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THE FOGGING BY ACIDS AND OXIDIZING AGENTS AND THE INTENSIFICATION OF THE PHOTOGRAPHIC LATENT IMAGE[1,2]

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It was discovered in 1901 by Lüppo-Cramer that various strongly diluted acids produce latent fog on certain types of high speed plates,[3] especially if the solution contains potassium bromide. That sulfurous acid causes the same effect was noticed by him in 1908.[4] In addition to this it was found by him that acidified ammonium persulfate causes latent fog as well as acting as a desensitizing agent.[5] The explanation which Lüppo-Cramer gave for these phenomena was that the acids and oxidizing agents tend to destroy the ripening germs, or the latent image specks, on the grains, producing a more dispersed condition of the silver in them. This tends at first, he says, to make the speck more active in producing developability.[6]

Recently, the writer offered a different explanation for the action of certain oxidizing agents and acids in producing latent fog.[7]

Lüppo-Cramer has since questioned this viewpoint[8] and reiterates his own hypothesis. He has also given some evidence which he considers supports his own view and is in opposition to that of the writer. The present paper offers a further discussion of the writer's hypothesis and some additional experimental evidence in its support. It also presents an explanation of the opposing facts cited by Lüppo-Cramer.

The hypothesis of the writer was, and still is, that since most plates and films contain an excess of soluble bromide (KBr), the oxidizing agents give with this some free bromine, a trace of which remains in the gelatin after the excess oxidizing agent is destroyed and washed away. It then gradually returns to that portion of the silver sulfide sensitivity speck which had not been affected by the oxidizing agent, and reacts in a manner described in a previous paper on the intensification of latent image by hydrogen peroxide.[9]

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[1] In memory of Ira Remsen.

[2] Presented at the Convention of the American Chemical Society, September, 1928.

[3] Lüppo-Cramer, *Phot. Korr.*, **38**, 159 (1901).

[4] Lüppo-Cramer, *ibid.*, **45**, 552 (1908).

[5] Lüppo-Cramer, *ibid.*, 39, 563 (1902).

[6] For the previous literature covering this subject and for a more complete discussion of the hypothesis see Lüppo-Cramer (a) "Grundlagen der phot. Negativverf," Eder's Handb Vol. II, Pt. 1, Halle, **1927**, p. 340; (b) *Camera (Luzern)*, **3**, 14 (1924).

[7] E. P. Wightman, *Brit. J. Phot.*, **74**, 447 (1927); see W. Clark, *ibid.*, **74**, 121 (1927).

[8] (a) Lüppo-Cramer, *Z. wiss. Phot.*, **25**, 121 (1928); (b) *ibid.*, **25**, 129 (1928); (c) *Phot. Korr.*, **64**, 49 (1928).

[9] E. P. Wightman and R. F. Quirk, *J. Franklin Inst.*, **204**, 731 (1927).

That very dilute bromine solution causes the formation of latent fog was discovered by Lüppo-Cramer,[10] and was more recently verified by the writer, who found that it also causes, in a concentration of 1:200,000, marked intensification of latent image. In addition to this, it was observed, as S. E. Sheppard and others had already stated,[11] that bromine is strongly retained by gelatin, even when the latter was set and washed with sodium bicarbonate solution or with a solution of oxalic acid containing a small amount of manganous sulfate, the bromine which remained after this washing having the power to react with colloidal silver to give colloidal silver bromide.

That potassium iodide solution without acid present, and more so when it is present, soon turns yellow with the formation of free iodine is a well-known fact. Light is no doubt a catalytic agent in this reaction for even in a dimly lighted room the decomposition seems to take place slowly.

Light also has an effect on the acid solutions of the alkali bromides. One per cent. potassium bromide solution containing sulfuric acid to $P_H = 3$, which when freshly made shows no trace of bromine, gives a definite free bromine reaction after standing for a few hours.[12]

Such a solution causes fog on the photographic plate, as Lüppo-Cramer has previously discovered;[6b] although if present during exposure it also causes a lowering of sensitivity. Neutral bromide under corresponding conditions causes lowering of sensitivity without the fog formation. When the plate is bathed before or after exposure with either acid or neutral bromide, there is no sensitivity decrease or latent light image alteration but merely a fog effect from the acid bromide.

