The Effects of Iodide Addition on Fog Characteristics of Cubic Silver Bromide Grains

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Dependence of fog on chemical sensitization and iodide amount in cubic AgBr emulsions has been studied. Similar fog curve shapes were obtained from the iodide-covered AgBr emulsions by varying the iodide amount and the sulfur-sensitized AgBr emulsions by varying the sulfur amount. Subsequent gold sensitization of the two kinds of emulsions produces two fog peaks in the curves with varying the iodide or sulfur amount. The surface properties of the emulsion grains have been discussed with reference to fog formation. The origin of fog is attributed to the reactivity difference between the chemical site and the bulk crystal surface. The reactivity sequences of different chemical sites were derived: $Ag_2S > AgI > AgBr > AgCl$ and $Au_n > Ag_n$, etc. Direct electron transfer development (DETD) and indirect electron transfer development (IETD) were supposed to be the two processes in development. Based on the proposed mechanisms, the main experimental results were successfully explained with a distribution model of chemical impurities at the cubic AgBr grain surface.

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Introduction

Sulfur and gold sensitization of silver halide emulsions are important methods to modify the surface properties of microcrystals. Birch, Farnell, and Flint¹ reported that development centers are formed preferentially on cubic faces for unsensitized AgBr grains of cubo-octahedral shape and shifted to octahedral faces on sulfur sensitization. These authors¹ observed a web-like deposit on the octahedral surfaces of the sulfur sensitized grains. A similar deposit was proved to be Ag₂S by Aznárez.² Moisar^{3,4} also observed that sulfur digestion leads to a higher dispersion of Ag₂S specks at (111)-faces than at (100)-faces. During gold sensitization, silver ions in the Ag₂S specks are replaced by gold.⁵ Tavernier and Faelens⁶ also reported that Ag₂S reacts in vitro with Au(III) ions. Many authors⁷⁻⁹ noted that gold increases the developability of the smallest silver specks. In the presence of sulfur sensitivity specks, gold lowers the size of silver specks required for development,⁹ etc. There is no need to repeat all the results for sulfur and gold sensitization. Good reviews on sulfur, gold, and sulfur-plusgold sensitization have been presented by Muller,10 Moisar,¹¹ Mitchell,¹² Spencer, Atwell, and Levy,¹³ and Kuge.14

The existence of iodide in silver halide grains is another factor influencing the properties of crystalline surfaces. Iodide-rich islands¹⁵ or discontinuous iodide-rich layers¹⁶ on crystalline surfaces can be obtained with different methods. It was reported by Hu, Wang, and Peng¹⁷ that sulfur specks are formed preferentially at iodiderich regions of T-grains. Li and Wang¹⁵ also proved by STEM-EDS analysis that sulfur sensitization leads to higher sulfur content at iodide-rich islands of a cubic silver halide emulsion. Great interest in studying the physical and chemical behavior characteristics of iodide in silver halide microcrystals has been shown by many other authors.¹⁸⁻²⁶

It can be concluded from the above comments that sensitization specks may be selectively formed at certain sites on grain surfaces. Because development also commences at separate sites on the grain surface, we may thus ask: Is there any connection between the sensitization specks and the development sites? How do the chemical impurities (iodide, sulfur and gold, etc.) at grain surfaces influence the development?

The purpose of this work is to study, according to the fog characteristics of emulsions, the influence of chemical impurities at grain surface on development. The surface properties are especially taken into account to understand the development mechanism.

Experimental

Monodispersed cubic AgBr emulsion with roughly 0.74 μ m edge length was used for studying the surface properties and fog characteristics. The emulsion was divided into several parts, and 0.03 to 10000 μ mol KI per mole AgBr was added separately into each part for the surface halide displacement at 70°C for 30 min. A series of emulsions was then obtained with different surface iodide content (Emulsion Series I).

Similar experimental steps as above were carried out except that the amount of $AgNO_3$ equivalent to KI was added simultaneously into each part of the emulsion. Another series of emulsions was thus obtained with different surface iodide content (Emulsion Series II).

The two series of iodide-covered emulsions were treated, at 70° C for 60 min, with different amounts of sodium thiosulfate for sulfur sensitization (S), differ-

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TABLE I. Formula of Surface Developers for Fog Development, (30 min at 20° C)

	M-AA-1	M-AA-a	M-AA-b	
Metol	2.5 g	2.5 g	2.5 g	
Ascorbic acid Potassium bromide	10.0 g	10.0 g	10.0 g	
Sodium metaborate	35.0 g	35.0 g	35.0 g	
Distilled water to make	1000 mL	1000 mL	1000 mL	



Figure 1. Relationship between pAg and iodide amount in the two series of iodide-covered AgBr emulsions: Series I — KI were added; Series II — equivalent amount of $AgNO_3$ and KI were added.

ent amounts of gold-nitrilotriacetic-acid (Au-NTA) complex for gold sensitization (Au), and different amounts of sodium thiosulfate plus Au-NTA for sulfur-plus-gold sensitization (S+Au). Emulsions without chemical sensitization are represented as (U).

For comparison, sulfur and sulfur-plus-gold sensitizations of pure AgBr emulsions were also carried out.

