Electron Microscope Studies on Radiography. III.[1,2] Formation of Lumpish Developed Silver in Radiography

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The shape of developed silver in industrial X-ray films exposed to a high energy radiation has been found mainly lumpish, which differs from the filamentary shape observed in ordinarily-developed photographic films. The formation process and crystalline states of lumpish silver were studied with an electron microscope in comparison with those of filamentary silver. Lumpish silver cannot be in a single uniform crystalline state under a kind of hindrance due to too active a development for regular crystal growth, the thickness of emulsion layer and the concentration of silver halide also have some effects.

It has been thought[3] that the developed silver of photographic film has a filamentary structure (Fig. 1) in normal development and that the reduced silver grows on development nuclei. However, according to the author's observation, the develoed silver in industrial X-ray film has a shape to be called "lumpish" (Fig. 2) and grows at sites apart from development nuclei. On the shape and the formation process for such silver, no paper has been reported with discrimination from ordinary ones.[3] To make clear the development characteristics of industrial X-ray film, the difference between the structures of lumpish and filamentary silvers and their formation conditions were studied.

Many electron microscopic studies on developed silver have been reported, and a lot of morphologic knowledge on developed silver is available. We also applied a transmission type electron microscope for this stuby. This equipment was also applied for an electron diffraction study to analyze the crystal structure and crystalline state of developed silver.

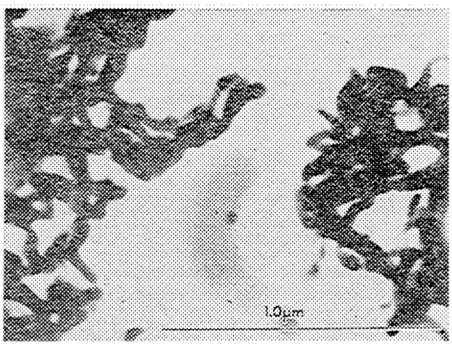


Fig. 1. An electron micrograph of developed silver in FUJI NEOPAN SS film developed with FUJIDOL. Crystalline state of the silver correspond to Figs. 4B—D.

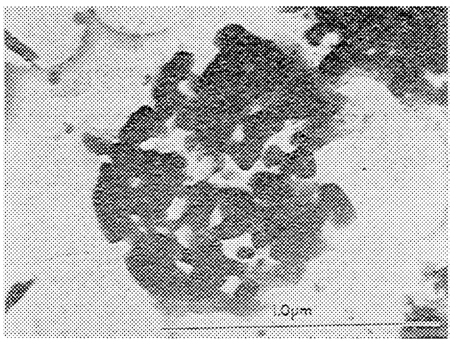


Fig. 2. An electron micrograph of developed silver in SAKURA RR industrial X-ray film developed with KONIDOL-X. Crystalline state of the silver correspond to Figs. 4B—G.

Many experimental methods which appeared in the past were carried out mostly under special conditions, *i.e.*, by using diluted monodispersed emulsion or by using partial development with a particular developer. These experiments disclosed that the tubic, Mueller's type developed silver[5] is formed in the dilute monodispersed emulsion layer and very thick filamentary silver[4] is formed via a particular physical development. These developed silvers are not observed in the conventional development. Therefore, in this study, the author has carried out an experiment by using commercial films under the ordinary conditions, *i.e.*, by exposing and developing them according to manufacturer's instruction, and the morphological variation of silver has been systematically observed in course of development.

Although the crystal structure of developed silver has already been determined by some workers, no information has been supplied of the structure of developed silver in course of development. In this study, therefore, the variation of the crystalline state of silver during development has also been traced systematically by the electron diffraction method.

