

Effect of Iridium doping in Cubic and Octahedral AgBr Grains on the Latent Image Formation Process.

M. Slagt and Y. Iwasa
Tilburg Research Laboratory, Fuji Photo Film BV
Tilburg, The Netherlands
T. Owaki and A. Hirano
Ashigara Research Laboratories, Fuji Photo Film Co. Ltd
Minami-Ashigara, Japan

Introduction

Metal dopants have often been incorporated into silver halide grains in order to manipulate their photographic behavior. For example, complexes of iridium, rhodium or iron have been used for various purposes. Among these complexes, especially the iridium salts have been investigated in detail in relation to their photographic and physical effects[1].

It was reported that iridium doping in AgBr and in AgCl grains result in different kinetic properties (decay time, activation energy, etc.)[4,6]. These facts suggest that the environment surrounding the doped iridium in silver halide crystals is important in the process of latent image formation. It was also reported that the different shapes of AgBr grains exhibit different physical properties, for example the ionic conductivity[5,8] and the concentration of R-centers[7].

In this paper, it will be shown how the difference of crystal shape affects on the role that doped-iridium is playing in the process of latent image formation. Some remarkable differences in photographic properties, especially in retarded latent image formation will be discussed, in relation to the difference of their physical properties. Gold latensification will be applied in order to characterize latent image centers which are involved in these processes.

Experimental

Sample preparation

Two different types of silver bromide grains were prepared: cubic AgBr and octahedral AgBr. The cubic AgBr grains were precipitated at a pH of 4 and a pAg of 6.1, using a controlled double jet technique. The length of the edge is 0.3 µm.

The octahedral AgBr grains are of same size but were precipitated at a pAg of 7.8 (pH also 4).

Doping of iridium into the grains was done by addition of potassium hexachloroiridate into the bromide solution. This solution was added during crystal formation. The iridium doping was incorporated into the major shell region of the crystals (shell/core = 36/1) in both the cubic and the octahedral grains. The grains have not been spectrally or chemically sensitized.

Results and Discussion

Photographic behavior of cubic and octahedral AgBr with different concentrations of iridium

The $[IrCl_6]^{2-}$ complex was incorporated into the major shell of cubic and ocahedral AgBr grains. The dopant amount was varied up to 10^{-5} mol iridium per mol silver. In the first experiment the time between exposure and development was kept constant at 60 minutes. The results are presented in Figs. 1 and 2.

For investigating the retarded latent image formation, the aging time between exposure and development was varied from 15 seconds to 48 hours. The retardation process can be found in Fig. 3 (cubic) and Fig. 4 (octahedral).

In order to determine the location of the latent images, the density after total development was compared to the density after surface development. The density difference between total development and surface development is considered to be the result of latent images which are present in the interior of the grains. The results are shown in Figs. 5 and 6.

Reactions concerned with latent image formation.

It is known that an iridium center doped into a silver halide crystal can play a role as a temporary trap for photo-electrons[3]. For the latent image formation concerned with doped iridium, the basic reactions (see bellow) are important to discuss the observed photographic behavior. These reactions will happen successively and/or competitively.

Reaction 1: the reversible trapping of electrons by iridium centers.

$$e^- + Ir^{3+} \rightarrow Ir^{2+}$$
$$Ir^{2+} \rightarrow e^- + Ir^{3+}$$

Reaction 2: the reversible trapping of electrons by intrinsic electron traps followed by trapping an interstitial silver ion.

$$e^- + Ag_i^+ \rightarrow Ag^0 \quad (\rightarrow Ag_n)$$
$$Ag^0 \rightarrow e^- + Ag_i^+$$

Reaction 3: the irreversible recombination of photoelectrons with positive holes.

$$e^- + h^+ \rightarrow \text{recombination}$$

Reaction 4: the irreversible destruction of latent images.

$$Ag_n \rightarrow n\,Ag_i^+ + n\,e^-$$

In Reaction 2, not only electrons produced by photolysis but also electrons released from iridium contribute to the formation of Ag^0 ($\rightarrow$finally latent image center; Ag_n with $n \geq 4$). Regarding the latter process, recently it was reported that the electron for contributing to the latent image formation is not directly supplied from an iridium center, but by decomposition of Ag^0 formed near the iridium center[6)]. However, in this paper, a simplified model is adopted for each reaction for the sake of its convenience.