The emulsions were coated at about 10 g of silver per square meter. They were developed in doubly diluted D-72 developer, for 5 min at 20°C without exposure, to measure fog density. Three M-AA developers (listed in Table I) with different amounts of potassium bromide were also used to study the surface properties and fog characteristics of the emulsions.

Experimental Results

The Fog Variation Tendencies of the Two Emulsion Series. The formation processes of surface AgI in Emulsion Series I may be different from that in Series II. The former is a process of surface bromide displaced by iodide, while the latter may be a process of silver iodide growing onto the grain surface. Suppose the two methods produce a roughly equivalent number of chemical sites (in the same size distribution) on the grain surface when the same amount of iodide is added. The obvious difference is that their pAg values at high iodide level are greatly different (see Fig. 1).

As a comparison of the two methods, Figs. 2 and 3 demonstrate the fog variations of the two Emulsion Series on different chemical sensitization. They show the similar fog variation tendencies with changing iodide amount. The (U)- and (S)-emulsions (small sulfur amount) hardly produce any fog in D-72, while the (Au)-



Figure 2. Dependence of fog on the iodide amount in Emulsion Series I at each chemical sensitization condition.



Figure 3. Dependence of fog on the iodide amount in Emulsion Series II at each chemical sensitization condition.

and (S+Au)-emulsions produce high fog levels and two fog peaks appear in the curves with varying iodide amount. The influence of pAg on the fog variation tendencies was not significant.

Though bromide should influence fog formation, it did not influence the fog variation tendencies of the two series of emulsions. Subsequently, the slight fluctuation of bromide concentration in emulsions was neglected for studying the fog characteristics, especially in a bromiderich developer such as D-72. Therefore, the following fog results are based only on Emulsion Series I.

The Fog of (U)-Emulsions. Though the fog of (U)-emulsions is very small, the influence of iodide amount at AgBr surface on the fog variation was observed with three M-AA developers. On reducing the bromide concentration in the M-AA surface developer, both Figs. 4 and 5 clearly show that the fog of (U)-emulsions increases slightly at high iodide levels with increasing iodide amount. This result suggests that chemically active sites exist at high iodide-covered cubic AgBr grains, but the activity of the sites is readily lowered by bromide.

The Fog of the (S)-Emulsions. Figure 6 shows the fog curves of (S)-emulsions. The amount of sulfur sensi-



Figure 4. Dependence of fog on the iodide amount in Emulsion Series I in surface developers.



Figure 5. Dependence of fog on the iodide amount in Emulsion Series II in surface developers.

tizer for each curve is constant with varying iodide amount. It reveals that the fog increases with increasing sulfur amount, but the curve shape does not significantly change with varying iodide amount. In other words, the fog value for each amount of sulfur usage keeps roughly constant with increasing or decreasing the iodide.

The Fog of (Au)-Emulsions. Figure 7 shows the fog curves of (Au)-emulsions. It demonstrates that small amounts of gold sensitizer (less than 6.5 μ mol/mol Ag) hardly produce any fog, and high fog values appear with increasing gold amount at each iodide level. The curve shapes for gold over-sensitized emulsions show two peaks with varying iodide amount. However, the fog variation is not completely proportional to gold at each point. The fog increases with increasing gold amount at low iodide levels, but large amounts of gold sensitizer leads to fog decrease at middle to high iodide levels. Therefore, fog variation in the (Au)-emulsion largely depends on both the iodide and the gold amount at emulsion grain surfaces.

The Fog of (S+Au)-Emulsions. Figure 8 shows the fog curves of (S+Au)-emulsions. The amount of either gold or sulfur sensitizer is constant for each curve with varying iodide amount. As with (Au)-emulsions, most of the



Figure 6. Influence of iodide amount on fog in sulfur-sensitized AgBr emulsions.



Figure 7. Fog as a function of iodide amount at different levels of gold in sensitized AgBr emulsions.



Figure 8. Fog as a function of iodide amount at varying amounts of sulfur-plus-gold in sensitized AgBr emulsions.

fog curves of (S+Au)-emulsions exhibit two peaks with varying iodide amount, except that the position of the first peak at low iodide level is extended toward higher iodide levels, but that of the second fog peak does not shift. The relative fog density at each iodide level changes irregularly with increasing sulfur amount.



Figure 9. Dependence of fog on the amount of sulfur sensitizer in the sulfur and the sulfur-plus-gold sensitized AgBr emulsions.

The Fog of Sulfur-Sensitized AgBr Emulsions. Complicated fog results were obtained by sulfur, gold and sulfur-plus-gold sensitization of iodide-covered emulsions. Figure 9 shows the influence of sulfur and sulfur-plus-gold sensitization on the fog of cubic AgBr emulsions. In the case of sulfur sensitization (see the curve "no Au" in Fig. 9), the fog increases sharply when the amount of sulfur sensitizer reaches a certain level. This is consistent with the common knowledge of sulfur sensitization.

