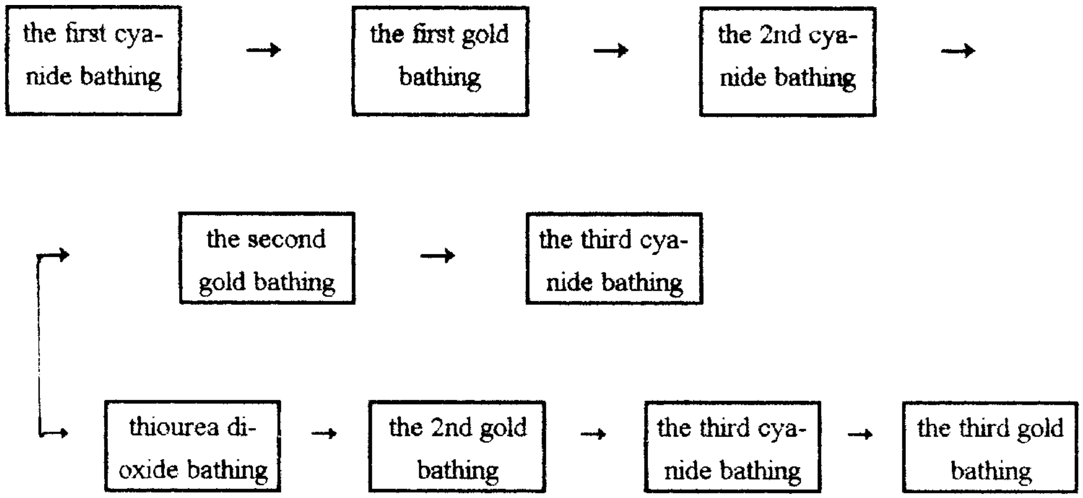


Figure 2. Bathing procedure for coated Emulsion F2-2.

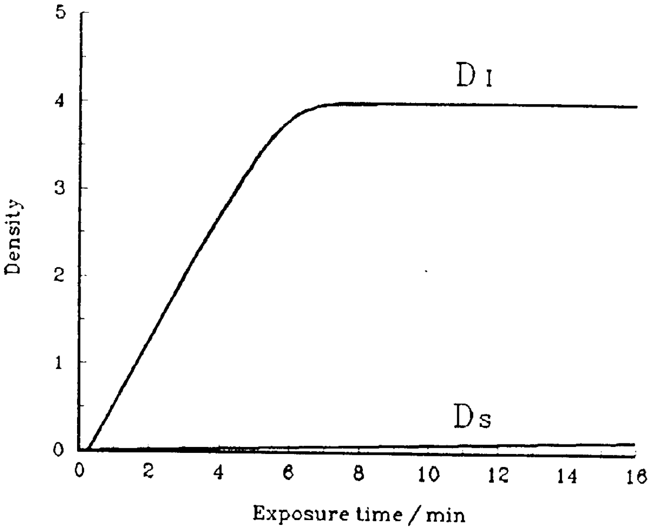


Figure 3. The fog density versus exposure time when photofogged. Curve D_S—surface development, Curve D_I—internal development.

The concentration of the potassium bromide solution used for washes after each bathing was 0.5 g potassium bromide per liter.

