# Study on Fog Development of Silver Halide Microcrystals

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## Abstract

*The fog development of silver halide emulsion with sensitizers of sulphur and gold in developers D-19b and CD-4 were studied. The experimental results showed that the fog density produced by both sensitizers of sulphur and gold in D-19b developer is greater than that in CD-4 one, Moreover, in some sulphur levels the fog produced by sulphur sensitization is much larger that gold sensitization in developers D-19b, and whereas it is smaller in the CD-4 in comparison with that by the same gold level sensitization. These result were in consonant with the study of the fog developing dynamics of sulphur and gold sensitization in the developers D-19b and CD-4. These results indicated that sulphur sensitization is distinctly different from gold one for the influence on the fog formation in the fog developing processes. The fog formation rate constants of emulsion with the sensitizer of sulphur is greater than one with sensitizer of gold ,and the fog development activation energy of the emulsion with the sensitizer of sulphur is smaller than one with the sensitizer gold in the developer D-19b .conversely, the fog formation rate constants of the emulsion with sensitizer of sulphur is smaller than one with sensitizer gold, and the fog development activation energy of the emulsion with sensitizer of sulphur is greater than one with sensitizer gold in the developer CD-4.*

## Introduction

Fog is the development of a grain which has not been exposed and which hence does not bear a latent image silver speck. In the practice of photo taking, low level of fog is always required. As far as any emulsion is concerned, both the sensibility and the time of development are limited by fog. Therefore, various means such as the adoption of anti-fog agent and stabilizer preparation as adopted to curb the formation of fog.

The fog resulted from the unexposed silver halide grains in the development is in the same process as photolytic silver produced the exposure. In the fog development, the unexposed silver halide grains collisions with the molecules of the developer, but most of the collisions produces no effect, with only a small part of the active molecules with high energy can give out two electrons. After absorbing two electrons, the silver halide grain reacts with two silver ions to produce $Ag_2$. Comparatively speaking, $Ag_2$ is stable. The reaction is as follows:

$$2Ag^+ + R^{2-} \rightarrow Ag_2 + OX \qquad (1)$$

On the one hand, the further collisions between the molecule of the developer the surface of the silver halide grain may produce more $Ag_2$ particles; on the other hand, the collisions on $Ag_2$ particle will result in $Ag_4$, thus becoming developable.

$$Ag_2 + 2Ag_I + R^{2-} \dashrightarrow Ag_2 + Ag_2 + OX$$
$$\dashrightarrow Ag_4 + OX \qquad (2)$$

In this study, the researchers has sensitized emulsion AgBr I(111) respectively with sulphur and gold and analyzed the difference of fog development between the two sensitized emulsions in the developers D-19b and CD-4. At the same time, a study of the dynamics of the fog development of the two sensitized emulsions in developers D-19b and CD-4 respectively. For comparison, the result of dynamic experiment of the fog development of emulsion AgBr has also been given.

## Discussion and Conclusion

In Fig. 1 and Fig. 2 the following results are shown:

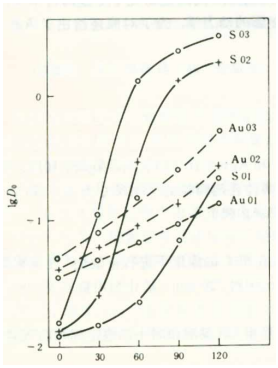


*Fig.1 The dependence of fog formation on sensitizing time in developer D-19b.*

(1) In two developers D-19b and CD-4, the density of fog development goes up along with the increase of the amount of sulphur and gold within the same time of sensitization;
(2) In said two developers, the density of fog development goes up along with the extension of the time of sensitization under the condition of same amount of sulphur and gold;
(3) The fog development density of the sulphur-sensitized emulsion varies sharply in two developers under the condition of the same time of sensitization and same amount of sensitizer, while the fog development density of the gold-sensitized emulsion varies slightly in two developers when the time of sensitization and the amount of sensitizer are the same;