The fog curve shape for sulfur-sensitized emulsions is similar as that of (U)-emulsions, though the fog of the (U)-emulsions is very small. Figures 2 and 4 also demonstrate a slight fog increase at high iodide level of the (U)-emulsions. This similarity implies that the sites with components of both silver iodide and silver sulfide at AgBr grain surface may act as reactive fog centers. However, the maximum fog of sulfur-sensitized AgBr emulsions is much larger than that of iodide-covered AgBr emulsions. The minimum sulfur amount initiating a fog increase is hundreds of times less than that of iodide (see Figs. 2, 4 and 9). Therefore, the interaction mechanisms of sulfur center and iodide center with developer may be somewhat similar, but the reactivity of sulfur centers is much higher than that of iodide centers.

The Fog of Sulfur-Plus-Gold Sensitized AgBr Emul-

sions. In the case of sulfur-plus-gold sensitization, Fig. 9 shows that the addition of a relatively small amount of gold sensitizer (less than $6.5 \,\mu$ mol/mol Ag) decreases the fog density at the high sulfur level, but a large amount of gold sensitizer (more than 10 μ mol/mol Ag) greatly increases fog density at each sulfur level, and two fog peaks appear. This is similar to the (Au)-emulsions, which implies that silver iodide and silver sulfide may function similarly in the process of gold sensitization and development.

Discussion

From the above experimental facts, we conclude that fog varies with composition and amount (which may affect the deposit size and dispersion) of chemical impurities at crystalline surfaces. Therefore, several questions are raised by our results; how to explain: (1) the similarity of the fog curve shapes between the (U)-emulsions and the sulfur-sensitized AgBr emulsions; (2) that the sulfur centers are much more reactive to developing agents than iodide centers; (3) the appearance of two fog peaks; and (4) the similarity of the fog curve shapes between the (Au)-emulsions and the sulfur-plus-gold sensitized AgBr emulsions. Obviously, proper answers to these questions depend on our detailed knowledge of why the introduction of such chemical impurities at the AgBr surface results in the formation of fog.

Surface Properties and the Ionic Concentration

Sequence. The experiments have demonstrated that the surface Ag_2S site is much more reactive to developer than the AgI site, which means that the reactivity sequence of the surface sites is $Ag_2S > AgI > AgBr$. Because silver ions and developer agents are the entities of development, the introduction of chemical impurities should have resulted in activity variation of the silver ions at these surface sites. The following concentration sequences were thus derived based on the subsequent discussion: $[Ag^+]_{silver sulfide} > [Ag^+]_{AgI} > [Ag^+]_{AgBr} > [Ag^+]_{AgCI}$, $[Au^+]_{silver sulfide} > [Red]_{AgI} > [Au^+]_{AgBr} > [Au^+]_{AgCI}$ and $[Red]_{silver sulfide} > [Red]_{AgI} > [Red]_{AgBr} > [Red]_{AgCI}$. Ag⁺ and Au⁺ represent the surface adsorbed ions and "Red" represents the developing agent adsorbed at different surface sites.

Influence of Water on the Stability of Silver Halide. Silver halides are not ideal ionic crystals. It is important to consider their covalent character simultaneously with discussion of the microcrystal properties.²⁷ The ionic character sequence is AgCl > AgBr > AgI, and the covalent character sequence is AgCl < AgBr < AgI.

The ionic and covalent character of silver halide may affect its stability in a solvent. Table II shows that the stability sequence of silver halides in the gas phase is AgCl > AgBr > AgI, but in water it is AgCl < AgBr < AgI. This means that the least stable AgI species in the gas phase becomes the most stable one in water. According to the principle of the hydrophobic effect,³⁰ the more covalent character a compound has, the more hydrophobic it is. In other words, the compound with more covalent character may be more stable in water and easier to dehydrate. In a previous work,³¹ we showed that the dehydration sequence of silver halide is AgI > AgBr > AgCl, according to their hydrophobic character. Therefore, the reverse stability sequence of silver halides in water and gas phase may be attributed to the solvent effect³² of water.

Theoretical Account of the Stability Sequence. The empty bonds of microcrystal surface may interact with gelatin, solvent, bromide, and other ions by forming Lewis acid-base complexes, even before developing agents approach it. Therefore, the stability of these compounds

TABLE II. Bond Energy and Dissociation Constants of Silver Halide

	Strength of the chemical bonds ²⁸ (kJ mol ⁻¹ at 25°C)	Dissociation constants ²⁹ in water at room temperature (pK)			
AgCl	341.4	3.3			
AgBr	293±29	4.5			
Agl	234±29	7.5			

TABLE III. Frontier Orbital Energy by I	Klopman'	s Calculation
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	F-	H ₂ O	OH⁻	Cl⁻	Br⁻	SH⁻	I-
$E_m(eV)$	-12.8 Ca ²⁺	−10.73 Fe³+	-10.45 Fe ²⁺	–9.94 H⁺	–9.22 Na⁺	-8.59 Ag⁺	–8.31 Au⁺
<i>E</i> _{<i>n</i>} [*] (eV)	2.33	2.22	0.69	0.42	0	-2.82	-4.35

TABLE IV. Nucleophilic Order (from Ref. 32)			
E _n *	Nucleophilic order		
-7 -5 +1	HS > I ⁻ > Br ⁻ > CI ⁻ > HO ⁻ > F ⁻ HS > I ⁻ > HO ⁻ > Br > CI ⁻ > F HO ⁻ > HS > F > CI ⁻ > Br > I		

and complexes is of great importance for development.