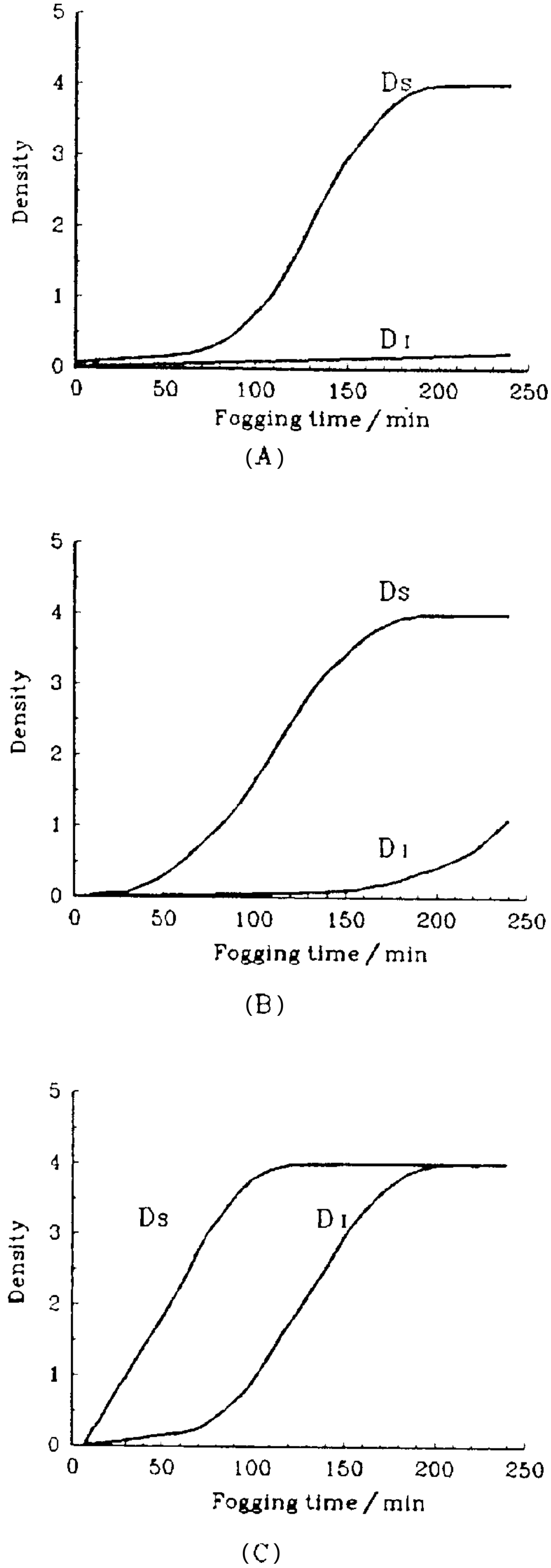
All the baths and washes were replicated at room temperature. Gold baths and KBr washes were agitated by bursts of nitrogen. Every bathing experiment was done four times for each emulsion. After processing, the densities of each step were measured and averaged.

Results and Discussion

Behavior of Photoelectrons and Electrons Provided by a Fogging Agent. When the emulsion that had not been chemically fogged was photofogged, both the surface and the internal fog densities varied with fogging time. The dependency of the surface and internal fog densities of the emulsion on photofogging time (exposure time) are shown in Fig. 3. When the silver halide crystal is exposed, the photoelectrons can be excited to the conduction band where they can move about within the crystal and are preferably trapped by the lattice imperfections at the interface between the core and the shell, forming internal latent images. Very few surface latent images were formed on the shell, even when the exposure time was prolonged.

When the same emulsions were chemically fogged, the results were quite different. Both the surface and the internal fog densities varied with the chemical fogging time as shown in Fig. 4 for emulsions F1-1 to F1-3 and in Fig. 5 for emulsions F2-1 to F2-3. Figures 4 and 5 indicate that for both chemical fogging methods the fog centers were not preferably formed at the interface between the core and the shell, although there were a lot of deep electron traps. Instead, fog centers were preferably formed at the grain surface. The internal density increases only after the surface density reaches a certain value (For example $D_s = 4$ for emulsions F1-2, F1-3, F2-2, and F2-3, as shown in Figs. 4(b), 4(c), 5(b) and 5(c), respectively). The formation of the internal fog center always lags behind that of the surface fog center. When the amounts of fogging agent and gold salt are small, the formation rate of the surface fog center is low and few internal fog centers can be formed as shown in Figs. 4(a) and 5(a) for emulsions F1-1 and F2-1, respectively. The rate rises with increasing amounts of fogging agent and gold salt and so does the formation rate of the internal fog centers. The retardation time of the formation of the internal fog center decreases, as shown in Figs. 4(a) to 4(c) and 5(a) to 5(c).

James[2] thought that the developer interacted with silver halide to form isolated silver atoms or to transfer electrons to surface states. The atoms or electron-occupied surface states could then thermally dissociate to inject electrons to the conduction band of silver halide. Similarly, when the emulsion is fogged by a fogging agent, which reduces the surface silver ions to silver atoms, the surface fog centers are formed first. When some of the silver atoms thermally dissociate, electrons can be transferred to the conduction band and trapped at the interior of the grain. However, because the silver halide grains were Rh^{3+} doped in this study, the incorporated Rh^{3+} ions provided internal sinks for electrons and Ag_0^+ ions that could otherwise combine to give Ag atom or Ag_2 molecules.[1] The electrons transferred from surface silver atoms might be competitively trapped by Rh^{3+} instead of forming internal fog centers. When the surface fog center grows to a certain size, there are then enough electrons in the interior