As an argument against the hypothesis of the writer that latent fog is produced through bromine formation, Lüppo-Cramer cites the fact that a sulfurous acid solution or sulfur dioxide gas causes fog and that, obviously, bromine would not be formed in the presence of such a solution.[4,8c] When potassium bromide also is added the fog is increased, he found.

Another very interesting fact which he observed was that while ordinary plates of various kinds when bathed for two minutes in a solution containing 20 g. of potassium bromide and 1 cc. of concentrated sulfurous acid per liter showed marked fog on development in metol–hydroquinone; several different brands of ortho-chromatic plates showed even less fog than the control plate which was given no treatment before development.[8a]

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[10] Lüppo-Cramer, "Phot. Probleme," Halle, **1907**, p. 132.

[11] See S. E. Sheppard, "Gelatin in Photography," Monograph No. 3, Vol. 1, **1923**, pp. 153–156.

[12] E. P. Wightman and S. E. Sheppard, "Effect of Certain Salts on the Photographic Sensitivity," paper presented at the Detroit Meeting, American Chemical Society, September, 1927, in press.

The same phenomenon was observed with special plates to which various color-sensitizing dye solutions were added for two minutes prior to the KBr–H_2SO_3 solution treatment. Even 0.1% hydrogen peroxide for two minutes did not cause fog on the dye-impregnated plates.

Recently, in another connection, the writer found that ordinary air containing up to 0.08% by volume of sulfur dioxide did not cause the formation of latent fog or appreciable change of sensitivity of either an Eastman Speedway plate or of a W. and W. panchromatic plate in fifteen hours of treatment; whereas an even less quantity of sulfur dioxide in air saturated with moisture in only a few hours caused bad fog on similar plates. Moderately dry air containing 0.16% sulfur dioxide caused a slight increase in sensitivity of a pan plate but no increase in fog.

It seems very likely that the action of sulfurous acid in producing fog is first an absorption into the plate and then an increase of solubility of the silver bromide grains on the surface. A certain amount of silver bromide goes into solution; the amount may be very minute, only a few molecules or ions. Then this in the presence of some of the larger sensitivity specks acting as nuclei oxidizes the sulfurous acid to sulfuric acid and a trace of silver deposits on the specks, increasing the size of the largest ones to the developable condition, thus[13]

$$2Ag^+ + 2Br^- + 2H^+ + SO_3^{--} + H_2O = 2Ag + 4H^+ + 2Br^- + SO_4^{--}; \quad \Delta F = -40{,}216 \text{ cal.}$$

The addition of potassium bromide increases this effect by increasing the solubility of the silver halide.[14] When the sensitizing dye is present it forms a protective layer, preventing the silver halide from going into solution and in some cases absorbing the sulfur dioxide.

As was said above, the author's hypothesis was based partly on a previously proposed mechanism of latent image intensification by hydrogen peroxide.[9] In a paper presented before the recent International Congress of Photography, some additional evidence for this mechanism has been set forth.[15]

It was found, for instance, that a latent image produced by x-rays on either fast or slow plates cannot be intensified by hydrogen peroxide. A. P. H. Trivelli had suggested that this should be the case since "an x-ray quantum of energy is of the order of 100 to 1000 times greater than

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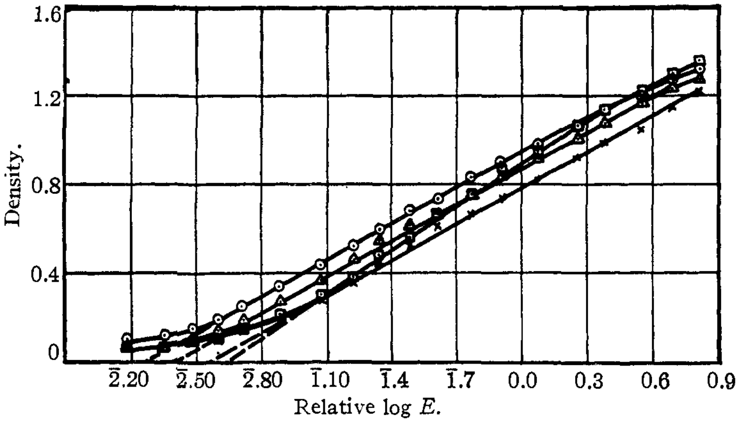
[13] The reason a sulfite containing developer does not do this is probably because of the interstabilizing effect of the developer reducing agent on the sulfite and *vice versa.*