The stability sequences of different compounds in water may be explained by the principle of hard and soft acids and bases³³ (HSAB). HSAB says, based on numerous experimental facts, that the interaction between compounds obeys the rule of hard acid preferentially reacting with hard base and soft acid preferentially reacting with soft base. Klopman³² agrees with the HSAB principle and describes a general treatment of chemical reactivity with a polyelectronic perturbation theory involving both reactants and solvent. In Klopman's view, when two reactants approach each other, a mutual perturbation of the molecular orbitals of both reactants occurs. The total energy variation in a Lewis acid-base reaction can be evaluated by three terms: electrostatic, covalent, and solvent terms. The nucleophilic order and the relative reactivity (or stability of complexes in solution) will be determined by the empty frontier orbital energy of acceptors (E_n^{*}) and the occupied frontier orbital energy of donors (E_m^{*}) . According to Klopman's calculations, the nucleophilic order of the anions changes with the variation of the empty frontier orbital energy of cations. The frontier orbital energy and nucleophilic order are separately listed in Tables III and IV. As examples, the stability sequences of several types of compounds in water solution are given: $CaF_2 > CaCl_2 >$ $CaBr_2 > CaI_2$; HF > HCl > HBr > HI; AgCl < AgBr < AgI $< Ag_2S; AuCl < AuBr < AuI < Au_2S; Au_2S > Ag_2S, and$ AuI > AgI.

The Stability Sequence of Selective Adsorption. There are a large number of empty bonds at the microcrystal surfaces of AgCl, AgBr, AgI, and Ag₂S. These empty bonds will selectively bind certain ions or molecules. According to the nucleophilic order shown in Table IV, both Au⁺ and Ag⁺ should be preferentially bound by sulfur or by iodide at the silver halide surface. A surface site with a component of silver and/or gold should preferentially bind sulfide or iodide anions for the same reason. According to HSAB principle, the stability sequences for adsorbed ions are listed as follows.

 $\begin{array}{ll} \mbox{for } Ag^{+}, \ AgCl-Ag^{+} < AgBr-Ag^{+} < AgI-Ag^{+} < Ag_2S-Ag^{+} \\ AuCl-Ag^{+} < AuBr-Ag^{+} < AuI-Ag^{+} < Au_2S-Ag^{+} \\ Ag_2S-Ag^{+} < Au_2S-Ag^{+} \\ AgI-Ag^{+} < AuI-Ag^{+}, \\ \mbox{for } Au^{+}, \ AgCl-Au^{+} < AgBr-Au^{+} < AgI-Au^{+} < Ag_2S-Au^{+} \\ AuCl-Au^{+} < AuBr-Au^{+} < AuI-Au^{+} < Au_2S-Au^{+} \\ AgI-Au^{+} < AuI-Au^{+}, \\ \mbox{for } I^{-}, \ I^{-}AgI < I^{-}Ag_2S \\ I^{-}AuI < I^{-}Au_2S \\ I^{-}Au_2S < I^{-}Au_2S \end{array}$

We note from the nucleophilic order shown in Table IV that the OH⁻ ion is also essential to the silver halide system. Exposing a silver halide grain to high pH leads

 $I^{-}-AgI < I^{-}-AuI.$



Figure 10. Scheme for the surface charge layers of AgBr, AgI, Ag_2S , and their surface charge variation with varying pAg and with positively charged gold ions: (a) at a low pAg, such as 9 at 25°C; (b) at a high pAg, such as 10 at 25°C; (c) silver ions or gold salts are added into (a).

to the formation of AgOH and Ag_2O at the grain surface, which may be one origin of both surface sensitivity and fog.

Surface Charge and the Concentration Sequence of the Surface Adsorbed Silver Ions. Fatuzzo and Coppo^{34–36} supposed that, based on work on large single crystals of silver halides, a space charge layer is located in the sub-surface of the crystal. The space charge layer was suggested to be "positive" or "negative" depending not only on the impurity content and temperature but also on the composition of surroundings. Honig and Hengst^{37,38} also studied the dependence of the space charge layer of grains on the pAg of an electrolyte in contact with their surface. Levy and his co-workers^{39–41} agree with the space charge model.

According to the stability sequence of ionic adsorption, $AgCl-Ag^+ < AgBr-Ag^+ < AgI-Ag^+ < Ag_2S-Ag^+$, we propose a model of the surface adsorption sequence: there is a higher silver concentration on the surface of Ag_2S than on the surface of less stable AgI or AgBr. When these crystals are in water solution, their surface charge sequence (from positive to negative) is $Ag_2S > AgI > AgBr > AgCl$ (see Fig. 10).

