Electron-Microscopic Observation of Photographic Emulsion. I
Appearance of the "Halos" in Electron Micrographs

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Synopsis

Using emulsion of "Fuji" process photographic plate and emulsion produced by the ripening of colloidal silver bromide, the "halos" in electron micrographs were observed under various conditions. It was found that (1) the "halos" appeared with intense electron bombardment, (2) this was more remarkable in the case of using the emulsions before sensitization produced in the dark room than that after sensitization, (3) the ring pattern was clearer in the case of suddenly increasing an electron beam density than the case of slowly increasing it, and (4) the appearance of the "halos" depended on the thickness of gelatine and it appeared only in the case of proper thickness of gelatine. The cause of the "halos" was discussed and a model experiment was carried out to confirm the physical consideration obtained.

From the standpoint of ionic crystal theory the problem of latent image formation of photographic emulsion is very interesting and important. Notwithstanding, electron-microscopic observations of photographic emulsions have been very poor. Only the appearance of the "halos" in the electron-microscopic image of photographic emulsion had already been known(1). A few investigators also indicated that, in general, some of electron-microscopic specimens were remarkably deformed and changed in quality due to intense electron bombardment and there were often possibilities of misjudging these original characters because of so-called pseudostructure. John H. L. Watson(2) studied this effect on inorganic substances such as tetracupper calcium oxychloride, tungsten oxide and etc., and concluded that this cause may be attributed to the heat effect of the electron bombardment. E. F. Burton, R. S. Sennett and S. G. Ellis(3) also observed this phenomenon mainly on ionic crystals such as sodium chloride, potassium bromide, potassium iodide, silver chloride, etc., and suggested that this effect may not be entirely due to the heat effect of the electron bombardment. Systematic studies and physical interpretations of the "halos", however, have scarcely been made. In order to clarify the cause of the "halos" in electron micrographs of photographic emulsion for beginning of solution on the problem of latent image, electron-microscopic observations of the emulsion were carried out under various conditions.

(1) Y. Oyama, Shimazu Hyoron **5** (1948), 17.
(2) John H. L. Watson, J. Appl. Phys. **19** (1948), 713.
(3) E. F. Burton, R. S. Sennett and S. G. Ellis, Nature **160** (1947), 565.

Emulsion of "Fuji" process photographic plate and emulsion produced by the ripening of colloidal silver bromide were used. Fig. 1 and Fig. 2 are electron micrographs of the "Fuji" process emulsions in the case of medium thickness of gelatine after sensitization and before it produced in the dark room respectively. In both specimens it was found that ooze from the crystal was performed, great or little, but the "halos" and the change of the inner structure of the crystal did not appear at all in the case of weak electron bombardment (a)

