THE DECOMPOSITION OF HYDROGEN PER-OXIDE AND THE MECHANISM OF LATENT PHOTOGRAPHIC IMAGE INTENSIFICATION¹

IN a previous paper² some interesting experimental facts concerning the effect which was called the intensification of latent image by H_2O_2 and some other substances were presented. This phenomenon consists of an increased developability above the normal of the exposed portions of a plate treated after exposure with H_2O_2 .

The object of the present work was to find the reason for the intensification of latent image. In the course of it, certain possible underlying mechanisms suggested themselves.

It was the work of Bray and Livingston³ on the catalytic decomposition of H_2O_2 in solutions containing H and Br ions which gave the first possible clue as to such a mechanism. They showed that prior to a steady state, which may require an hour or more in being reached, the following reactions take place when acid and soluble bromide are mixed with H_2O_2 solution:

$$H_2O_2 + 2 Br^- + 2 H^+ = Br_2 + 2 H_2O$$
 (1)

$$H_2O_2 + Br_2 = O_2 + 2 Br' + 2 H^+$$
 (2)

The sum of these, or the steady state gives

$$2 H_2O_2 = 2 H_2O + O_2$$
 (3)

Soluble bromide is present in practically all ordinary dry plates, and in all the previous work on latent image intensification acid was present in the solution of H_2O_2 used.

The second possible clue to an explanation of the action was a chemical mechanism of latent image formation recently proposed by K. C. D. Hickman.⁴ He has obtained evidence that while in bulk, in a test tube, Br in water solution reacts quantitatively with Ag_2S to give AgBr, H_2SO_4 and HBr, in the photographic plate on the other hand, when the Ag_2S is isolated in the so-called sensitivity specks⁵ and the Br is formed only in very limited quantity,

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² E. P. Wightman and R. F. Quirk, J. Franklin Inst. 203, 261 (1927).

³ W. C. Bray and R. S. Livingston, J. Am. Chem. Soc. 45, 1251 (1923); R. S. Livingston and W. C. Bray, Ibid.,

45, 2048 (1923); R. S. Livingston, *Ibid.*, 48, 45 (1926).
4 K. C. D. Hickman, *Phot. J.* 67, 34 (1927).

⁵ S. E. Sheppard, Colloid Symposium Monograph 3, 76 (1925); Phot. J. 65, 380 (1925).

by the photochemical decomposition of AgBr grains, then certain reactions take place which he believes give rise to metallic Ag instead of AgBr. He further believes, as we do also, that it requires a smaller speck of Ag than of Ag_2S to produce developability of the grain and he gives some evidence in support of this contention.

We have found that when H_2O_2 solution is added to a suspension of Ag_2S in a solution of acid and soluble bromide that some of the sulfur of the sulfide is oxidized to H_2SO_4 and, in a bulk reaction such as this, AgBr is formed. When no soluble bromide is present, however, the Ag_2S apparently remains unattacked.

Taking the previous facts into consideration and assuming that Hickman is correct in his contention, it seems reasonable to suppose that when the photographic plate is treated with acid H_2O_2 the trace of bromide formed from the soluble bromide in the plate attacks the silver sulfide of the sensitivity or latent image speck (where it has not all been transformed into silver during the light exposure) and thus renders the grain developable.

The fact that acid H_2O_2 converts metallic Ag to Ag ions should not alter this hypothesis since Ag ions, when adsorbed to AgBr, are at least as effective as metallic silver, if not more so, in producing developability of the grain.

W. Clark has contended⁶ that the action of H_2O_2 in producing latent fog on a photographic plate is purely chemical and not one of chemiluminescence as previously supposed by Sheppard and one of us.⁷ The present hypothesis and experimental work, while they do not disprove the chemiluminescence view, do furnish the basis for a chemical explanation of H_2O_2 action.

An additional experiment which supports the chemical view is that if we remove almost all the KBr from a plate prior to H_2O_2 treatment, by addition of a small amount of AgNO₃, not enough to give excess of Ag ions, the intensifying effect of H_2O_2 is considerably lowered.

A full paper on this subject will be published shortly.

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⁶ W. Clark, Brit. J. Phot. 70, 763 (1923); Phot. J. 66, 78 (1923).

⁷ S. E. Sheppard and E. P. Wightman, J. Franklin Inst. 195, 337 (1923).