The surface charge type depends on the ionic adsorption. According to the solubility products²⁹ of silver halides, the isoionic points pAg of silver halides should be 4.88 for AgCl, 6.16 for AgBr, 8.04 for AgI, and approximately 16.23 for Ag₂S. When AgBr, AgI, and Ag₂S are co-existing in a solution of pAg = 9 [see Fig. 10(a)], to keep the equilibrium between the solution and the bulk crystals, the intimate surface layer (Stern adsorption layer) of AgBr may contain excess adsorbed bromide ions $(pBr = 3.32; [Br^-] >> [Ag^+])$, and hence the surface is negatively charged. The intimate surface layer of AgI should be less negatively charged because fewer halide ions and more silver ions are adsorbed (pI = 7.08, [I⁻] > [Ag⁺]); and the surface layer of an Ag₂S crystal should be positively charged by adsorbing excess silver ions (pS $= 31, [Ag^+] >> [S^{2}]$). In other words, the concentration sequence of surface adsorbed silver ion is $[Ag^+]_{silver sulfide}$ $> [Ag^+]_{AgI} > [Ag^+]_{AgBr} > [Ag^+]_{AgCl}$. The concentration sequence of surface adsorbed gold(I) ions may be obtained by similar reasoning: $[Au^+]_{silver sulfide} > [Au^+]_{AgI} > [Au^+]_{AgBr}$ $> [Au^+]_{AgCl}$.

With increasing bromide concentration in solution, the

charge of each crystal surface will shift from positive to negative [Fig. 10(b)]. On the contrary, their surfaces may become more positively or less negatively charged by adding silver and/or gold ions [Fig. 10(c)].

Though our depiction on surface charge model agrees with Fatuzzo and Coppo's assumption³⁶ to a certain extent, we did not analyze the influence of interstitials and vacancies that are the basis of Fatuzzo and Coppo's model. Our concern is a real emulsion system and we believe that whether the surface is positively or negatively charged depends on the surface adsorption. pAg variation will change the surface adsorption character and hence the surface charge layer.

Accessibility Sequence of Developer Agent to the Crystalline Surfaces. It is easy for two separated hydrophobic groups to be "pushed" together by intermolecular forces in water. Therefore, a hydrophobic group may be more easily adsorbed by a more hydrophobic silver halide surface. For example, the fact of uncharged developer being adsorbed on a negatively charged silver iodide surface⁴² can be explained by the hydrophobic effect.

Because the dehydration sequence of silver halides is $Ag_2S > AgI > AgBr > AgCl$, the sequence for any hydrophobic group accessing the crystalline surface should be $Ag_2S > AgI > AgBr > AgCl$. As a result, the concentration of developing agent at the grain surface is not uniformly distributed. The concentration sequence of developer at different surface sites may be $[Red]_{silver sulfide} > [Red]_{AgI} > [Red]_{AgBr} > [Red]_{AgCl}$.

It has been demonstrated that the surface charge sequence (from positive to negative) is $Ag_2S > AgI > AgBr$ > AgCl. When developer anions diffuse near a sulfursensitized AgBr grain surface, they may be attracted to the positively charged silver sulfide speck and repelled from the negatively charged AgBr surface. If the speck is large enough, more developing agents may aggregate around the speck (Ag_2S) than on the AgBr surface. Therefore, the concentration sequence of developer at different surface sites may still be $[Red]_{silver sulfide} >$ $[\text{Red}]_{\text{AgI}} > [\text{Red}]_{\text{AgBr}} > [\text{Red}]_{\text{AgCl}}$, but the concentration difference is exaggerated. This means the selectivity of developing agents to these surface sites may be increased by increasing the negative charge on the developing agents. But, if the developing agents are positively charged, their concentration differences at different surface sites may be reduced and the selectivity decreased.

The Metallic Clusters. The concentration sequences of the surface adsorbed silver ions and developing agents can explain why the chemical impurities such as sulfur specks easily initiate development. With the exhaustion of adsorbed silver ions, metallic silver atoms or clusters will be formed and the chance of developer agents directly interacting with silver ions will be decreased. Whether the development continues is then dependent on the function of the newly formed silver atoms or clusters.

If silver or gold cluster exists on a AgBr grain surface, the surface of such site may be equally approachable by most of the surrounding chemicals, but the negative charge in the surface layer of the bulk crystal may repel the developer anions. Therefore, the developer agents will preferentially approach the metallic cluster.

On the other hand, electron transfer is a key process in the development. Because electron affinity (EA) is a measure for the affinity of the metallic cluster towards electrons, the EA data may be helpful in understanding the function of the metallic cluster during development. Ho, Ervin, and Lineberger⁴³ obtained the EA data of Ag_n (n = 1 to 10) and Au_n (n = 1 to 5) clusters by negative ion photoelectron spectroscopy. Several important suggestions may be derived by applying their major results to the silver halide system: (1) Owing to its very large EA (more than 1 eV), Ag_n (or Au_n) is an excellent electron acceptor. (2) An overall increase in EA occurs with increasing cluster size. The development may thus be accelerated by increasing the cluster size. (3) The EA's of Au_n are much larger than that of Ag_n ; This means that Au_n is a more excellent electron acceptor than Ag_n .