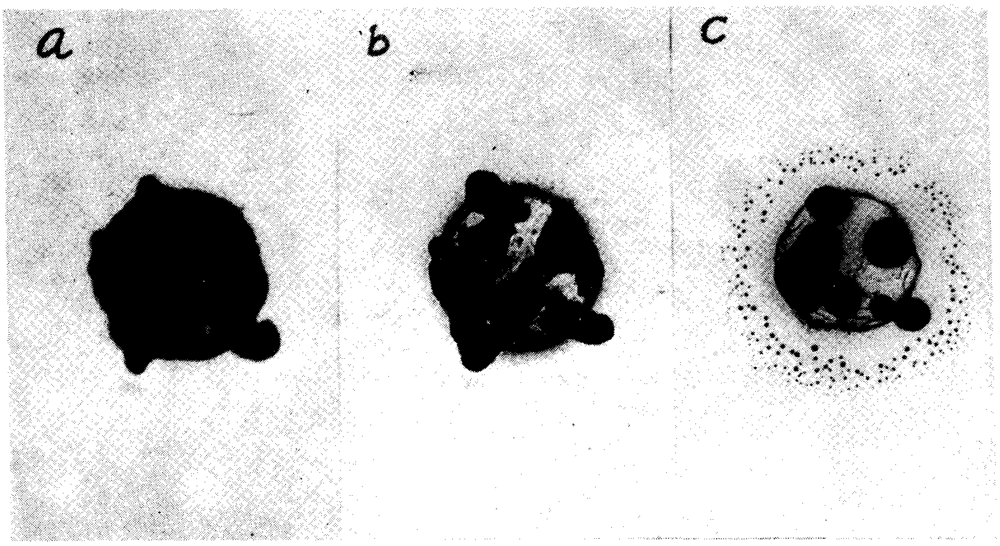

Fig. 1. Electron micrographs of the "Fuji" process emulsions in the case of medium thickness of gelatine after sensitization. (a), (b) and (c) correspond to the cases of weak, intense and more intense electron bombardment, respectively. 28,000×

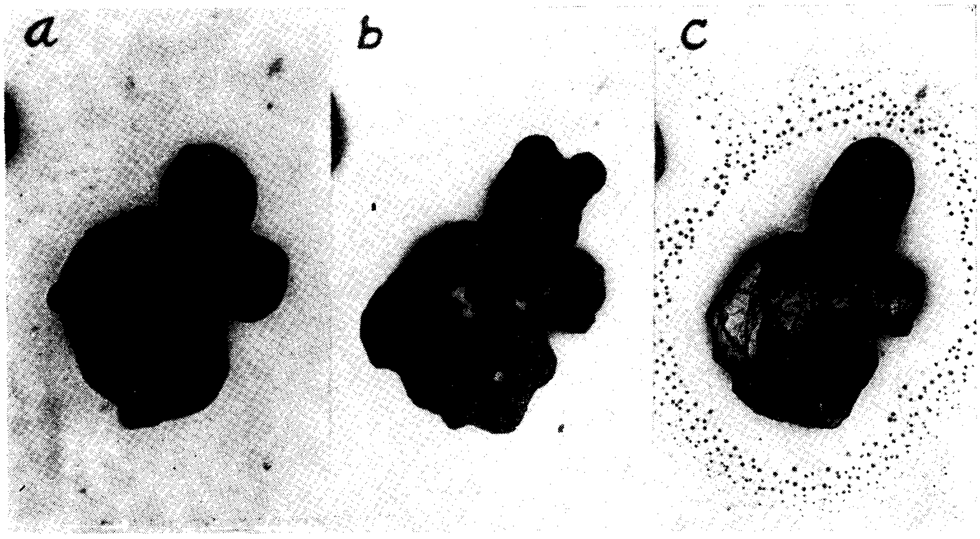

Fig. 2. Electron micrographs of the "Fuji" process emulsions in the case of medium thickness of gelatine before sensitization produced in the dark room. (a), (b) and (c) correspond to the cases of weak, intense and more intense electron bombardment, respectively. 28,000×

It was also seen that the inner structure of the crystal changed at first with intense electron bombardment (b) and the "halos" appeared with more intense electron bombardment (c). This phenomenon was more remarkable in the case of using the emulsions before sensitization produced in the dark room than that after sensitization as seen from the comparison of both figures. The ring pattern, as seen in the both figures, is clearer in the case of suddenly increasing an electron beam density than the case of slowly increasing it. From the observation with the naked eye it also seemed that the "halos" appeared at an instant of sudden change of the inner structure of the crystal. Fig. 3 is an