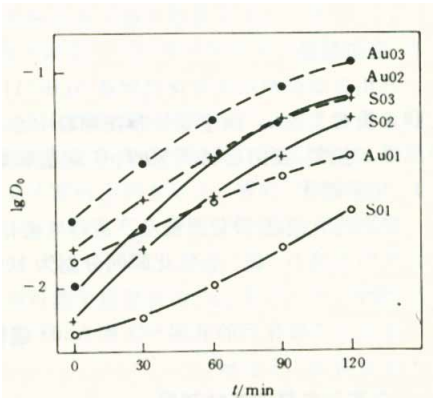


*Fig.2 The dependence of fog formation on sensitizing time in developer CD-4.*

(4) The fog development density of the sulphur-sensitized emulsion and the gold-sensitized emulsion in the developer D-19b is bigger than that in the developer CD-4 if both the time of sensitization and the amount of sensitizer are the same;

Fig. 3 and Fig. 4 reveal the relation between fog formation and developing time in two developers D-19b and CD-4 at the development temperature of $20^0$C. It can be seen in Fig. 3 that within the time span of fog development, the developing rate of the sulphur-sensitized emulsion is greater than that of the gold-sensitized emulsion in the developer D-19b. It is shown in Fig. 4 that the developing rate of the sulphur-sensitized emulsion is smaller than that of the gold-sensitized emulsion in the developer CD-4 within the time span of fog development.

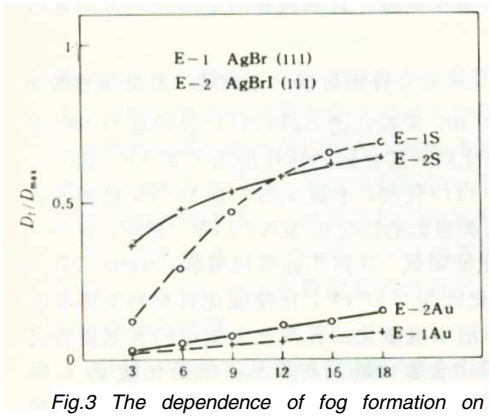


*Fig.3 The dependence of fog formation on developing time in developer D-19b at 20℃*

According to following formula for calculating chemical reaction rate:

$$LnCo/(Co-X)= kt \qquad (3)$$

By replacing $C_o$ in formula (3) with $D_{max}$ and replacing $X$ with $D_t$, then the formula becomes:

$$K_t=1/t\ LnD_{max}/(D_{max}-D_t) \qquad (4)$$

In formula (4), $D_{max}$ refers to the maximum density of the film, $t$ refers developing time and $D_t$ refers to the fog development density when the developing time is $t$. According to formula (4), the rate constants of fog formation can be calculated. In the following Table 2, the rate constants of fog formation of both the sulphur-sensitized emulsion and the gold-sensitized emulsion in developers D-19b and CD-4 respectively at 18⇒.

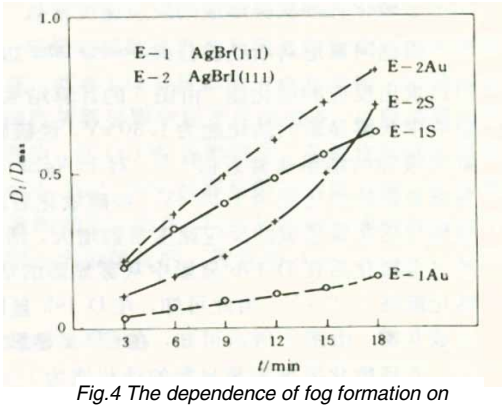


*Fig.4 The dependence of fog formation on sensitizing time in developer CD-4 at 20℃.*

According to the data in Table 1, the rate constant of fog formation of the sulphur-sensitized emulsion is bigger than that of the gold-sensitized emulsion in the developer D-19b, while the rate constant of fog formation of the sulphur-sensitized emulsion is smaller than that of the gold-sensitized emulsion in the developer CD-4.

**Table 1 The rate constants of fog formation**

| Time of dev. (min) | S-sensitized | | Au-sensitized | |
|---|---|---|---|---|
| | D-19b | CD-4 | D-19b | CD-4 |
| 6 | 14.0 | 8.8 | 1.02 | 11.1 |
| 9 | 12.1 | 7.4 | 1.24 | 9.1 |
| 12 | 10.8 | 6.8 | 1.25 | 8.3 |
| 15 | 9.0 | 6.9 | 1.18 | 7.6 |
| 18 | 7.8 | 6.6 | 1.06 | 7.6 |