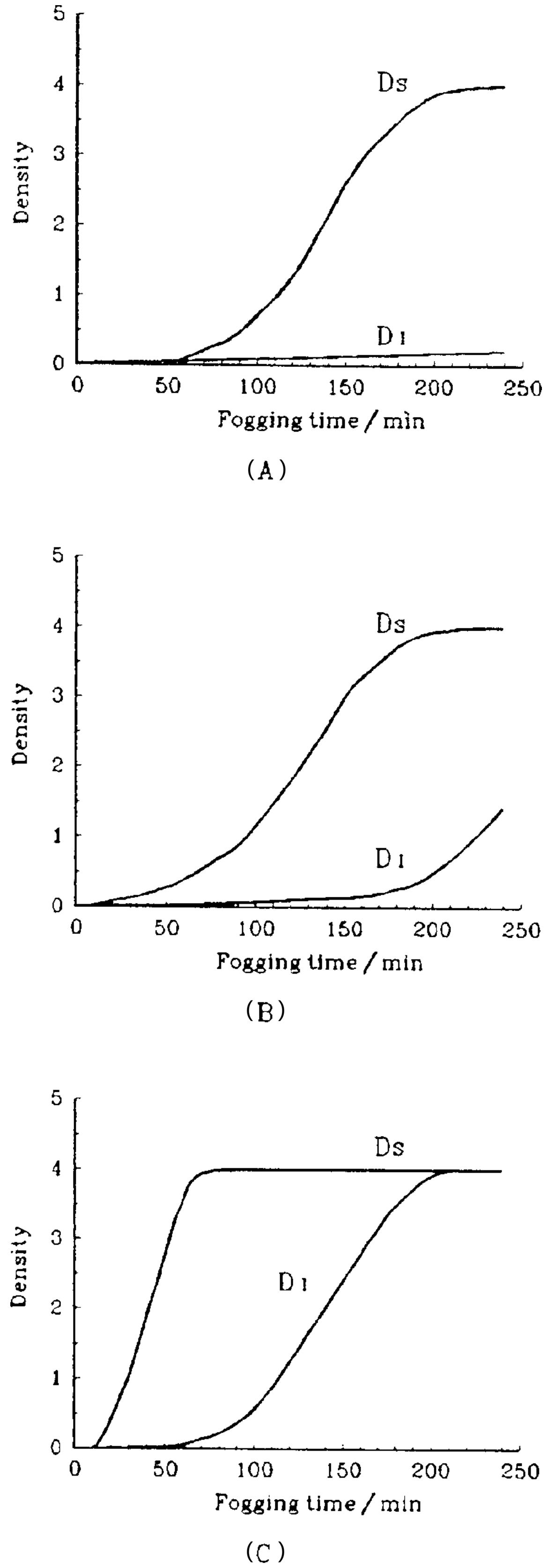


(A)

(B)

(C)

Figure 4. Fog density versus fogging time when fogged by thiourea dioxide alone: (a) Emulsion F1-1, (b) Emulsion F1-2, and (c) Emulsion F1-3, D_S—surface development, D_I—internal development.



(A)

(B)

(C)

Figure 5. Fog density versus fogging time when fogged by thiourea dioxide plus gold salt: (a) Emulsion F2-1, (b) Emulsion F2-2, (c) Emulsion F2-3, Curve D_S—surface development, Curve D_I—internal development.

of the grain to form internal fog centers. These two factors cause the retardation of the formation of internal fog centers. Therefore, during the formation and growth of the internal center, electrons indirectly come from the fogging agent. Thus, the transfer is quite different from that of the electron induced by light and the preferable fog location formed by the fogging agent is different from that formed by photofogging.

Effect of Silver Halide Solvent on the Fog Center. The addition of a silver halide solvent after fogging can increase the fog density for both emulsions F1-2 and F2-2, but the increment depends on the solvent and the fogging method, as illustrated in Table II. Table II shows that the effect of KSCN is less than that of KBr and the response of the emulsion fogged by thiourea dioxide plus gold is less than that of the emulsion fogged by thiourea dioxide alone.

Collier[11] proposed that when a silver halide solvent, NaSCN or NaBr, was added to a reduction-sensitized AgBr emulsion, a small amount of AgBr might dissolve on a microscopic level and some nondevelopable silver centers might migrate together forming developable fog centers. The situation is similar in this study. The small nondevelopable fog centers may aggregate to form developable fog centers under the effect of the solvent, resulting in an increase of fog density.

TAI was added to stop the fogging treatment. TAI molecules are adsorbed to the silver halide crystal as its silver salt and can retard Oswald ripening of the silver halide crystal in which the rate-determining step is silver halide dissolution. Therefore, restraint of AgBr dissolution rate by TAI may be the main cause of the restraint of the fog center formation. Bromide ion can compete with TAI^- for being adsorbed on the silver halide crystal.[12] When KBr is added, Br^- can replace TAI^- so that the dissolution of silver halide and the coalescence of nondevelopable fog centers is prompted. However, SCN^- cannot compete with TAI^-. The effect of KBr on the fog density is thus greater than that of KSCN.