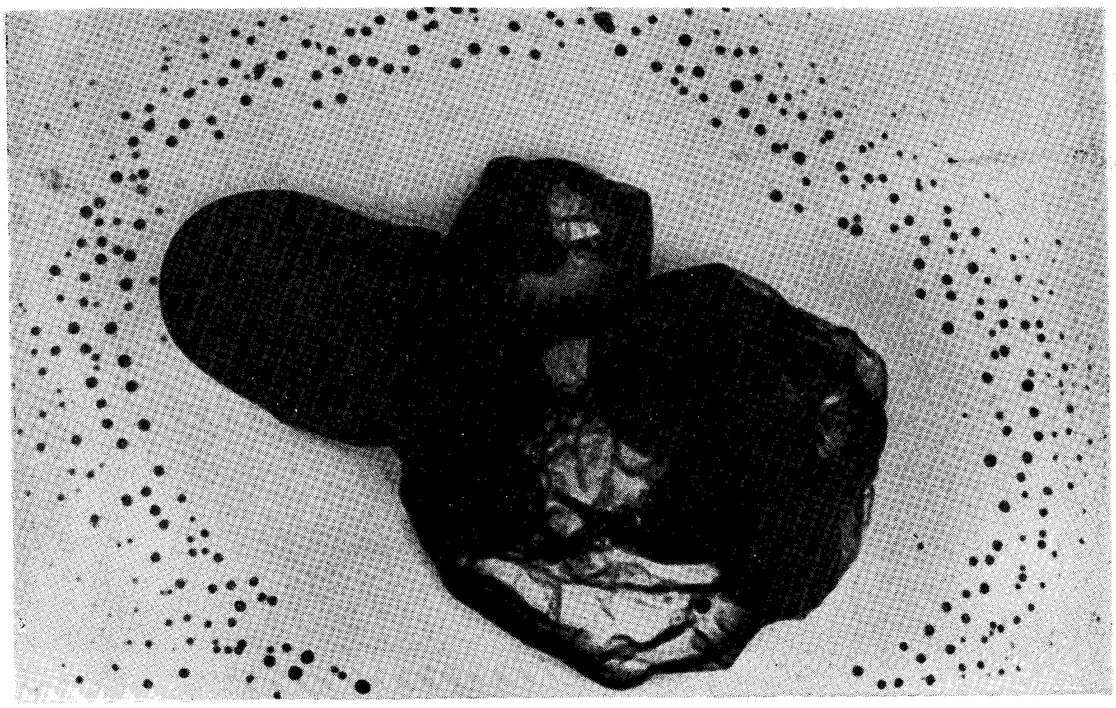

Fig. 3. Enlarged electron micrograph of one part of Fig. 2 (c). 50,000×

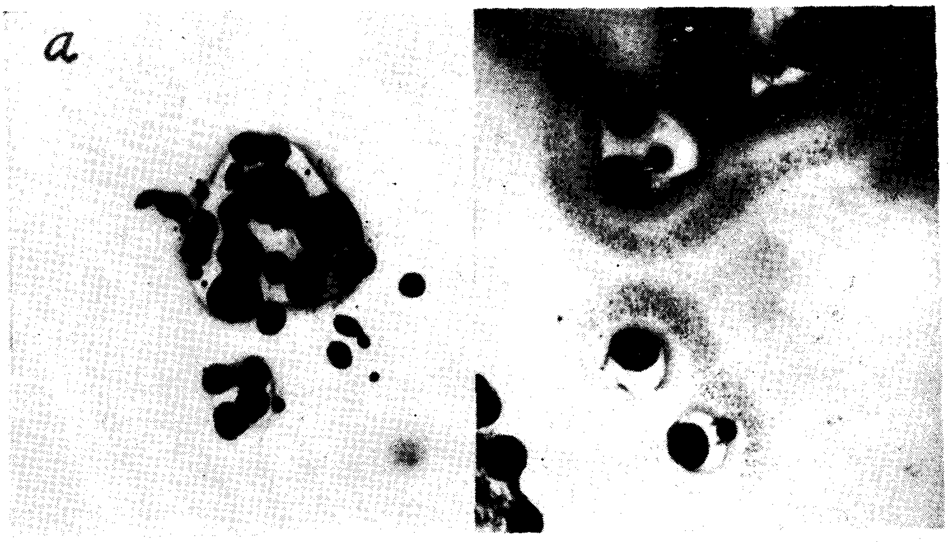

Fig. 4. Electron micrographs of the "Fuji" process emulsions after sensitization in the cases of gelatine having thin and various thicknesses, respectively ((a) and (b)). 28,000×

enlarged electron micrograph of one part of Fig. 2 (c). From this the behaviour of very beautiful "halos" can be seen. The emulsions were also observed at various thicknesses of gelatine. As the results it was found that the appearance of the "halos" depended on the thickness of gelatine*. Fig. 4 (a) and (b) are electron micrographs of the "Fuji" process emulsion after sensitization in the cases of gelatine having thin and various thicknesses respectively. From these it is clear that "halos" do not appear in the case of no or thin gelatine. Fig. 5 are also electron micrographs of the "Fuji" process emulsion before sensitization