Experimental

Specimens for electron micrscopic observation were prepared from several strips of Sakura RR industrial X-ray film in the following procedure. Test film strips were exposed uniformly to 150 kVp X-ray beam of optimum dose, 0.2 R (5.16×10^{-5} C/kg), and developed for 10, 30, 60, 90, 120, 150, 180, 240, or 300 s with Konidol-X, the commercial developer for Sakura industrial X-ray film. The specimens were prepared[6] from developed and stop-bathed, but not fixed, film strips. The degree of the degradation of gelatin in emulsion layer with enzyme which allows silver halide particles to be isolated, was controlled so that deformation of developed silver might be prevented. The rotation speed of the centrifuge used for washing silver and silver halide particles was also controlled so as to be kept as low as 800 rpm for the same purpose. The finished specimens were observed with a JEM Type-100 transmission electron micrscope, and morphological and crystallographical variations of silver in every step of development were studied. Magnifying powers of 5000—60000 were applied according to the size of silver and silver halide particles

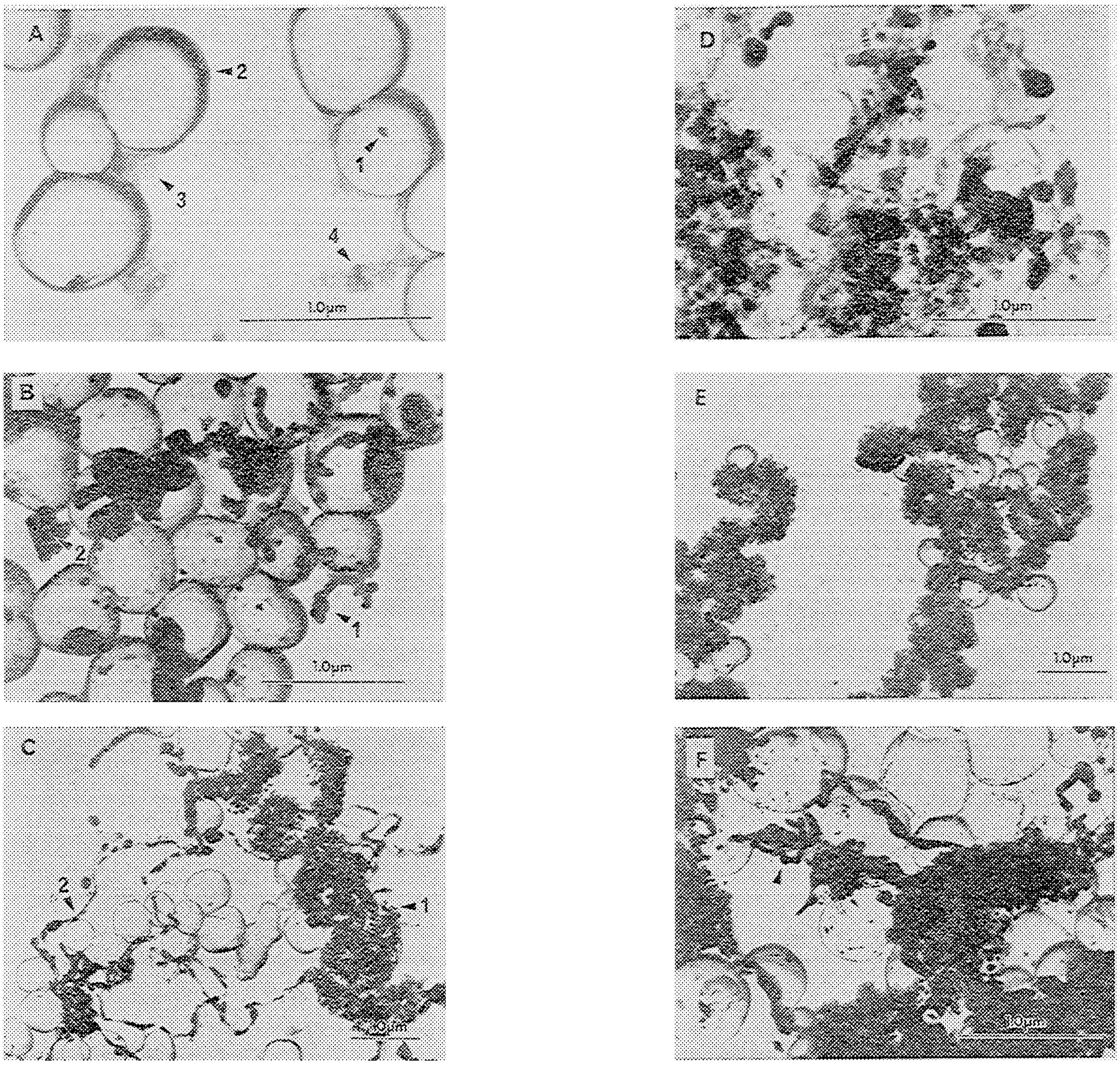


Fig. 3A—F. Variation of shape and crystalline state of the developed silver in SAKURA RR industrial X-ray film exposed to 150 kVp X-ray is developed for various times with KONIDOL-X.
Figs. A and B are for developed 30 s, Fig. C for 60 s, and Figs. D—F for 150 s respectively. Figs. A and B correspond to Figs. 4A and 4B, Fig. C to Figs. 4B—D, and Figs. D—F to Figs. 4B—G respectively.

and the electron diffraction apparatus equipped with the JEM Type-100 electron microscope was used for the measurement[7] of crystalline states of silver.