The fact that the response of Emulsion F2-2 to the solvent is less than that of Emulsion F1-2 seems to indicate that the size distribution of the fog center is wider, and more nondevelopable fog centers exist on the grain surface for the emulsion grain fogged by thiourea dioxide alone than for the emulsion fogged by thiourea dioxide plus gold. The addition of silver halide solvent may help small nondevelopable fog centers to migrate together forming developable ones so that the increment of the density for emulsion fogged by thiourea dioxide alone is greater. This result suggested that the addition of gold salt in the fogging treatment could reduce the number of nondevelopable fog centers and reduce the dispersity of fog centers. Fewer fog centers and narrower size distribution of fog centers are favorable to the bleach of fog centers by positive holes and hence to increasing the sensitivity of the direct positive emulsion. Further study on the size distribution of the fog centers is necessary to confirm the supposition.

Deposition of Gold on the Fog Center. All the bathing experiments were replicated four times for each emulsion. The data points in Figs. 6 and 7 are the average values of the four experiments. The maximum density deviations were 0.11 for higher densities and 0.06 for lower densities. Certainly, the deviations are far less than the differences between the two density levels before and after bathing.

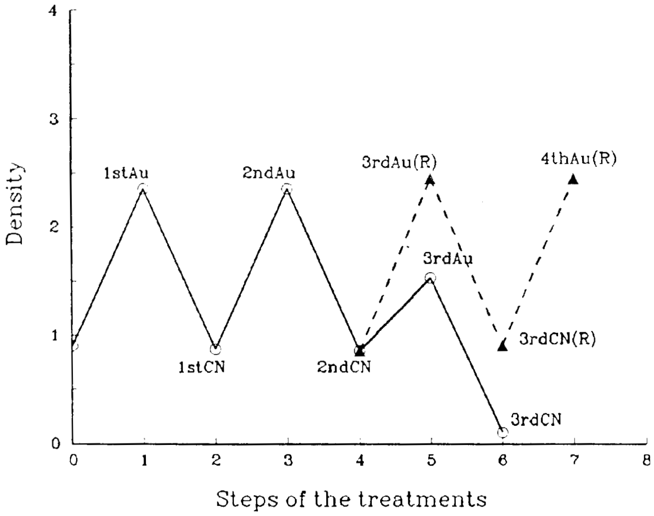


Figure 6. Densities of coated Emulsion F1-2 after each bathing. (R), triangles and dashed lines represent that the sample was bathed after the treatment of the thiourea dioxide solution.

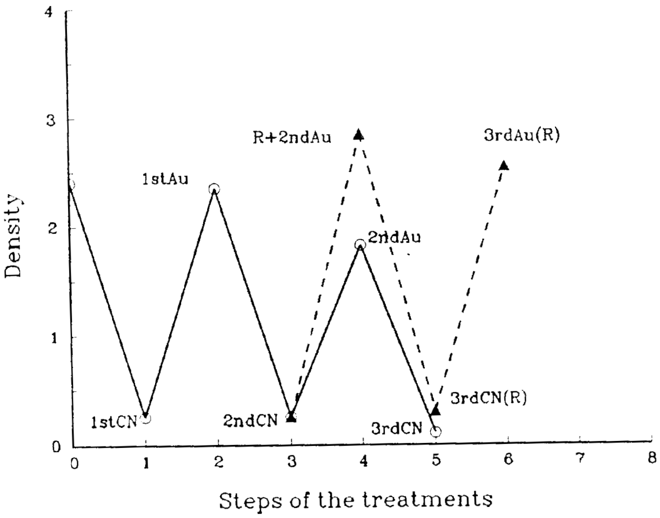


Figure 7. Densities of coated Emulsion F2-2 after each bath. (R), triangles and dashed lines represent that the sample was bathed after the treatment of the thiourea dioxide solution.

In comparison with Spencer's experiments,[8] two main differences exist. First, Spencer's work was on negative emulsions while our study dealt with prefogged direct positive emulsions. Second, we extended the number of gold and cyanide cycles so our results could show whether replacement or plating was the more important process was dependent on the amount of the fogging agent.