Effect of doped iridium concentration

Different behavior in the process of latent image formation was observed, depending on the concentration of iridium doping in both octahedral and cubic AgBr grains. Therefore the discussion on the function of iridium doping will be divided into 4 classes with different concentration of iridium doping: no iridium, low concentration, intermediate concentration, and high concentration.

<u>No iridium doping</u>

In case where no iridium is incorporated, photoelectrons can only be trapped via Reaction 2 to form latent images, or recombine with positive holes (Reaction 3).

<u>Low concentration of iridium doping</u>

In case where a small amount of iridium (~ 10^{-7} mol Ir/mol Ag) is incorporated, an increase of the sensitivity is observed (see Figs. 1 and 2). This increasing sensitivity can be explained by Reaction 1. A small amount of iridium enables electrons to be trapped by the iridium centers (Reaction 1). Therefore less electrons will recombine with positive holes, resulting in a sensitivity increase, as can be seen Figs. 1 and 2.

<u>High concentration of iridium doping</u>

A tremendous desensitization (see Figs. 1 and 2) has been observed at a high concentration of iridium doping (~ 10^{-5} mol Ir/mol Ag). When the iridium amount is drastically increased, electron trapping via Reaction 1 is considered to becomes dominant over the trapping via Reaction 2. That is, most of electrons are trapped by the many iridium centers which are present in the grains. After being released from the iridium centers, these electrons will immediately be re-trapped by other iridium centers close to them. Trapping electrons by iridium centers occurs successively and more frequently than the reaction of electrons with interstitial silver ions. It is considered that the lack of available electrons in Reaction 2, caused by the high amount of iridium centers is responsible for the low sensitivity and the slow rate in the retarded latent image formation.

<u>Intermediate concentration of iridium doping</u>

In case of an intermediate amount of iridium doping (~ 10^{-6} mol Ir/mol Ag), several interesting phenomena were observed. In cubic grains, desensitization has already started (see Fig. 1) while in octahedral grains sensitization is still proceeding (see Fig. 2). This difference between cubic and octahedral grains will be discussed in more detail later.

Regardless of sensitization or desensitization, just after exposure a remarkable enhancement of latent image formation, that is a well known retarded latent image formation, is recognized for both cubic (see Fig. 3) and octahedral grains (Fig. 4). After reaching the maximum sensitivity, a strong latent image fading occurs at the aging time from 1 hour onwards.

With an intermediate iridium concentration electrons which are released from the iridium centers will be trapped by other iridium centers but will finally be incorporated into a latent image (Reaction 2) resulting in a steady increase of the sensitivity.

Characterization of latent image centers

At an iridium concentration of 10^{-6} mol Ir/mol Ag, a typical retarded latent image formation due to the presence of doped iridium followed by a latent image fading is visible, especially for octahedral grains. For these grains, it was tried to characterize the latent image centers which are involved in these processes.

In order to investigate the presence of sub-latent images, gold latensification was applied to octahedral AgBr grains. The results are presented in Fig. 7.

In the region where retarded latent image formation is observed, gold latensification did not result in an increase in sensitivity, as shown in Fig. 9. This suggests that the big increase in sensitivity is not caused by the presence of many sub-latent images which can grow into latent images later on. Instead the latent image centers (Ag_n $n \geq 4$) seem to grow up efficiently and instantly. This observation is in line with the theory that in unsensitized grains the growth rate of sub-latent images into latent images is dominant over the formation rate of sub-latent images (nucleation). As a result sub-latent images will grow immediately into latent images [2)].