The formation process of filamentary silver, whose shape is well known as a general one, was also studied by the same method as used for lumpish silver, and the difference between these processes has been studied. The specimens for filamentary silver were prepared from Fuji Neopan SS (fine grain panchromatic negative film), uniformly exposed to sunlight, and developed for 30, 60, 90, 120, 150, 180, 240, 300, or 420 s with Fujidol, the commercial developer for Fuji Neopan SS.

Furthermore, factors influencing the shape of silver were also studied on other types of photographing materials by changing exposure and development conditions. These materials include Fuji 150 industrial X-ray, Sakura Konipan SS, Fuji Minicopy HR II, Sakura Color III, and Sakura NR-M2 nuclear liquid emulsion. For Sakura RR, Fuji Neopan SS, and Sakura NR-M2, some special materials were also prepared for which the concentration of silver halide and the thickness of emulsion layer were modified after decomposing film emulsion with enzyme. These materials were used for studying the relation between the shape of silver and the physical constitution of film material. All the materials were exposed to 150 kVp X-ray or to sunlight for studying the influence of radiation. Two type of developers, Konidol-X as an active developer and Fujidol as a moderate one, were used. Each developer was diluted so as to have a concentration of 100, 50, 25, 10, 5, 2, or 1% with water for studying the influence of developing conditions. The microscopic procedures used for these materials were the same as those for Sakura RR film used to observe lumpish silver, and the shape and crystalline state of silver on each material were studied at various stages of development.

Results and Discussion

The change in the shape of silver observed in the conventional development process of Sakura RR film is shown in Figs. 3A—F, and the change in the crystalline state of silver accompanying that in the shape is shown in Figs. 4A—H by electron diffraction patterns. The pattern of Fig. 4A indicates that the silver is in an amorphous state since it has no diffraction dot. Ac-

