On the Pseudo-Photographic Effect of Coal and the Photographic Plates

By

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Abstract

The pseudo-photographic effect of coal was studied from the phenomena at the side of the plate. By using the KI-starch paper and the photographic plates, some properties of latent images induced by coal were observed. The pseudo-photographic sensitivity of photographic plates was also examined. It was found that the pseudo-photographic sensitivity seemed to be increased by the fog, and the photographic plates were sensitized by heating and light-exposure. The action of coal on the sensitized plates was analogous to that of H_2O_2. It may, therefore, be considered that the direct active agent in the coal is H_2O_2.

Coal has ability to affect a photographic plate in the dark. When the photographic plate is developed in the usual manner, a " contact photograph " is obtained which varies in character with the structure of the surface of the coal which is laid in contact with it. Such pseudo-photographic effect of coal has been studied by Halsam and Wheeler[1] and Ito.[2]

Recently, the writer has also been concerned in the study of this effect of coal in cooperation with H. Sawada and K. Morikawa.[3] There we studied the mechanism of this effect from the side of the coal and proposed the view that the peroxide (either H_2O_2 or O_3) which is formed during the oxidation of coal is the agent that affects the photographic plate.

In the present paper the author studies this effect from the side of the plate and compares the effect of coal with that of H_2O_2.

Preparation of Contact Photographs

To prepare contact photographs, the surface of a lump of coal is

1. G. S. Halsam and R. V. Wheeler: Fuel, **1**, 43, (1922). G. S. Halsam: Fuel, **7**, 253, (1928).
2. K. Ito: Bull. Inst. sci. Res. Manchukuo, **3**, 562, (1939).
3. H. Sawada, K. Morikawa and Y. Yamamoto: This will be published in J. Fuel Soc, (Japan).

polished by sand paper No. O; this surface is laid upon the film of a plate and heated during exposure at 30°C in a light-tight box in which humidity is kept at 79.5% by means of a saturated NH_4CL solution to accelerate the action of coal.

In the case of H_2O_2, a solution containing one part of commercial oxydol in 100 parts of water is used. 40 c.c. of this solution is measured into a glass crucible, and a plate is laid film-side down on the edge of the crucible, the film being 10 mm. apart from the liquid surface, and left in the dark at room temperature during 24 hours; then it is developed in the usual manner.

Investigation with KI-Starch Paper

In the previous investigation, when KI-starch paper was used instead of a photographic plate, a brown-violet iodine-starch figure was obtained on the paper which was identical with the normal contact photograph. When KI-starch paper was laid between the coal and the plate, the image on the plate was much weakened. From these facts, we proposed the view that the fogging agent in coal is absorbed by the KI-starch paper, that coal does not affect the plate directly, that the active agent is a peroxide (either H_2O_2 or O_3) which affects the KI-starch paper, and that H_2O_2 is more likely to be it than O_3.

The writer has now repeated this investigation. KI-starch paper was laid between coal and Ilford Process plate, and after a long exposure of 40 hours, the plate was carefully developed; in the region of the plate where the KI-starch paper was in contact with it, the image was not developed at the surface layer of the film, while at the deeper layer the image was clearly developed. Hence, by brief light exposure from the glass side of the plate, the image at the deeper layer is reprinted on the surface layer emulsion. Plate I, Fig. 1 (a) shows the contact photograph thus obtained, and Fig. 1 (b) in the same plate shows the iodine-starch figure on the KI-starch paper. This indicates that coal affects the KI-starch paper and the plate simultaneously, while the excess of iodine which is librated in the paper by coal diffuses into the film of the plate and diminishes the latent images at the surface layer. To confirm this diffusion of iodine, a plate exposed for a long time to coal through KI-starch paper is dipped in a 3% starch solution before development and after sufficient adsorption of the solution, it is dried in the dark room.

When it is taken out of the dark, no change is at first detectable on the film, but gradually a violet figure proper to the iodine-starch reaction begins to appear and this figure is observed to be also identical to the normal contact photograph as shown in Plate I, Fig. 2; (a) showing the iodine-starch figure produced on the plate, (b) the normal contact photograph of the same sample. This shows first, that the excessive iodine which diffuses into the plate from the paper produces AgI by combination with silver that is liberated as latent image and diminishes the latent image at the surface layer of the film of the plate; second, that when the plate is taken out to light, the photo-decomposition of AgI begins to take place, and iodine is again liberated and this time it reacts with the starch previously adsorbed in the film and shows the violet figure, as shown in Plate I, Fig. 2 (a).