On the other hand, in the region of latent image fading gold latensification reveals less fading. This means that latent image centers have broken down gradually in time via sub-latent image centers. The fading rate is considerably fast, compared to that of non doped grains or grains with lower concentration of iridium (see Fig. 4). This implies that the latent image centers formed in the process of retarded latent

image formation affected by the existence of iridium centers are less stable than those formed without doped iridium.
To investigate the cause of latent image fading after long aging (longer than 1 hour between exposure and development), exposed samples have also been aged under vacuum condition. As an example, results obtained for the octahedral grains with 10^{-6} mol Ir/mol Ag are presented in Fig. 8. The samples kept under vacuum condition do not reveal a fading behavior of the latent indicating that oxygen/ moisture are the cause of the latent image fading.

Effect of crystal shape

The shape of AgBr crystals has a remarkable effect on the process of latent image formation. Several striking differences are observed between cubic and octahedral AgBr grains, as shown already.

No iridium doping

The comparison of Figs. 1 and 2 shows that the sensitivity of the octahedral AgBr is much lower than that of cubic AgBr, when iridium is not incorporated. This difference in sensitivity indicates that the latent image formation process in octahedral grains is less effective than in cubic grains. One of possible causes for the lower effectiveness of latent image formation in octahedral grains can be the formation of sub-latent images (dispersion) instead of latent images due to the high concentration of interstitial silver ions (Reaction 2 forming Ag_n with $n<4$) [8] or more frequent recombination in octahedral grains (Reaction 3). Experimental results (see Fig. 7) revealed that the difference in sensitivity between octahedral and cubic grains is not caused by different number of sub-latent images, since the evidence supporting the existence of sub-latent image centers can not be obtained through gold latensification treatment. It is therefore likely that the lower effectiveness of latent image formation in octahedral grains is caused by a larger amount of recombination (Reaction 3).
Comparison between the density after total development and after surface development (see Fig. 6) revealed that in octahedral grains latent image formation occurs not only at the surface of the crystals but also at the inside of crystals. On the other hand, in case of cubic grains the latent image formation occurs mainly and effectively at the surface of crystals (see Fig.5). It was indicated by Takada that the potential difference between the surface and the inside of AgBr crystals is bigger in octahedral crystals than in cubic crystals.[5] The potential difference is caused by the formation of a space charge layer in the vicinity of the crystal surface in which a higher concentration of interstitial silver ions is present. It was suggested that such a band bending may drive electrons to the inside of the crystal and positive holes to the surface of the crystals. It has also been reported by Tani that a bigger potential difference between the surface and the inside of the crystals leads to the formation of more internal latent image[9]. Our results are consistent with these finding. That is the different distribution of latent images in crystals observed for octahedral grains may be explained in terms of the different structure of the space charge layer for these grains.

Iridium doping

In case where intermediate concentrations of iridium ions (~ 10^{-6} mol Ir/mol Ag) are doped, the most noticeable difference between cubic and octahedral grains is that the enhancement of sensitivity is much bigger in octahedral grains than in cubic grains during the retarded latent image formation (during the first 10 minutes after exposure) (compare Fig. 3 to Fig. 4). It is considered that some of the electrons which are produced after exposure have directly contributed to form latent image centers, while other electrons are transiently trapped by iridium centers. Trapping and re-trapping of electrons by iridium centers cause the retarded latent image formation. The enhancement of sensitivity in the process of the latent image formation is bigger in octahedral grains. In these grains a higher amount of electrons seem to be temporarily trapped. It seems that these are several possible reasons why in octahedral grains more electrons are temporarily trapped. These reasons are:

1. A higher amount of remaining electrons which have not been involved in the latent image formation just after exposure.
   The number of electrons which contribute to form latent images immediately after exposure is smaller in octahedral grains than in cubic grains, because octahedral grains show a lower effectiveness of latent image formation just after exposure. The remaining electrons which have not been involved in the process of latent image formation can be trapped by iridium ions (although some of them will still recombine with positive holes). After being released the electrons can contribute to a density increase during retarded latent image formation. Since the amount of these remaining electrons is higher in octahedral grains, the density increase during retarded latent image formation will be bigger in the octahedral grains.
2. More frequent migration of electrons to the interior of octahedral grains.
   As discussed already earlier in this paper, due to the larger potential difference in the space charge layer electrons can migrate more easily into the inside of octahedral crystals where most of doped iridium ions are present,. This means that electrons which are migrating into the inside of octahedral crystals can be trapped by iridium ions with a higher probability.
3. More stable position of electrons near iridium ions. Octahedral crystals have a larger number of Ag^+ ion vacancies as Frenkel defects, because octahedral AgBr have a higher concentration of interstitial Ag^+ ions[8]. Doped iridium ions are probably incorporated at the position of these vacancies as more stable sites. This implies that iridium doped into octahedral grains can trap electrons more stable compared to iridium doped into cubic grains.

Due to some of above reasons, electrons produced just after exposure can be trapped more frequently and more easily by iridium ions in octahedral grains. In case of intermediate concentration of iridium, the electrons trapped and released successively by iridium ions will finally be combined with interstitial Ag^+ ions. Consequently, the retarded latent image formation occurs more remarkably in octahedral grains than in cubic grains. It is interesting to note that the maximum sensitivity reached after aging (~100 minutes) in octahedral grains is rather close to that in cubic grains. The proper concentration of iridium ions can compensate the lower effectiveness of latent image formation observed in octahedral grains.

Conclusions

The effect of iridium doping on the latent image formation process was investigated for octahedral and cubic grains with different concentration of iridium. The following conclusions were obtained.

1. Regardless of the iridium doping amount, in cubic grains the latent images are almost all located at the grain surface, while in case of octahedral grains a substantial part of the latent images is located at the interior of the grains. This difference in location of latent images between cubic and octahedral grains may be explained by the difference in the space charge layer between them reported by Takada[5].
2. In case of no iridium doping, octahedral grains showed a lower sensitivity which is caused by more frequent recombination of electrons with holes, compared to cubic grains.
3. In case of iridium doping, especially with intermediate concentration of iridium (~10^{-6} mol Ir/mol Ag), octahedral grains exhibited a larger increase in sensitivity and a larger retardation in the process of latent image formation, compared to cubic grains. Sub-latent images are not so much involved in these stages.

4. Different behavior of latent image formation observed for octahedral and cubic grains can be explained in terms of higher amount of electrons temporarily trapped by iridium doped in octahedral grains, due to several possible reasons: higher amount of remaining electrons which have not been involved in the latent image formation just after exposure/ more frequent migration of electrons to the inside of octahedral grains/ more stable position of electrons near doped iridium ions.
5. The retarded formed latent images are easily destroyed again under influence of oxygen/moisture.

References

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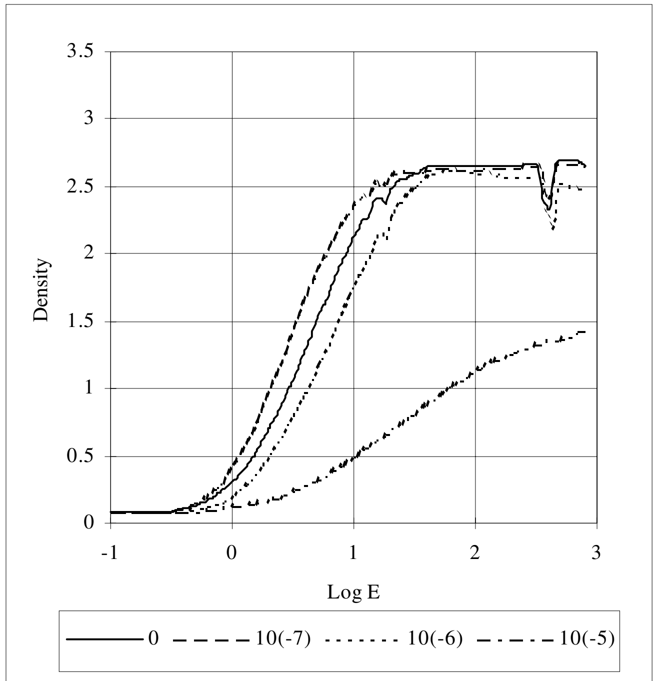

Figure 1: Incorporation of $[IrCl_6]^{2-}$ into cubic AgBr. $[IrCl_6]^{2-}$ concentration in mol/mol Ag.