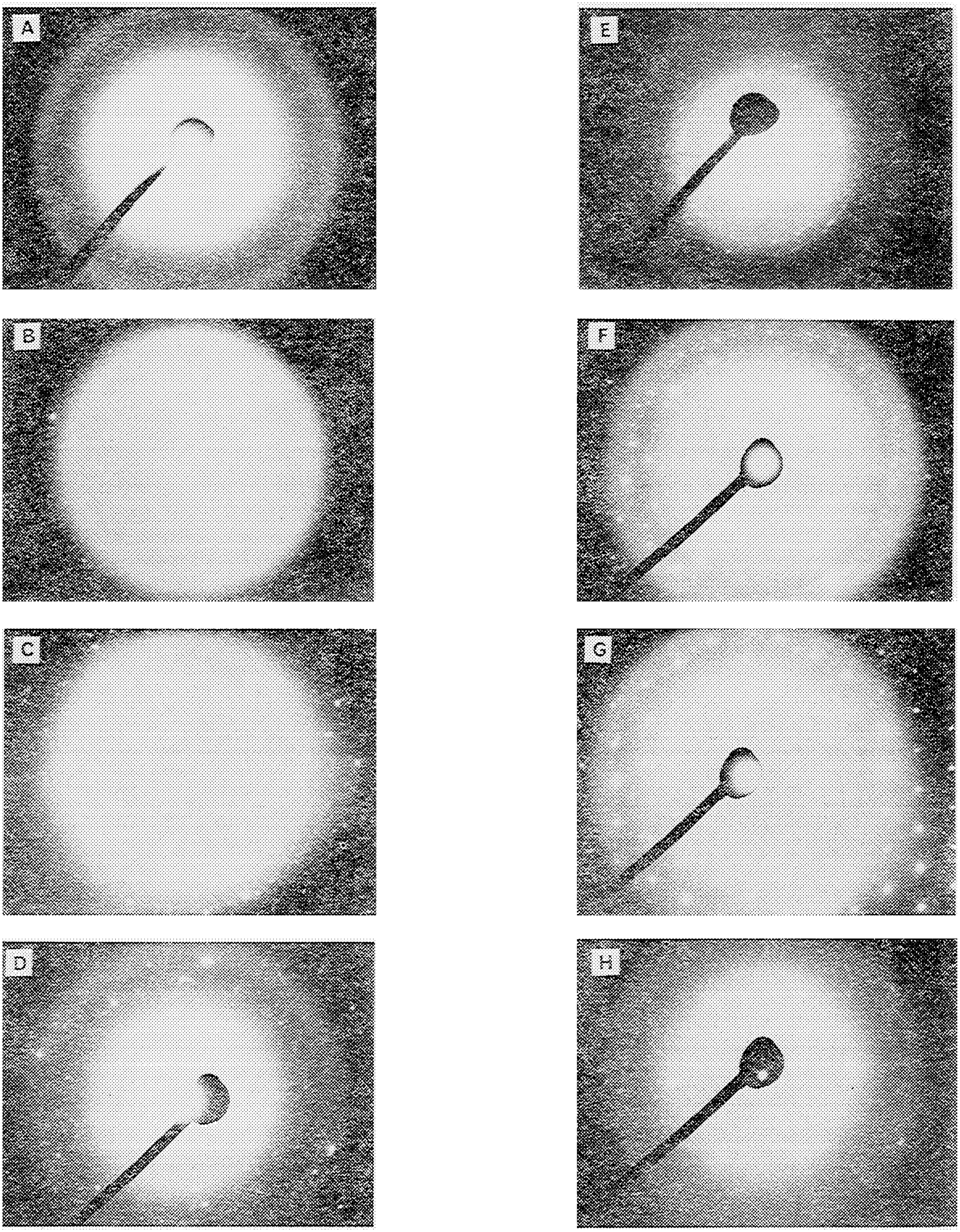


Fig. 4A—H. Electron diffraction patterns of silver on various conditions.
A: Amorphous, B—G: Progress of crystallization, H: Big crystal.

cording to the patterns of Figs. 4B—D, some crystallites are generated in the amorphous silver because some dots are found in the field. The increase in the number of dots means the increase in the amount of crystallites to be due to the progress of the crystallization of silver. The patterns of "Debye-Scherrer ring" in Figs. 4E and F indicate that almost all silver is finely crystallized in crystallites. The pattern in Fig. 4 G indicates a crystal growth of silver from a fine to coarse state. The pattern of "Laue" in Fig. 4 H indicates that the silver takes a structure of single crystal, and the Laue pattern of hexagon indicates that the crystal structure of developed silver is a face-centered cubic lattice.[7]