Zinc also shows a very strong pseudo-photographic effect, but it does not affect KI-starch paper. The cause of the effect of zinc thus seems to be essentially different from that of coal. In the case of zinc, besides Russell's hydrogen peroxide theory,[1] it may be considered that atomic particles which are activated at the fresh metal surface affect a plate as proposed by S. Aoyama, T. Fukuroi and others.[2]

Different Kinds of Photographic Plates

The pseudo-photographic sensitivity for coal and H_2O_2 of the photographic plates and films used in this investigation is roughly shown in Table 1. The Fuji Al, Panchromatic and Process plates were new-

Table 1. Pseudo-photographic sensitivity of plates and films for coal and H_2O_2

	Coal	H_2O_2
Ilford Process plate	very strong	very strong
Ilford Special Rapid plate	strong	strong
Apem Noskrene	strong	strong
Kodak X-Ray film	strong	strong
Fuji X-Ray film	faint	faint
Fuji Al plate	faint	faint
Fuji Panchromatic plate	very faint	very faint
Fuji Process plate	non-sensitive	non-sensitive

1. W. J. Russell: Proc. Roy. Soc. London (A), **61**, 424, (1897); **63**, 102, (1898).
2. S. Aoyama, T. Fukuroi and I. Takahashi: Bull. I. P. C. R. (Tokyo), **12**, 493, (1933); **14**, 481, (1935). S. Aoyama, T. Fukuroi and N. Susuki: Bull. I. P. C. R. (Tokyo), **15**, 923, (1936).

ly purchased while the others have been stocked so long that they had sustained a natural ageing fog. The pseudo-photographic sensitivity in the case of coal and H_2O_2 seems to increase as the natural fog increases; namely, the primary silver which has been liberated as the natural fog in or very close to the so-called sensitivity specks of AgBr grains seems to operate as a necessary factor in the process of the action of coal and H_2O_2. If so, the removal of the primary silver will decrease the pseudo-photographic sensitivity of the plates. In order to remove the primary silver, a solution containing

5% $K_2Cr_2O_7$ solution	1 part
10-fold dilution of conc. HCL	2 parts
H_2O	15 parts

was used.

Ilford Process plates, which are most strongly fogged, are dipped in this solution for 15 sec. and washed with running water for one hour. Then their pseudo-photographic sensitivity for coal and H_2O_2 is found to have clearly decreased. As shown in Figs. 3 and 4 in Plate I, the action on the treated (right half) plates is weaker than on the untreated (left half) plates, because the primary silver has been transformed into AgCl by the reaction,

$$2Ag + K_2Cr_2O_7 + 2HCL \longrightarrow 2AgCl + \text{Reduction Products of } K_2Cr_2O_7,$$

and thereafter can not operate as the sensitizing factor.

Since the natural fog is stronger in the edge of the plate than in the central part, a certain amount of unchanged primary silver will remain, even after the treatment, in the edge in an amount proportional to the original fog. Hence, the desensitization effect of the solution must be weaker in the edge than in the central part. This tendency is apparent in Plate I, Fig. 3, in that the edge is used for treatment; on the treated plate from right (the central part of the original plate) to left (the edge part) the desensitization effect gradually decreases. Thus the primary silver in the fog acts as the necessary factor in the pseudo-photographic effect of coal and H_2O_2 and it thus sensitizes the plates.

Sensitization of Plates

Coal and H_2O_2 do not affect Fuji Process plates. If, however, plates are pseudo-photographic-sensitized by their natural fog as mentioned above, the artificial fog also should sensitize them. In order to sensitize them, i. e., to give them the artificial fog, the writer has adopted the following methods which are often used in the usual sensitization of plates.

(a) By Heating

When a Fuji Process plate is heated at 40°C for two weeks, 8 hours a day, it is still not fogged, and so it is not sensitized for coal and H_2O_2. When it is heated at 55°C for 4—6 days, 8 hours a day, it is strongly fogged and becomes very pseudo-photographic-sensitive for coal and H_2O_2, as shown in Plate I, Fig. 5. In Fig. 5 the time of exposure is 29 hours, and the contact photograph was developed before the undesirable temperature fog appeared. The action on the plates heated for 6 days (left half) was stronger than that on those heated for 4 days (right half).

In the case of H_2O_2, it becomes so sensitive that the temperature fog is solarized. In this heating method, not only the silver liberated during the heating sensitizes the plate, but the relaxation of the gelatin film also allows a rapid penetration of the active agent in the coal through it.

(b) By Light-Exposure

When Fuji Process plate is light-exposed by a brown lamp (for the sensitive paper, 100V–10W) at a distance of 55 cm. for 5–10 sec., it also becomes pseudo-photographic-sensitive as shown in Plate I, Fig. 6, where the left half is exposed for 10 sec. and the right half for 5 sec. In this case, the sensitization effect is not so strong as in the case of heating.

According to Wightman and Quirk,[1] H_2O_2 intensifies the latent images before development, and the undevelopable latent images in the unintensified state are brought into the developable state owing to the reduction effect of H_2O_2; and AgBr grains with liberated primary silver in or very close to their sensitivity specks are very easily subject to the reduction effect of H_2O_2, because the reduction of the AgBr grains proceeds more easily from these silver-specks than from other points.

In the case of coal, the analogous intensification effect is detectable. The plate having the latent fog is pseudo-photographic-sensitive for coal just as mentioned above. In this case coal acts like H_2O_2 as the intensifier of the latent fog.