Development Mechanisms. A large amount of work has been done on photographic development. $^{\rm 44-49}$ However, there is not a single mechanism of development that has completely explained all the experimental phenomena in development. For example, the electrode theory explains most of the experimental facts by supposing that latent image is an electrode, but it neither proves that the very small silver cluster (latent image) can act like a general electrode, nor explains why large sulfur or gold specks at the silver halide surface produce high fog levels. The charge barrier theory explains developability by suggesting that the approach of developer ions to the developable nucleus is hindered or promoted by the surface charge of the grain, representing a special form of rate-determining transport process, but the existence of uncharged or positively charged developers shows this not to be the case.^{50,51}

These mechanisms were mainly based on the development of exposed silver halide grains, but the unexposed silver halide grain has been discussed less. The mechanistic proposals also paid less attention to the influence of surface composition, the solvent effect, etc. As is shown in our experimental results, the reactivity of different surface sites (I+Ag, I+S+Ag, I+Au+Ag, I+S+Au+Ag, etc.) may be very different. Because development is indeed a chemical process, an effective mechanism should try to discuss the development phenomena at both latent image and fog centers.

Electron transfer is a key process in both development of fog and of latent image. Consequently, some connections among the previous mechanisms of development may be established by analyzing the process of electron transfer. During development, developing agents are the electron donors, Ag⁺ and Au⁺ the electron acceptors. As discussed above, Ag_n and Au_n may also act as electron acceptors because of their high electron affinities. However, the final electron acceptor should still be the bound or free silver ion. Because gold and silver are also excellent electron conductors, it may be justified to suppose the metallic silver or gold clusters are electron conductors. As an electron conductor, the metallic cluster first obtains an electron from the developer and then immediately transfers the electron to any reactive interface between the cluster and the bulk crystal, where a lattice or interstitial silver ion accepts the electron. Therefore, development may occur in two ways-the silver ions directly or indirectly obtain electrons from the developing agent. We would call it direct electron transfer development (DETD) for $Ag^+ \leftarrow e^-$ Red and indirect electron transfer development (IETD) for $Ag^+ \xleftarrow{e} Ag_n$ \underbrace{e}_{e} Red or Ag⁺ \underbrace{e}_{e} Au_n \underbrace{e}_{e} Red. Red represents developer agents and \underbrace{e} indicates the electron transfer direction.

IETD. Pontius and Willis et al.^{52–55} demonstrated that silver grows in proportion to the surface of the individual silver centers and electron transfer at the electrode sur-

face is the rate-determining process of development. Many other authors⁵⁶⁻⁶⁶ reported that the electrochemical potential of a silver cluster depends on its size. A minimum critical size⁶⁷⁻⁶⁹ of a silver cluster is also needed to initiate development. These results can be explained by the proposal of IETD.

An IETD process is indeed consistent with the electrode mechanism. The reaction can be shown as Eqs. 1 and 2. If n = 1, it is obvious that the reaction will go on very slowly, because both the electron affinity and the contacting area of a single atom are small. With increasing the atom number in the cluster, both the electron affinity and the contacting area of the cluster increase, the electron transfer will be therefore accelerated. Therefore, the larger the cluster size is, the faster the development reaction.

$$Ag_n + e^- \to Ag_n^-, \tag{1}$$

$$Ag_n^- + Ag^+ \to Ag_{n+1}.$$
 (2)

DETD. From Eq. 3, it is clear that whether a DETD at a surface site will start depends largely on the concentrations of both surface silver ions and developer agents around the site. The concentration sequence of reactants at different surface sites is $[Ag^+]_{silver sulfide} > [Ag^+]_{AgI} > [Ag^+]_{AgBr} > [Ag^+]_{AgCl}$ for surface silver ions and $[Red]_{silver sulfide} > [Red]_{AgI} > [Red]_{AgI} > [Red]_{AgCl}$ for developer agents. Therefore, the reactivity sequence of these surface sites triggering DETD is: $Ag_2S > AgI > AgBr > AgCl$.

$$Ag^+ + Red \rightarrow Ag + Ox.$$
 (3)

If Au⁺ is adsorbed on the surface sites instead of Ag⁺, it should become easier for DETD to be triggered. This is attributed to two reasons: the lower standard potential of Au⁺ and the ease for Au⁺ ion to be approached by developer. (The desolvation energy³² is 3.41 eV for Ag⁺ and 3.24 eV for Au⁺ in water.) The reactivity sequence of these surface sites towards DETD is: Ag₂S+Au > AgI+Au > AgBr+Au > AgCl+Au.

Explanation on the Experimental Results. The Similarity of Fog Curve Shapes Between the (U)-Emulsions and the Sulfur-Sensitized Emulsions. Excess amounts of either iodide or sulfide at the surface of AgBr will result in fog formation: the fog of sulfur-sensitized emulsions increases sharply with increasing sulfur amount. These results can be explained by the development mechanisms proposed in the previous sections.

We have demonstrated that the concentration sequence of surface adsorbed silver ion is $[Ag^+]_{silver sulfide} > [Ag^+]_{AgI} > [Ag^+]_{AgBr} > [Ag^+]_{AgCI}$ and that of approaching developing agents is $[Red]_{silver sulfide} > [Red]_{AgI} > [Red]_{AgBr} > [Red]_{AgCI}$ at the same pAg level. This means that the existence of either AgI or Ag₂S at AgBr surface should result in DETD as is shown in Eqs. 4 and 5.

$$Ag_2S-Ag^+_{surface} + e^- \rightarrow Ag_2S-Ag$$
 (4)

$$AgI-Ag^{+}_{surface} + e^{-} \rightarrow AgI-Ag$$
 (5)