Several different shapes of developed silver are found in the early stage of development, *i,e.*, at 30 s development time, pointlike (Fig. 3A-1), bandlike (3A-2), and mistlike (3A-3) which are amorphous (Fig. 4A), and dendrite (3B-1). It seems that the mistlike silver will emerge from the silver-gelatin (complex) envelope[8] which is covering the silver halide particles (Fig. 3A-3 and -4). The mistlike silver thus having emerged then aggregates (Fig. 3B-2) as the amount of reduced silver increases and the crystallization progresses slightly (Fig. 4B). A further crystallization of aggregate silver was observed in the middle stage of development, *i.e.*, at 60 s, (Figs. 3C-1 and 4B—D). In the later stage of development, *i.e.*, at 150—300 s, the developed silver turned lumpish because of rapid progresses of aggregation and crystallization (Figs. 3D and 3E). The crystalline state of lumpish silver is complicated because the electron diffraction patterns obtained for several parts of the same lumpish silver are not the same (Figs. 4B—G). This means that the lumpish silver is produced as the result of a disorderly progress of crystallization.

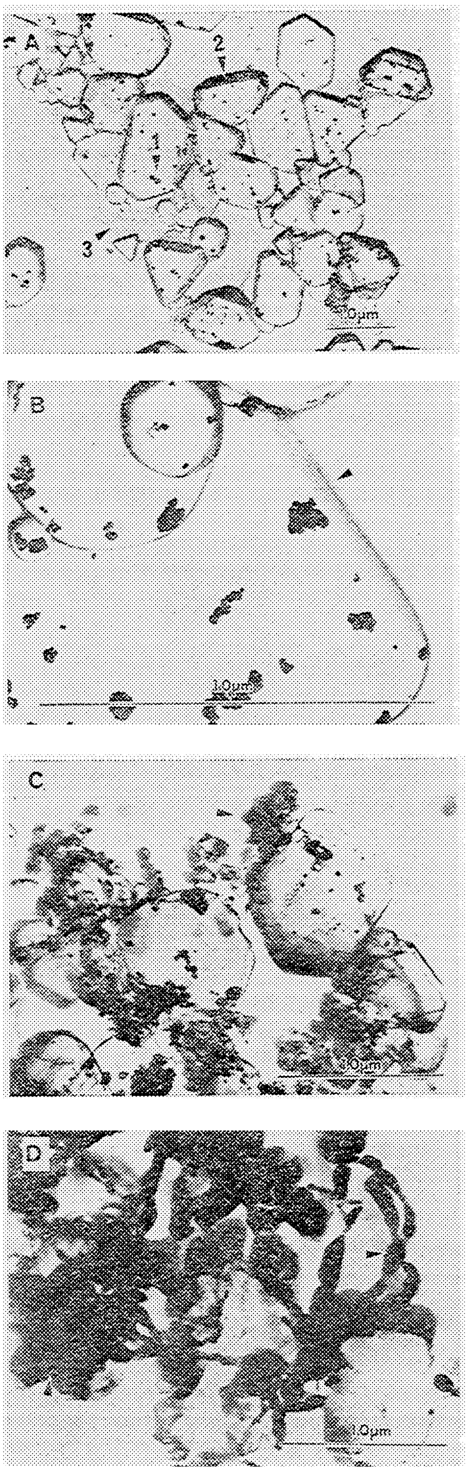
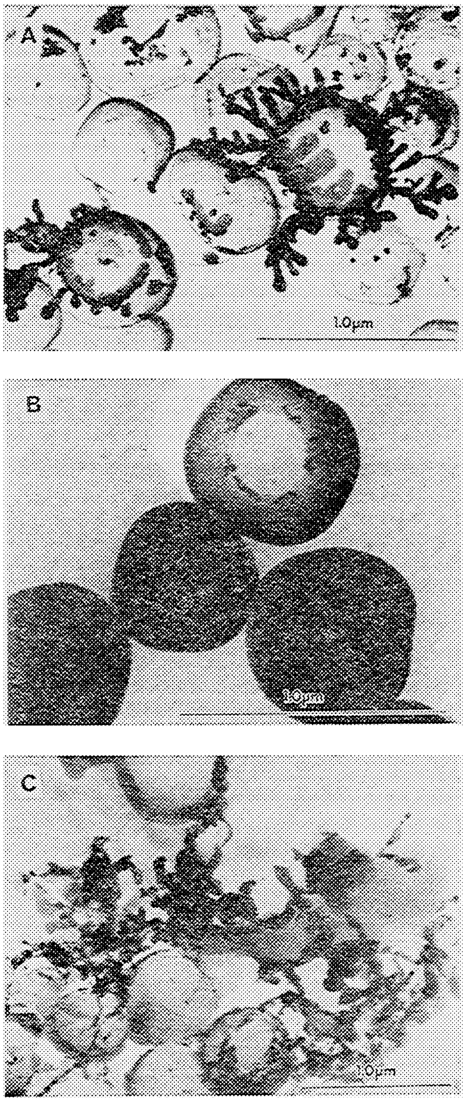