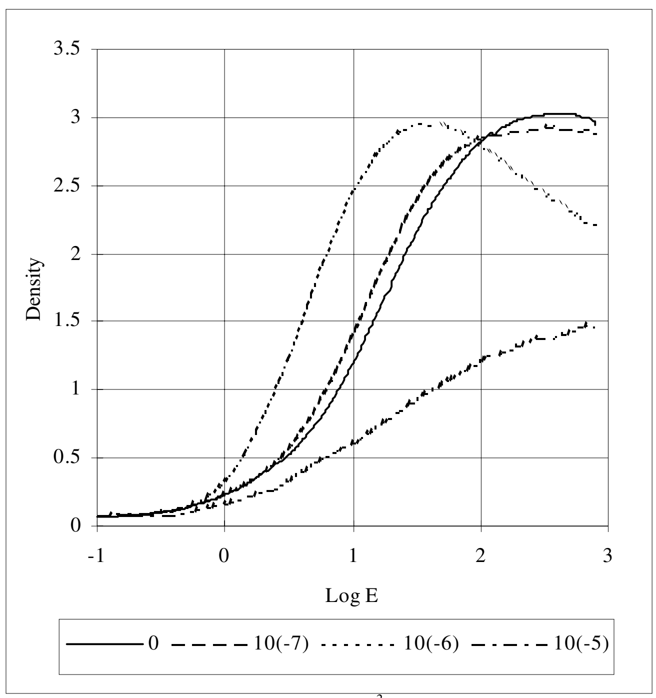

Figure 2: Incorporation of $[IrCl_6]^{2-}$ into octahedral AgBr. $[IrCl_6]^{2-}$ concentration in mol/mol Ag.

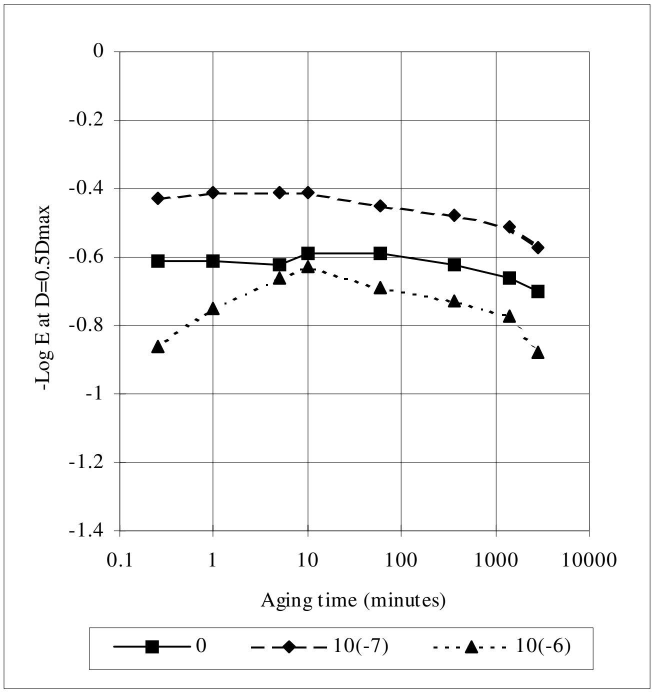

Figure 3: Sensitivity of cubic AgBr with different amounts of $[IrCl_6]^{2-}$ at different aging time between exposure and development. $[IrCl_6]^{2-}$ concentration in mol/mol Ag.