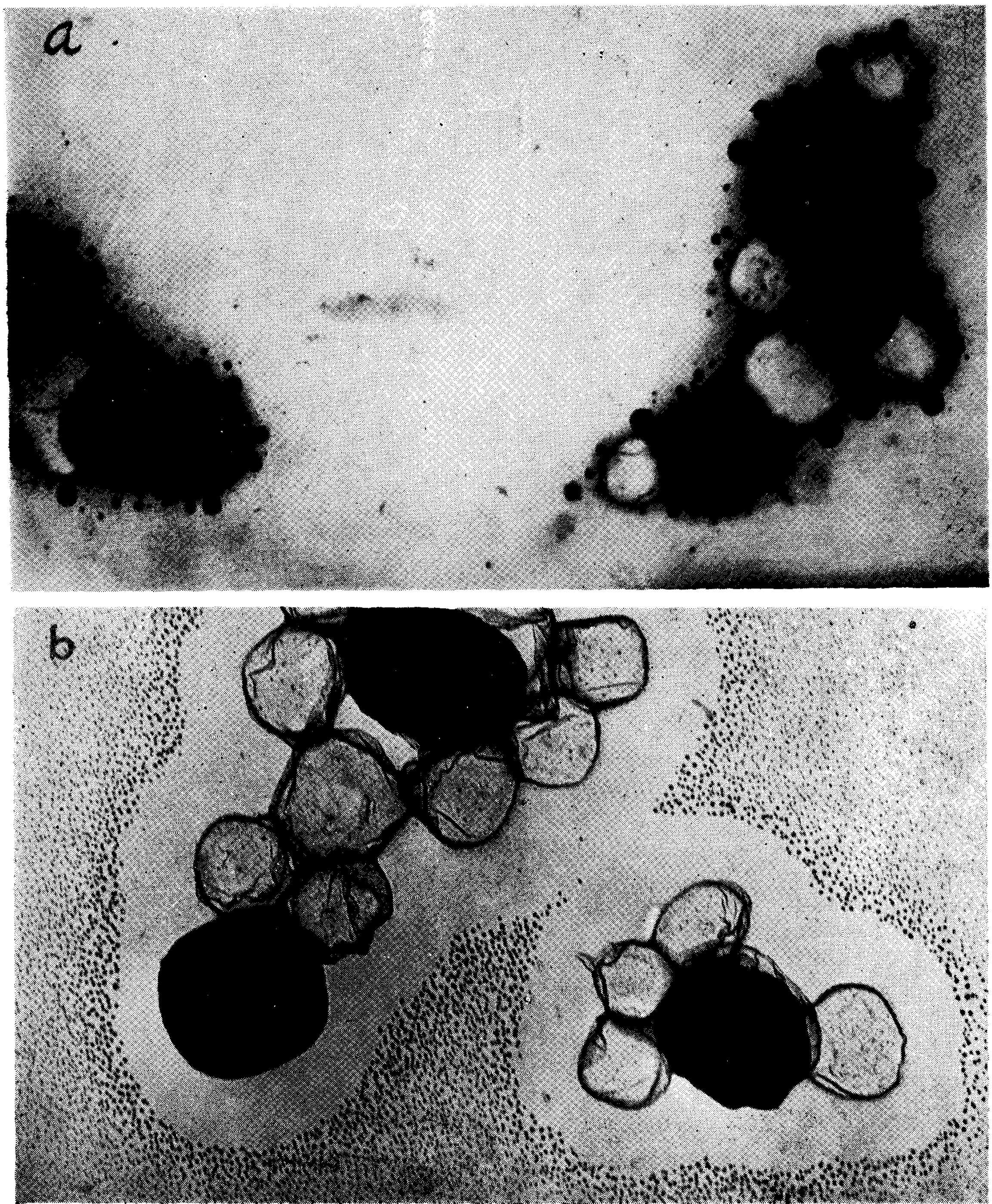

Fig. 5. Electron micrographs of the "Fuji" process emulsions before sensitization in the cases of gelatine having thin and proper thicknesses, respectively ((a) and (b)).
28,000×