Fig. 5A—D. Variation of shape and crystalline state of the developed silver in FUJI NEOPAN SS film exposed to sunlight and developed for various times with FUJIDOL.
Figs. A and B are for developed 30 s, Fig. C for 60 s, and Fig. D for 150 s respectively. Figs. A and B correspond to Fig. 4A, Fig. C to Figs. 4A and 4B, Fig. D to Figs. 4B—D respectively.

Silver particles other than lumpish shape, such as dendritic, tubular, filamentary and pointlike ones, have also been found in a slight amount on Sakura RR film fully developed. The tubular silver generated in and after the middle stage of development is similar in shape to the silver which has been found by Mueller[5] (Fig. 3C-2), and their crystallization degrees are almost the same as that of the aggregate silver (Figs. 4B—D). A filamentary silver was also found in a somewhat unusual shape (Figs. 3F and 4B—D). The size and number of pointlike silver particles produced in the early stage of development change little, though the development progresses to the final stage (Figs. 3A and 3E). It has been clarified that the development process in radiography is complicated because of the existense of silvers having various shapes and being in various states of crystallization.

On the other hand, the shapes of silver observed in the process of ordinary development of Fuji Neopan SS film are shown in Figs. 5A—D and 1, and their crystalline states are shown in Figs. 4A—D. The silver reduced in the early stage of development, at 30 s, has a pointlike (Fig. 5A-1), bandlike (A-2), mistlike (A-3), or dendrite (in a rare case) shape, which are amorphous (Fig. 4A) except for dendrite. These results are the same as those obtained with Sakura RR (Fig. 3A). The mistlike silver was found to emerge from the silver-gelatin (complex) envelope (Figs. 5B and 4A) in the early stage and to aggregate in the next process (Figs. 5C, 4A, and 4B). However, the aggregate silver does not take a lumpish shape in the middle stage of development, at 150 s, but the filamentary silver grows up there (Fig. 5D). The crystallization of aggregate and filamentary silvers at this stage scarcely progresses (Figs. 4B and 4C). The greater parts of aggregate silver change to filamentary silver in the later stage of development, at 300—420 s (Fig. 1). The crystallization of filamentary silver in the final stage shows only a slight progress, in contrast with the lumpish silver (Figs. 4B—D). The crystalline state of filamentary silver is almost the same at any parts in a filament. The shapes of silver other than the filamentary one, such as tubular, lumpish, and dendritic, were seldem been found in this experiment. No growth or increase in number of pointlike silver are found in the later stage, nor any formation process of lumpish silver. There seem to be little information on the shape of lumpish silver or its formation process, and then the new results obtained here on the formation process of filamentary silver, in comparison with that of lumpish silver, cannot entirely be explained on the basis of the formation mechanism[3] for developed silver widely accepted at present. It is thus pointed out



Figs. 6A—C. Electron micrographs of developed silver obtained from modified SAKURA RR industrial X-ray film at various treatment conditions.
A: Gelation free silver halide particles are isolated perfectly from the gelatin layer. B: Extremely thick emulsion layer with silver halide of low concentration. C: Thin emulsion layer with silver halide of medium concentration.