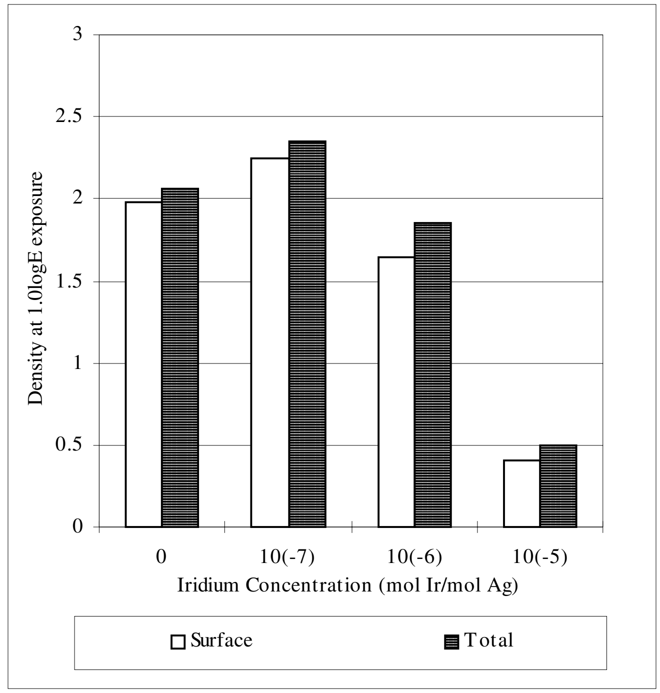

Figure 5: Surface and total development of cubic AgBr with different amounts of $[IrCl_6]^{2-}$. $[IrCl_6]^{2-}$ concentration in mol/mol Ag.

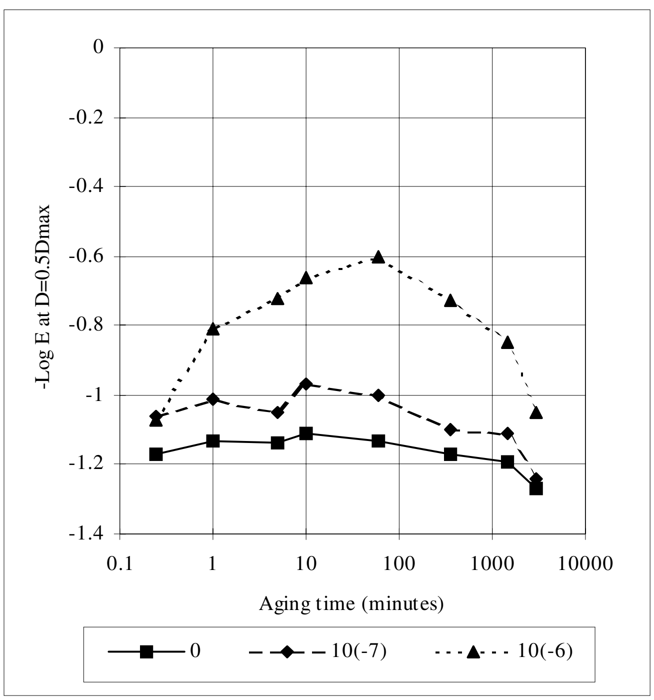

Figure 4: Sensitivity of octahedral AgBr with different amounts of $[IrCl_6]^{2-}$ at different aging time between exposure and development. $[IrCl_6]^{2-}$ concentration in mol/mol Ag.