[14] The solubility would be depressed only where very low concentrations of soluble bromide were used, that is, less than that already present in most emulsions. It is true that activity of silver decreases as solubility increases, but complex ions containing silver are formed which also may be reduced to metallic silver.

[15] E. P. Wightman and R. F. Quirk, "Intensification of the Photographic Latent Image," to be published in the Proceedings of the Seventh International Congress of Photography.

that of visible actinic light, so that even the smallest latent image speck produced by it is probably greater in size than that necessary to induce developability, and hence if there are no intermediate sized specks (as we had supposed to be present in the case of the ordinary light) there should be no intensification of an x-ray latent image."

Second, since the hypothesis supposed the formation of bromine by the acid-peroxide from the soluble bromide in the plate, the presence of a bromine acceptor along with the hydrogen peroxide should prevent or lessen latent image intensification. Acetone semicarbazone which Svedberg, Schunk and Andersson had used previously as such an acceptor to prevent solarization on the photographic plate[16] was tried. It was found, as anticipated, that since acetone semicarbazone increases developability of latent image to some extent in the middle and higher exposure regions, it does not prevent entirely intensification of latent image by hydrogen peroxide, but does lessen it instead of adding to it, as would be expected if there were no bromine absorbing action. The result is shown in Fig. 1.



⊡, Control, acetone semicarbazone treated; △, H_2O_2 and acetone semicarbazone treated; ×, control, H_2O treated; ⊙, H_2O_2 treated.

Fig. 1.—Effect of acetone semicarbazone on latent image intensification by H_2O_2.

Third, it has been found that an organic peroxide, benzoyl peroxide, also intensifies latent image, although to a less extent than hydrogen peroxide. One reason for the less vigorous action is, no doubt, the low solubility of the former in water.

We have now found some further evidence for our viewpoint. An Eastman Speedway plate was exposed behind an Eder-Hecht wedge and then one-half of it lengthwise was treated with a solution containing 1 part

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[16] T. Svedberg, O. H. Schunk and H. Andersson, *Phot. J.*, **64**, 272–274 (1924).

of chromic acid and 0.4 part of sulfuric acid in 500,000 of water. The treated half was bathed for one minute in 0.1% bicarbonate solution and the two halves were developed together. There was a distinct intensification of latent image, about two steps or 4° E. H., and a faint increase in fog on the treated plate as compared with the control. This experiment will be repeated varying the concentration of oxidizing agent and time of treatment, also using some other oxidizing agents.

In one of Lüppo-Cramer's recent papers,[8b] he shows an interesting result obtained by treating a Kranz-Ultra-rapid plate which had been exposed behind a neutral gray wedge tablet with hydrogen peroxide for varying lengths of time as follows: 1—control, no treatment; 2—15 minutes in 1% H_2O_2 solution after exposure; 3—3 to 7—fifteen, thirty, sixty, ninety and two hundred and ten minutes in 5% H_2O_2 solution. The result is shown in Fig. 2. In discussing it he says: "Already in Curve 2, but outspokenly in 3, we find besides the intensive fog formation, at the beginning of the rise of the curves, what I had already described in principle in 1915,[17] and what Wightman and Quirk recently designated as intensification of latent image."