* After this experiment this phenomenon was confirmed using cinema by M. Tajima, A. Fukami and K. Itô (to be published).

in the cases of gelatine having thin and proper thicknesses ((a) and (b)). "Halos" do not appear in the case of (a), but severalfold beautiful "halos" appear in the case of (b) and this change is more remarkable in the case of emulsion before sensitization than in the case of one after it. Fig. 6 (a), (b) and (c) are electron micrographs of the emulsions produced by the ripening of colloidal silver bromide in the cases of thin, medium and thick gelatine respectively.

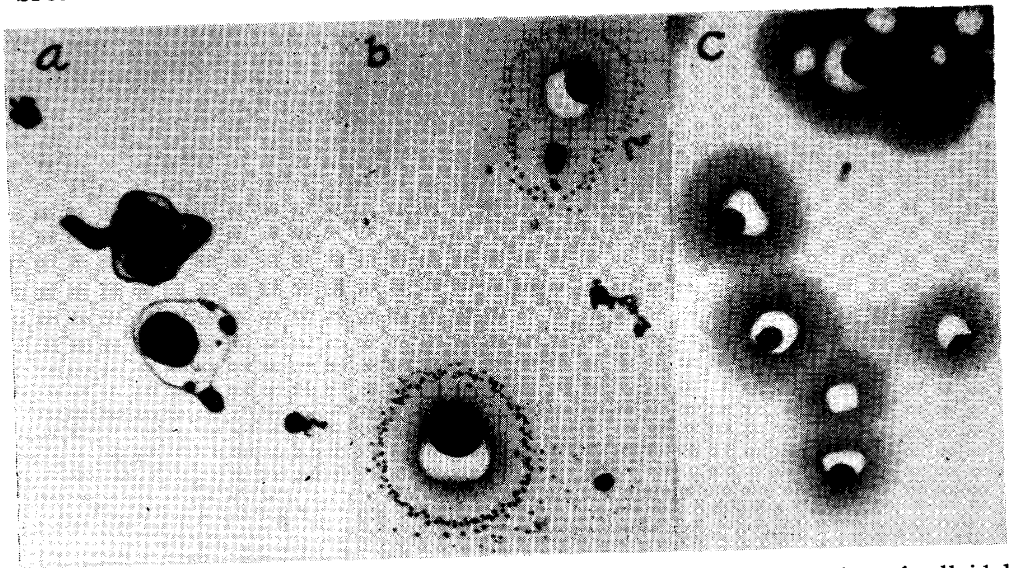

Fig. 6. Electron micrographs of the emulsions produced by the ripening of colloidal silver bromide in the cases of thin, medium and thick gelatine, respectively ((a), (b) and (c)). 28,000×

The "halos" do not appear in the cases of (a) and (c), but appear in the case of (b). In the case of (c) considerable ooze from the crystal can be seen.

Before considering the cause of the appearance of the "halos" it will be necessary to physically interprete the inner structure of the crystal appeared in electron micrographs mentioned above. Dark parts in the crystal should be