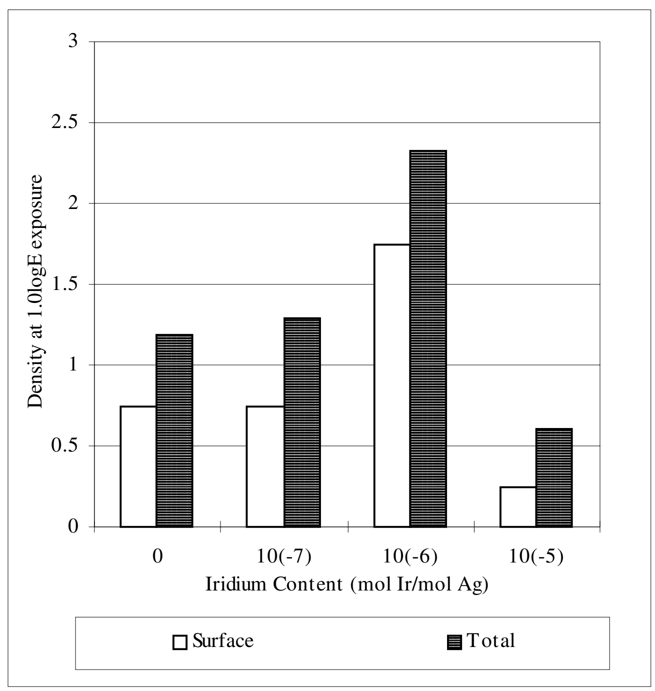

Figure 6: Surface and total development of octahedral AgBr with different amounts of $[IrCl_6]^{2-}$. $[IrCl_6]^{2-}$ concentration in mol/mol Ag.

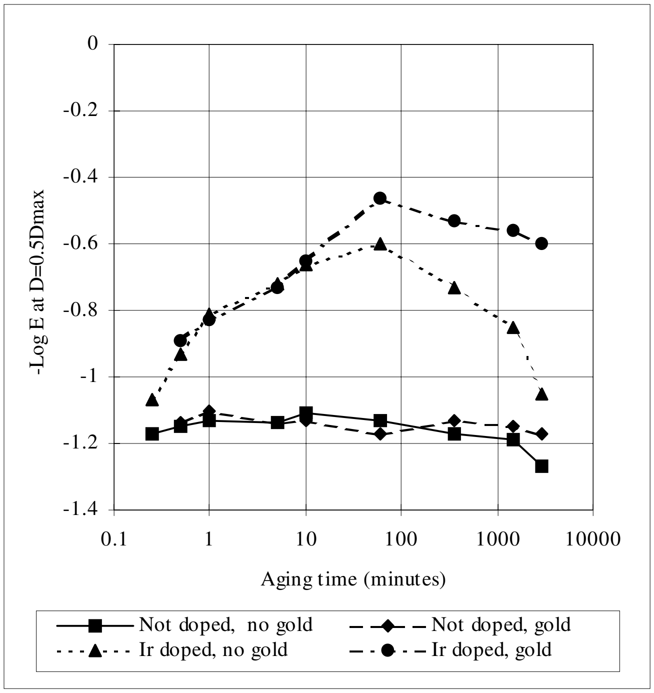

Figure 7: Gold latensification of octahedral AgBr with 10^{-6} mol $[IrCl_6]^{2-}$ per mol Ag and without doping.

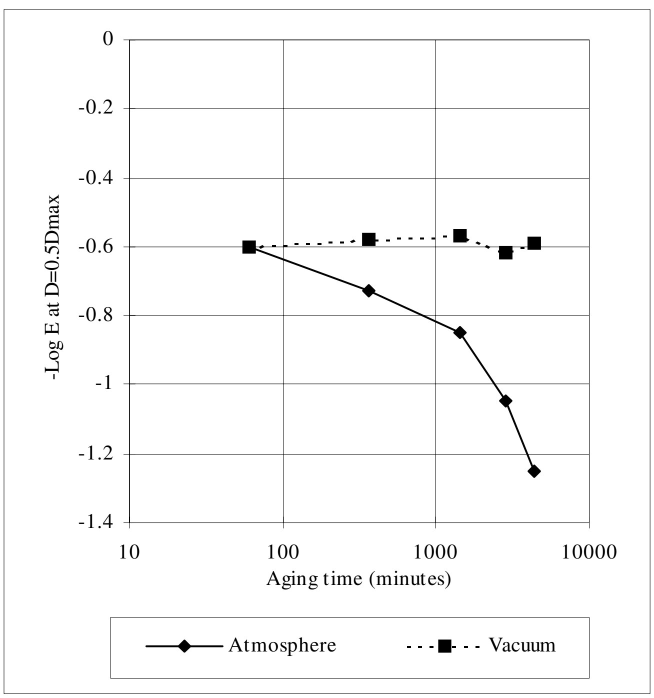

Figure 8: Sensitometric behavior of octahedral AgBr with 10^{-6} mol $[IrCl_6]^{2-}$ per mol Ag under vacuum condition