By using Arrhenius' empirical formula $k=Ae^{-E/RT}$, drawing L$nk$ against 1/T obtains a straight line, and by using the slope of the straight line, the activation energy of the reaction can be obtained. The calculation result in Fig. 5 indicates that the fog development activation energy of the unsensitized emulsion AgBr(111) in the developer D-19b is 1.50eV which becomes 1.27eV after being sensitized with sulphur. This is very similar to the result reported in relevant literature [2, 7]. As to emulsion AgBr(111), its fog development activation energy in the developer D-19b is 1.08 eV before being sensitized with sulphur, but becomes 0.75 eV after being sensitized with sulphur. Obviously, the constant of fog formation of the emulsion increases after being sensitized with sulphur, but the activation energy decreases after being sensitized with sulphur. It can also be seen in Fig. 5 that the fog development activation energy of AgBr,I in the developer D-19b is 0.98 eV after being sensitized with gold, an increase of 0.23 eV than that of the

sulphur-sensitized emulsion. Therefore, the sulphur-sensitized emulsion in the developer D-19b is more likely to form fog than the gold-sensitized emulsion. It is indicated in Fig. 6 that the fog development activation energy of the gold-sensitized emulsion in the developer CD-4 is 1.64 eV while that of the sulphur-sensitized emulsion is 1.88 eV. It is obvious that the gold-sensitized emulsion in the developer CD-4 is more likely to form fog than the sulphur-sensitized emulsion. (The activation energy of the unsensitized emulsion AgBr,I(111) in the developer CD-4 is so small that is cannot be calculated). On the basis of the above experiment results, it can be deduced that the most appropriate sulphur/gold ratio in the mixed sensitization with sulphur and gold for negative emulsion is different between color film and black-white film. In addition, after the negative emulsion for black-white film is sensitized with sulphur and gold, the sulphur component has bigger influence on the fog formation in the developer D-19b. But after the negative emulsion for color film is sensitized with sulphur and gold, it is the gold component that exerts bigger influence on fog formation in the developer CD-4.

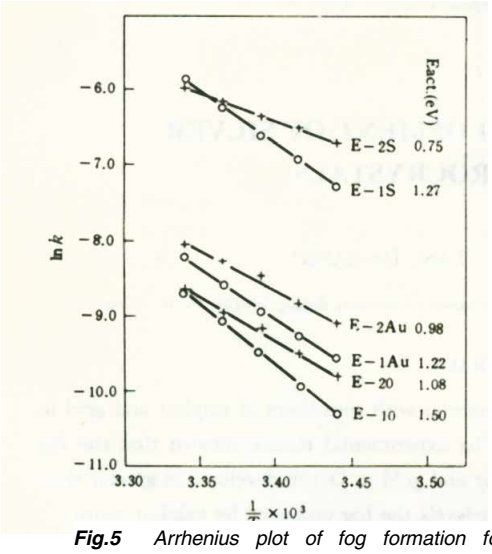


***Fig.5*** *Arrhenius plot of fog formation for different sensitizer added in developer D-19b, E-10, E-20 unsensitized emulsion.*

As stated above, the amount of the sensitive agent will not cause obvious change of the fog development activation energy, but will influence the fog development rate. That does not mean that, in the developer D-19b, the density of fog development caused by the sulphur-sensitized emulsion with any amount of sulphur is bigger than that caused by the gold-sensitized emulsion. Similarly, in the developer CD-4, it is not the case that the fog development density caused by the gold-sensitized emulsion with any amount of gold is bigger than that of the sulphur-sensitized emulsion.

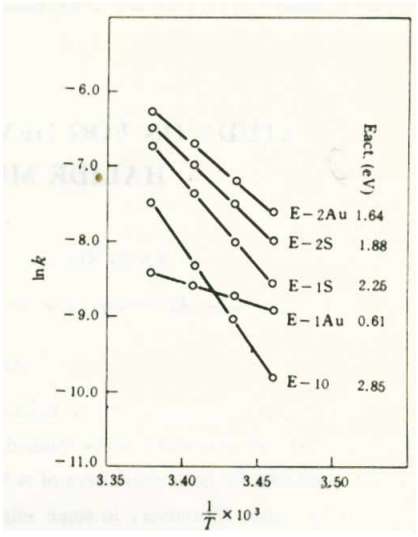


*Fig. 6 Arrhennius plot of fog formation for different sensitizer added in developer CD-4, E-10 unsensitized emulsion.*

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