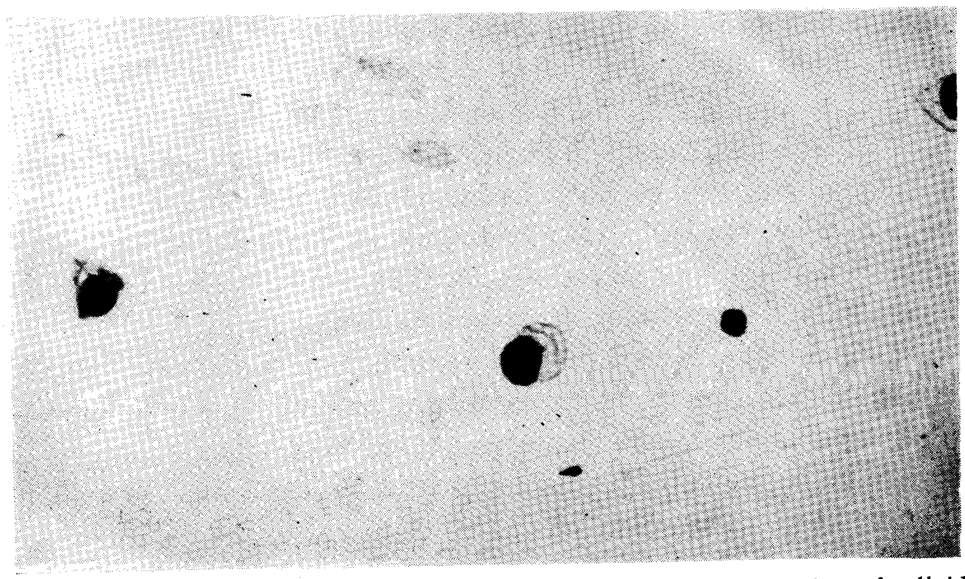

Fig. 7. Electron micrographs of the emulsions produced by the ripening of colloidal silver bromide without gelatine. 28,000×

considered to be metallic silver, because the melting point of bromine is about 60°C and bromine produced from decomposition may perhaps evaporate as gas. Fine inner structure of crystal may also be attributed to metallic silver because of the appearance of a similar structure in the specimen without gelatine as shown in Fig. 7. A residue left behind due to the electron bombardment is to be considered as the contaminating material already discussed by R. L. Stewart,(4) J. H. L. Watson,(2) E. F. Burton, etc.(3) It was also found that the bright part in the crystal was flat as the result of an examination of specimen in the case of Cr-shadowing (Fig. 8).

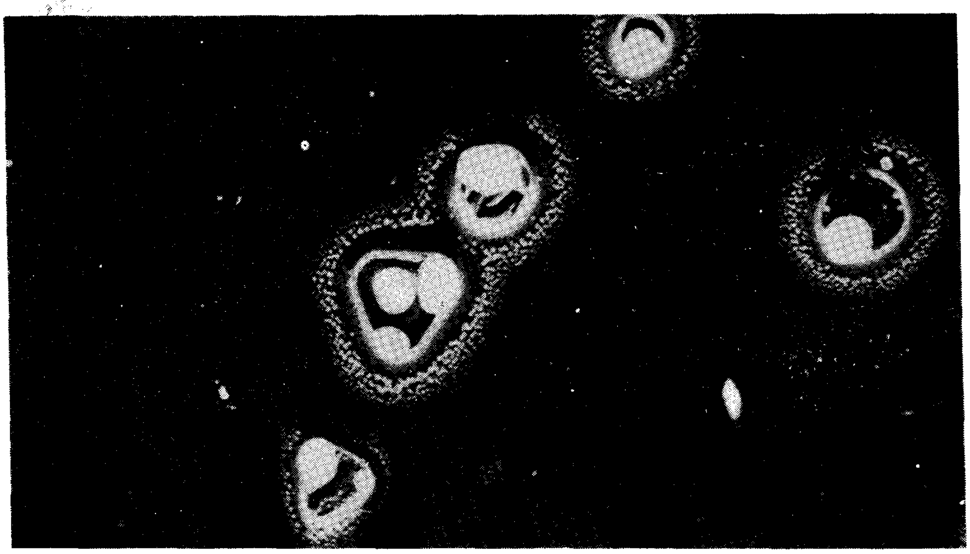

Fig. 8. Cr-shadowed electron micrographs of the "Fuji" process emulsions in the case of medium thickness of gelatine before sensitization. 22,000×