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1. E. P. Wightman and R. F. Quirk: J. Frank. Inst., **203**, 261, (1927); **204**, 731, (1927).

The plates, which are more or less developable owing to the natural or artificial fog, are also more pseudo-potographic-sensitive for coal. Therefore, the action of coal may be thought of as a kind of the intensification of the latent images, and H_2O_2 which is produced during the oxidation of coal seems to act as the intensifier. If O_3 is present, it will form H_2O_2 by combination with H_2O before acting on a plate, for the action of coal is accelerated by humidity and temperature as mentioned in the previous investigation.[1]

Consequently, the mechanism of the pseudo-photographic effect of coal at the plate side is the reduction of AgBr grains due to H_2O_2 which is the active agent in coal, and the reduction of AgBr grains by coal takes place easily when they are more or less developable due to certain factors.

In conclusion the writer wishes to express his sincere thanks to Professor U. Yoshida and Professor M. Miyata for their kindness and interest taken in this work. His hearty thanks are due to General Superintendent Dr. M. Sato, Mr. G. Okuno, Dr. K. Morikawa and Mr. H. Sawada for their kind encouragement throughout this work.

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Plate I

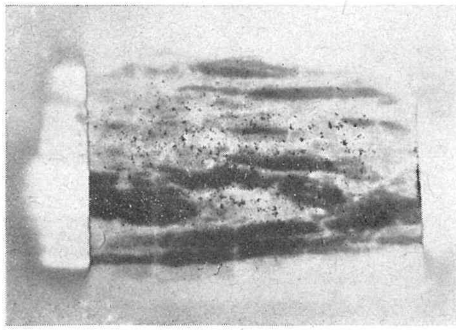

Fig. 1 (a)

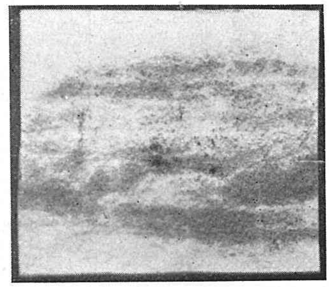

Fig. 1 (b)

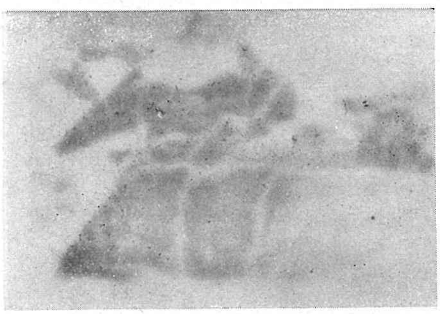

Fig. 2 (a)

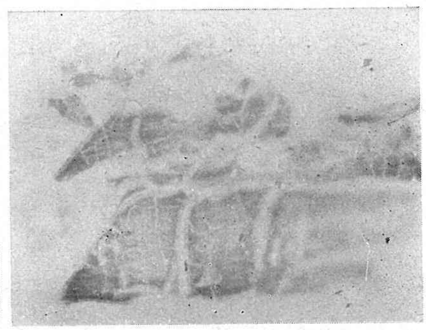

Fig. 2 (b)

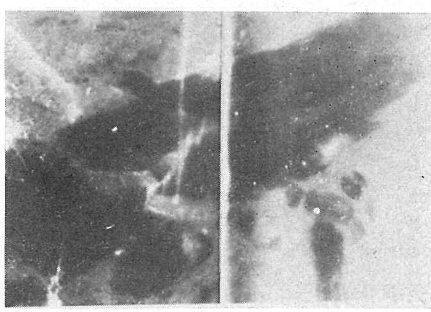

Fig. 3

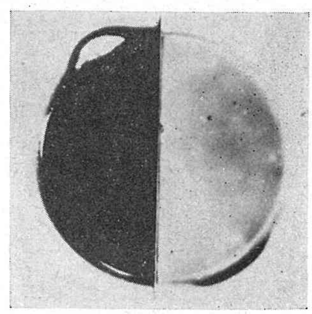

Fig. 4

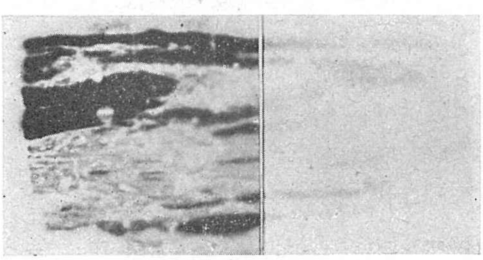

Fig. 5

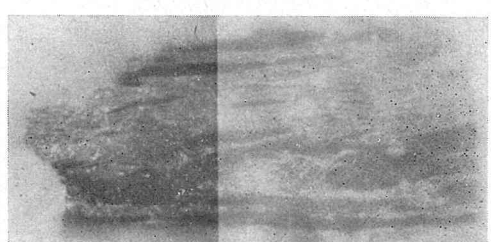

Fig. 6