With the occurence of DETD, the surface silver ions are consumed and silver clusters formed. The probability of IETD will therefore increase. When the impurity

deposit size is very small, the silver cluster formed by DETD may be too small to initiate an IETD, and the grain is therefore difficult to develop. When the impurity size is large enough, more silver ions can be adsorbed by it and more developing agents can approach it. Reactions 4 and 5 may therefore occur easily and more adsorbed silver ions may be reduced. The probability for separate silver atoms by DETD to grow into large silver clusters (see Eqs. 6 and 7) is thereby increased with increasing speck size. Some of the silver atoms reduced by DETD aggregate together to make IETD possible. Repeated IETD (Eqs. 1 and 2) allows the grain to be completely developed. Therefore, a large sulfur sensitization initiates the development more readily than a small speck, and a large amount of sulfide or iodide at the AgBr surface initiates fog development.

$$n \operatorname{Ag}_2 S - \operatorname{Ag} \rightarrow (\operatorname{Ag}_2 S - \operatorname{Ag})_{n-m} (\operatorname{Ag}_2 S)_m \operatorname{Ag}_m,$$
 (6)

$$n \operatorname{AgI-Ag} \to (\operatorname{AgI-Ag})_{n-m} (\operatorname{AgI})_m \operatorname{Ag}_m.$$
 (7)

Though both silver iodide and silver sulfide at the silver halide surface can initiate development, the reactivity of sulfide is at least hundreds of times higher than that of silver iodide as was shown above. This is partly attributed to the concentration differences of their surface adsorbed silver ions and attracted developing agents. Because $[Ag^+]_{silver sulfide} > [Ag^+]_{AgI}$ and $[Red]_{silver sulfide} > [Red]_{AgI}$, a sulfur center may more easily form a much larger silver cluster by DETD than will an iodide center of the same size. Therefore, the reactivity of a sulfur center is much larger than that of an iodide center.

Another problem that needs to be explained is the difference in maximum fog density. Though the same number of silver atoms can be formed by DETD at different impurity specks, their agglomerate status will affect the subsequent IETD. If the silver atoms are randomly dispersed over a large speck, such as a silver iodide center, they will need a long time to migrate and gather; the IETD is accordingly difficult. When the same number of silver atoms are formed at a tiny speck, it is obvious that the IETD should proceed rapidly, and a slight increase in impurity level should lead to many more grains being developed. Therefore, we observe a slight fog increase with iodide-covered AgBr emulsions with increasing iodide amount, but a sharp fog increase in sulfur-sensitized AgBr emulsions with increasing sulfur amount.

Why Subsequent Gold Sensitization of the (U)-**Emulsions and the (S)-Emulsions Produce Fog Eas**ily. According to the HSAB³³ principle and Klopman's calculation,³² Au⁺ is a softer acid than is Ag⁺. Therefore, Au⁺ ion is easier to bind by the soft bases I⁻ and S²⁻ than is Ag⁺ ion. We consequently suppose that gold sensitizer may be more easily adsorbed than silver ion by the surface iodide or sulfur sites on AgBr surfaces. As a result, more Au⁺ than Ag⁺ will be preferentially located at the sulfur or the iodide center rather than on the rest of the AgBr surface. On the other hand, the standard potential of Au⁺ is lower than Ag⁺. Consequently, if a tiny amount of gold sensitizer is located at the sulfur or the iodide center, it will not significantly affect the reactivity of these centers, but a large amount of gold sensitizer will greatly increase their developability. The DETD as Reactions 8 and 9 will therefore take place rapidly.

$$Ag_2S-Au^+_{surface} + e^- \rightarrow Ag_2S-Au,$$
 (8)



Figure 11. Surface distributions of AgI (o), AgI island (larger circle), and gold sensitizer (*) at cubic AgBr grains: (a) trace amount of KI is added, very few AgI molecules are formed; (b) AgI molecules are dispersed all over the grain surface with the addition of more KI; (c) small AgI island is formed; (d) large AgI island is formed. (a') through (d'). Same amount of gold sensitizer is added into (a) through (d) respectively.

$$AgI-Au^{+}_{surface} + e^{-} \rightarrow AgI-Au.$$
(9)

On the other hand, the electron affinity of a gold cluster is greater than of a silver cluster of the same size. Some of the gold atoms formed by DETD will migrate and aggregate into gold clusters (see Eqs. 10 and 11) and make the IETD (see Eqs. 12 to 14) at these sites easier than with silver clusters. Therefore, addition of gold sensitizer should greatly increase reactivity of the original sulfur or iodide speck at the AgBr surface. This is why the (Au)- and the (S+Au)-emulsions are easier to fog than the (U)- and the (S)-emulsions.

$$n \operatorname{Ag}_2 S - \operatorname{Au} \to (\operatorname{Ag}_2 S - \operatorname{Au})_{n-m} (\operatorname{Ag}_2 S)_m \operatorname{Au}_m,$$
(10)

$$n \operatorname{AgI-Au} \rightarrow (\operatorname{AgI-Au})_{n-m} (\operatorname{AgI})_m \operatorname{Au}_m,$$
 (11)

$$Au_n + e^- \to Au_n^-, \tag{12}$$

$$\operatorname{Au}_{n}^{-} + \operatorname{Ag}_{i}^{+} \to \operatorname{AgAu}_{n}, \tag{13}$$

$$AgAu_n + e^- \to AgAu_n^-.$$
(14)