Here, the reason why the "halos" appear should be considered. It is first found that the appearance of the "halos" cannot be caused by the Liesegang ring, because in the above-mentioned electron micrographs rings around the crystal become narrower and dark points become smaller on leaving the crystal. And also the aggregation of gelatine film due to the electron bombardment cannot be the cause, judging from the results that no changes were noticed in the cases of various thicknesses of gelatine only. This is also confirmed by the fact that the ring points cast fine shadows in the metallic shadowing image mentioned above. Accordingly, ooze or evaporation of metallic silver remains as the probable cause of the "halos". C. E. Hall and A. L. Shoen(5) reported that half-transparent substance oozed from the crystal with the electron bombardment of silver chloride and it might be partially metallic silver. Ooze from the crystal should be performed, great or little, but this is not the cause of the "halos". In this experiment the "halos" appeared in the case of intense electron bombardment, on the contrary, ooze appeared in the case of weak electron bombardment. Very remarkable ooze also appeared in the case of excessive

(4) R. L. Stewart, Phys. Rev. **45** (1934), 488.
(5) C. E. Hall and A. L. Shoen, J. Opt. Soc. Am. **31** (1941), 281.

thickness of gelatine film as seen in Fig. 2 (c), and this never aggregated with the intense electron bombardment. From the consideration of ooze, the "halos" should be dense immediately around the crystal and lighter on leaving the crystal; in reality, the "halos" did not appear at all immediately around the crystal as seen in the above-mentioned electron micrographs. So it is seen that the cause of the "halos" is not the ooze but the evaporation of metallic silver. From the consideration that the evaporation of metallic silver is not performed in the case of weak electron bombardment but is remarkable in the cases of intense and sudden ones, it can easily be explained that the "halos" only appears in the latter cases. The results that the "halos" did not appear in the case of thin gelatine but appeared in the case of medium thickness are very interesting from the standpoint of latent image formation of photographic emulsion. As silver sulphate in gelatine acts as centers of aggregation of metallic silver(6), it can be interpreted from the fact that silver particles are difficult of moving in the former case having small density of silver sulphate but in the latter case of having large density of it, they are easy of moving and aggregating due to the electron bombardment. Fig. 9 is the case in which unknown contamination attached on the circumference of specimen supporter was deposited on the specimen already having the "halos" because of the electron bombardment.

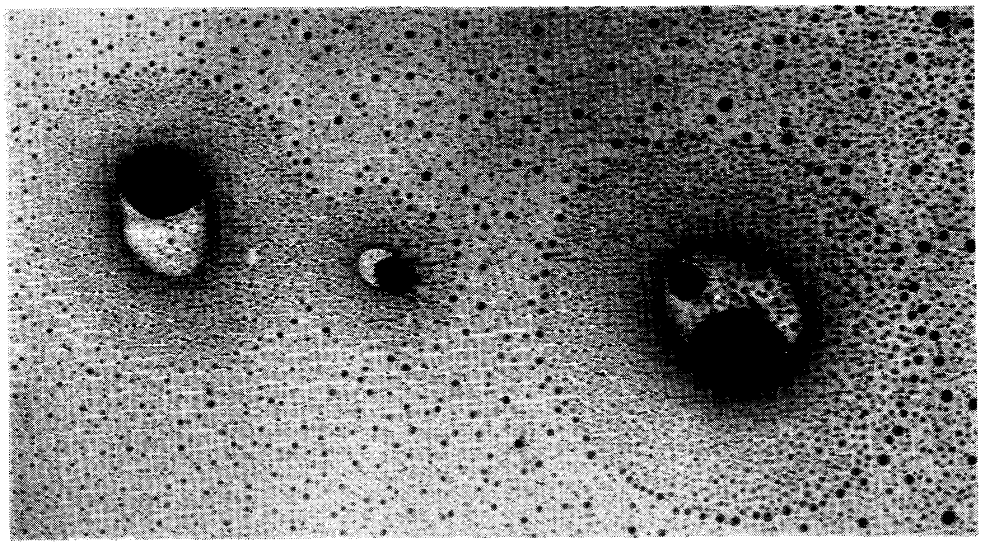

Fig. 9. Electron micrographs showing the unknown contamination deposited from the circumference of specimen supporter on the specimen already having the "halos" due to the electron bombardment. 28,000×

In this figure density of aggregation points is large at the inner part of the "halos", but small at the outer part of it, that is, it is easier for contamination particles to aggregate at the outer part of the "halos" than at the inner part of it. From this it is presumed that the gelatine is thin at the immediate circumference of the crystal, assuming that silver sulphate in gelatine acts as centers of aggregation of contamination particles similer to silver one.