For Emulsion F1-2, fogged by thiourea dioxide alone, the fog densities after each of the gold and the cyanide baths are shown in Fig. 6 (circles and solid lines). Figure 6 shows that after each of the first two gold baths, the fog density increases to the same value and after each of the first two cyanide baths the fog density decreases to the same lower value. However, after the third gold bath the fog density increases to a lower value than before, and after the third cyanide bath the fog density goes down to just 0.1. Thus, the increase of the fog density in the first two gold baths is mainly due to the plating of gold atoms on the fog centers. The replacement of silver atoms contained in the fog center by gold atoms contributes very little to the gain of density. Thus the size of the fog center, after each cyanide bathing that removes gold atoms only, does not decrease, as compared with that before gold bathing. Hence, the fog density can return to the same value. In the third gold bath, the increase of the fog density may result from the replacement of silver atoms by gold atoms, because by this time the residual fogging agent in the emulsion layer has been used up by reducing gold ions to gold atoms in the first two gold baths and also washed out by the KBr solution. The fact that after the third cyanide bath the fog density goes down to just 0.1 can also prove that in the fog center some silver atoms have been replaced by gold atoms. After removing gold atoms by the third cyanide bath, the sizes of the fog centers decrease and some fog centers become nondevelopable so that the fog density decreases a lot.

To confirm that the gold atoms can plate on the fog centers, another experiment was done. After the second cyanide bath but before the third gold bath, the sample was bathed by a thiourea dioxide solution (50-mg thiourea dioxide per liter) for a time to increase the content of the fogging agent in the emulsion layer, but the fog density did not increase after this bathing. When the third gold bath was carried out, the fog density increased to the same higher value as with the first two gold baths. The results are shown in Fig. 6 by triangles and dashed lines. The third cyanide bath and the fourth gold bath showed results similar to that of the first two gold and cyanide baths, respectively.

Emulsion F2-2, fogged by thiourea dioxide plus gold, was first treated by a cyanide bath. The densities after each cyanide bath and gold bath are shown in Fig. 7 (circles and solid lines). Fig. 7 indicates that the fog density of the sample decreases from 2.36 down to 0.23 after the first cyanide bath indicating a lot of gold atoms are contained in the fog center. The increase of the fog density after the first gold bath is also mainly due to the plating of gold atoms on the fog centers. Because after the first gold bath the density increases to the same value as obtained by the initial fogging treatment, the reaction mechanism of the fogging treatment by thiourea dioxide plus gold is the same as that of the gold bath, i.e., the plating of gold on the fog center is the main reaction in both cases. The density after the second cyanide bath is almost the same as that after the first cyanide bath. However, after the second gold bath the density does not reach a level as high as that after the first gold bath. Afier the third cyanide bath, the density decreases to 0.08. In comparison with Emulsion F1-2, the amount of the fogging agent was much less when emulsion F2-2 was fogged. When the sample of Emulsion F2-2 was bathed in the second gold bath, there was much less residual fogging agent in the emulsion layer. The replacement of silver atoms by gold atoms became the main reaction, resulting in a lower density value (0.08) after the third cyanide bath.

If the sample was treated by thiourea dioxide solution (50-mg thiourea dioxide per liter) after the second cyanide bathing, but before the second gold bath, to increase content of the fogging agent in the emulsion layer, and then was treated by the second gold bath, the fog density increased again to a value even a little bit greater than obtained by the first gold bath. The results are shown in Fig. 7 by triangles and dashed lines. The third cyanide bath and the third gold bath showed results similar to that of the first cyanide and gold baths. Whether gold atoms plate on the fog center or replace silver atoms contained in the fog center depends on the amount of the fogging agent present. If there is enough fogging agent, plating is the main reaction, otherwise replacement may occur. When a direct positive emulsion is fogged by a fogging agent plus gold, because of the great quantities of fogging agent gold ions are reduced to gold atoms that deposit with silver atoms forming fog centers.

Conclusion

In this study the location of the fog centers formed by photofogging is found to be different from that formed by a chemical fogging agent. When the Rh^{3+} doped, core-shell emulsion is photofogged the fog centers are preferably formed in the interior of the silver halide crystal indicating that photoelectrons can be transferred to the conduction band of the silver halide crystal directly. When the emulsion is fogged by a fogging agent, the internal fog centers are formed only where there is sufficient fogging agent, and the formation of the internal fog centers lags behind formation of the surface fog centers. Thus electrons provided by the fogging agent enter the conduction band indirectly. Addition of silver halide solvent can increase the fog density. In the fogging treatment, gold salt seems to make the fog center distribution narrower. When enough of the fogging agent is present in the emulsion, the plating of gold on the fog center is the main reaction, otherwise replacement occurs. Therefore, when a direct positive emulsion is fogged by a fogging agent plus gold, the gold ions are reduced to gold atoms that deposit with silver atoms, forming bimetallic fog centers.

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