Similarity of Fog Curve Shapes Between the (Au)-Emulsions and the Sulfur-Plus-Gold Sensitized AgBr Emulsions. Both the sulfur-plus-gold sensitized AgBr emulsions and the (Au)-emulsions produce two fog peaks with varying the sulfur or iodide amount. This similarity may be attributed to the selective adsorption of gold ions at the iodide or the sulfur sites. Because the amount of iodide or sulfur may influence their dispersion at the AgBr surface, it is important to suppose a surface distribution model of chemical impurities (see Fig. 11, taking the iodide and iodide-plus-gold centers as examples) to explain the experimental results:

- When a trace amount of KI is added, very few AgI clusters are deposited on the grain surface [Fig. 11(a)].
- With increasing KI amount, more AgI clusters are formed and distributed all over the grain surface [Fig. 11(b)].

- A new AgI phase (small island) is formed on adding more KI [Fig. 11(c)].
- A large AgI island is formed on adding large amount of KI [Fig. 11(d)].

Though the AgI molecules and clusters [in Figs. 11(a) through (c)] at the grain surface are too small to be seen under electronic microscopy, a large AgI island [Fig. 11(d)] has been found to form at the AgBr grain surface by the treatment with large amount of KI.¹⁵ A similar distribution model of sulfur specks at the cubic AgBr surface may be supposed as Figs. 11(a) through (d).

When the iodide-covered AgBr emulsions or the sulfur-sensitized AgBr emulsions are subsequently sensitized by gold, gold will selectively aggregate at the iodide or sulfur center according to the stability sequence of ionic adsorption: $[Au^+]_{silver sulfide} > [Au^+]_{AgI} > [Au^+]_{AgBr} >$ $[Au^+]_{AgCl}$. Therefore, the chemical impurities at the (Au)emulsions or at the sulfur-plus-gold sensitized AgBr emulsions may be distributed as Figs. 11(a') through (d'). Explanations on the formation of fog maxima and minima are as follows: (in the case of the same amount of gold-sensitizer being used for each of the emulsions).

- (a') When trace amount of KI was added, less amount of gold sensitizer (less than 6.5 mmol/mol Ag) does not produce fog, but large amount of gold sensitizer(more than 10 mmol/mol Ag) would aggregate around the few numbers of iodide centers to form much reactive centers, and large fog is hence easily produced.
- (b') With increasing iodide amount, the iodide centers are distributed all over the crystal surface with roughly equal size; gold should be equally distributed at each iodide center. Therefore, the gold amount at each iodide center is decreased and the reactivity of each site is lowered. The first fog minimum thus appears in the curve.
- (c') Increasing iodide will result in the formation of small AgI islands on the microcrystal surface. Therefore, more gold will aggregate around these islands than at the small AgI centers. The developability of the grain increases and the second fog peak appears again in the curve.
- (d'). When large amount of KI is added, a layer of AgI will cover almost all the microcrystal surface and large AgI islands are formed. Gold sensitizer is therefore distributed all over the microcrystal surface. The low

solubility of silver iodide and the reduced amount of gold at each island prevent it from producing high fog density. Therefore, a decline of fog density is observed at high iodide leveled.

The fog of sulfur-plus-gold sensitized AgBr emulsions demonstrates about the same variation tendencies as seen with the (Au)-emulsions (see Figs. 7 and 9). The exceptions are that the amount of sulfur is much smaller than that of iodide at the corresponding maxima and minima and the second peak in fog density does further decrease with increasing sulfur amount. Similar explanations as Figs. 11(a') to (d') may apply for the fog formation of the sulfur-plus-gold sensitized AgBr emulsions. The exceptions may be attributed to the reactivity differences between iodide-plus-gold centers and sulfur-plus-gold centers.

Conclusions

- 1. Similar fog curve shapes were obtained for iodidecovered AgBr emulsions with varying iodide amounts and for the sulfur-sensitized AgBr emulsions with varying sulfur amounts. The reactivity of the former is much lower than that of the latter.
- 2. For gold sensitization of iodide-covered AgBr emulsions, two peaks appeared in the fog curves with varying iodide amounts. Similar fog curve shapes were also obtained by sulfur-plus-gold sensitization of AgBr emulsions on varying the sulfur amounts.
- 3. The chemical impurities at the AgBr surface promote development to a certain extent. The fog characteristics of cubic AgBr emulsions are determined by the type, size, and distribution of chemical impurities at microcrystal surfaces.
- 4. When co-existing in aqueous solution, the reactivity sequences of different chemical sites are $Ag_2S > AgI >$ $AgBr > AgCl and Au_n > Ag_n$
- 5. Development may proceed by two paths: DETD and IETD. DETD depends on the surface concentrations of both silver ions and developer agents, while IETD reactivity largely depends on the sizes of silver or gold clusters.
- 6. Most of the fog development may be first initiated as DETD, and then followed by IETD.
- 7. The experimental results can be explained by the proposed development mechanisms given a distribution model of chemical impurities at the grain surface.

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