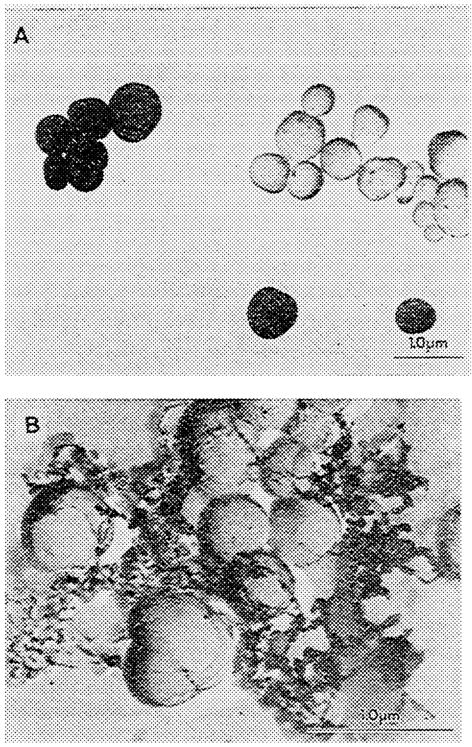


Fig. 7A—B. Electron micrographs of developed silver in SAKURA RR industrial X-ray film developed with KONIDOL-X of various dilution.
A: 1/25, B: 1/5.

that any appropriate development mechanisms should consider not only the reduction process of silver halide but also the crystallization process of reduced silver.

The factor determining the shape of silver has been studied more widely from the above point of view.

The popular shape of silver observed at a sufficient depth of ordinary development is either filamentary or lumpish. Neither the difference in film manufacturers nor the difference in exposure conditions is a dominating factor determining the shape of silver. Lumpish silver has been found to be formed only when industrial X-ray film is caused to be developed ordinarily and when other types of film materials are developed with higher-activity developers. However, the shape of developed silver of Sakura RR film which is lumpish, has been found to change variously according to the modification of the emulsion layer of film. For instance, gelatin-free silver halide particles obtained by an enzyme processing of Sakura RR film gave the dendritic silver after development (Figs. 6A and 4H). These gelatin-free silver halide particles were redispersed in gelatin solution and coated so as to have a thick emulsion layer with a low concentration of silver halide particles. This modified Sakura RR film gave spherical silver after development (Figs. 6B, 4A, and 4B). In the case of another type of film having extremely thin layer with a low concentration of silver halide particles gave the filamentary shape (Figs. 6C and 4B—D). Therefore, the constitution of emulsion layer, the concentration of silver halide, and the thickness of emulsion layer are effective factors determining the shape of silver.

On the other hand, another important factor determining the shape of silver is the activity of developer depending on the composition and development temperature. The shape of developed silver in Sakura RR film can easily be changed by varying the activity of the developer used; the spherical shape (Figs. 7A, 4A, and 4B) has been found at the lowest activity, the filamentary shape (Figs. 7B and 4B—D) at the medium activity, and the lumpish shape (Figs. 2 and 4B—G) at the highest activity.

Therefore, it has been clarified that the constitution of silver halide emulsion layers and the activity of developers are the most important factors that determine the shape of silver during the crystallization process of silver.

Conclusion

Most of developed silvers in industrial X-ray films formed with ordinary X-ray film developers have a lumpish shape, which differs from the filamentary silver formed in negative films not only in shape but also in crystalline state.

When lumpish silver is formed, some dendrite, tubular, and filamentary silvers are also formed. Lumpish silver consists of amorphous and crystalline parts, and the latter is composed of fine crystallites with various degrees of crystallization. Therefore, in the formation process of lumpish silver, the progress of crystallization of developed silver is highly influenced by the constitution of emulsion layer and the conditions of development as compared with the case of filamentary silver.

At the early stage of development with ordinary developers, developed silvers of both negative type films and industrial X-ray films exist in amorphous and formless states. Furthermore, the following processes occur: (1) amorphous and formless silvers emerge in the gelatin matrix around silver halide particles, (2) aggregate there, and (3) crystallize.

In this process, the developed silver shows several shapes resulting from the asymmetrical progress of crystallization governed by the above-mentioned factors.

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