(6) N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, 1940).

From the above-mentioned results it may be reasonable to explain the cause of the "halos" as follows; with electron bombardment the temperature of the crystal increases and ooze is formed. Gelatine film covering the crystal becomes half-molten and begins to flow with more intense electron bombardment, and because of the exposure of the silver bromide to vacuum directly, it is suddenly dissolved and the metallic silver evaporates from the crystal.* From this it can be considered that gelatine film becomes thin at the immediate circumference of the crystal and its thickness rises and falls in the parts of rings. Accordingly, the "halos" as seen in the figures hitherto shown appear because of aggregation of metallic silver due to the electron bombardment. To clarify such a consideration a model experiment was performed.

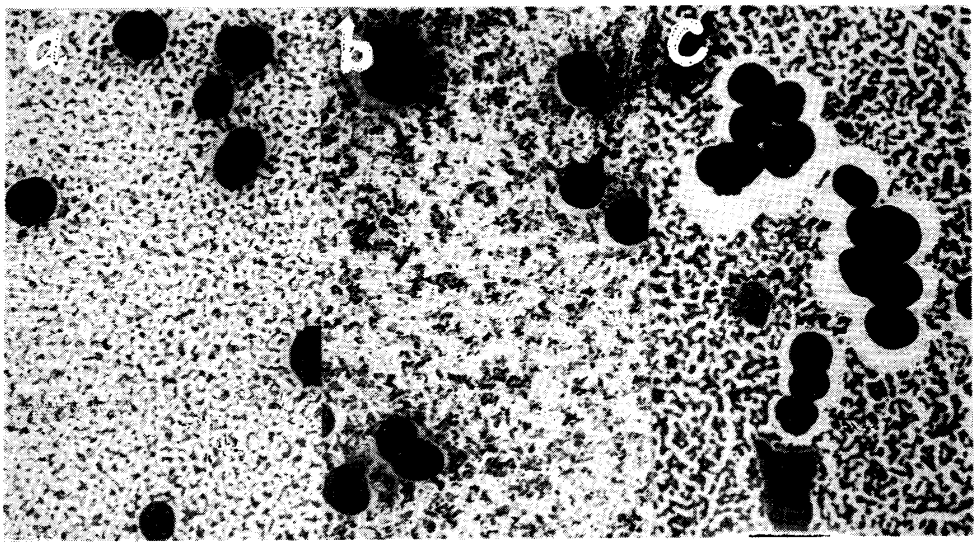

Fig. 10. Electron micrographs of the specimens of carbon black only, of carbon black placed on gelatine film, and of carbon black filled in gelatine film on the collodion foil, having very slightly deposited silver films under the same conditions ((a), (b) and (c)). 25,000×

With the specimens of carbon black only, of carbon black placed on gelatine film, and of carbon black filled in gelatine film on the collodion foil, very slightly deposited silver films were made under the same conditions. The results of electron-microscopic observation of these specimens showed that the "halos" did not appear and silver film was difficult of aggregation in the case of carbon black only (Fig. 10 (a)). On the contrary, in the case of carbon black placed on gelatine film (Fig. 10 (b)) the imperfect "halos" appeared, and in the case of carbon black filled in gelatine film (Fig. 10 (c)) the bright part appeared at the immediate circumference of carbon black and silver film was easy to aggregate. From the results of this model experiment it may be confirmed that the abovementioned physical interpretation is correct.

In conclusion the author wishes to express his thanks to Mr. S. Takahashi for his valuable assistance.

* Whether resolution of silver bromide due to the electron bombardment may be caused by pure heat effect as Watson(2) thought, or by ionic migration as Burton, etc.(3) suggested, cannot be concluded here from results obtained.