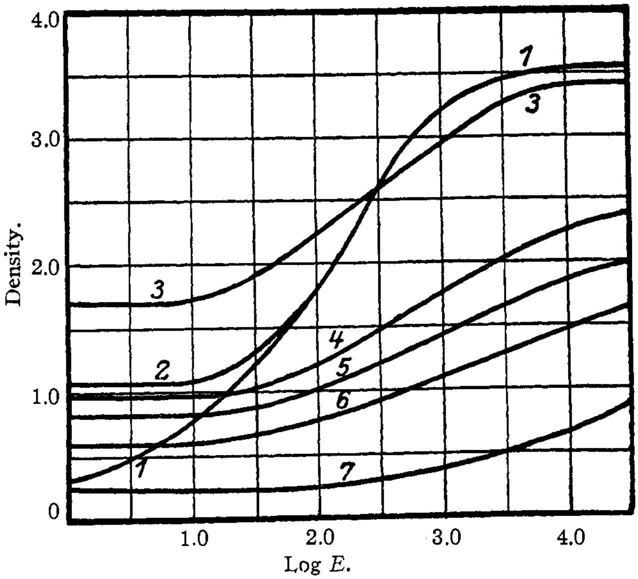

Fig. 2.—What Lüppo-Cramer calls intensification of latent image (Curves 2 and 3) and reversal of latent image (Curves 4 to 7) by hydrogen peroxide.

It would seem from this that there is a misunderstanding of what the latter investigators call intensification of latent image, since it was stated

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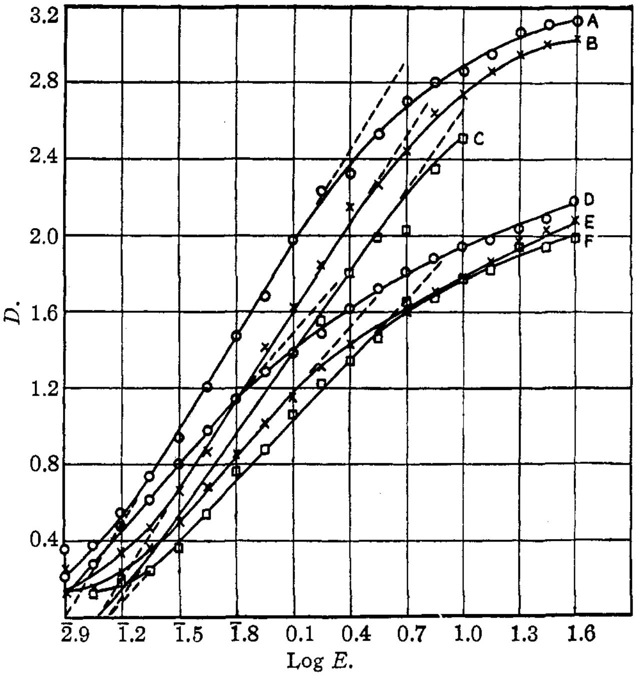
[17] Lüppo-Cramer, *Phot. Korr.*, 52, 135 (1915).

in their paper that the effect is produced by such a concentration of hydrogen peroxide as causes a practically negligible amount of fog. This happens to be, in the case of an Eastman Speedway plate, with which the Kranz-Ultra-rapid should more or less correspond, a concentration of about 0.008%, and the time of treatment is one minute. The intensification extends through most of the exposures. A comparison of Fig. 2 with Fig. 3, taken from Wightman and Quirk's paper, will show the fundamental difference. The entire effect in Curves 2 and 3, Fig. 2 (below where 3 crosses 1 and 2) appears to the writer to be a fog effect and not that of intensification as defined.



□, Blank; X, H_2O treated; O, H_2O_2 treated.

10-Minute development	Speed	λ	4-Minute development	Speed	λ
A, H_2O_2	876	1.60	D, H_2O_2	1102	1.12
B, H_2O	593	1.53	E, H_2O	593	1.15
C, Blank	516	1.42	F, Blank	516	1.05

Speed ratio: A/C = 1.70, B/C = 1.15, D/F = 2.15, E/F = 1.15

Fig. 3.—Intensification of latent image, high speed emulsion.

The reversal effect in the remaining curves in Fig. 2 is very interesting. As mentioned in a note in the *British Journal of Photography*[18] it seems likely that Lüppo-Cramer's idea of an increased dispersity of the latent image can be used to explain the reversal effect.

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[18] E. P. Wightman, *Brit. J. Phot.*, **75**, 189 (1928).

Summary

Further arguments are given in support of the viewpoint of Wightman that the cause of latent fog formation from the action of certain oxidizing agents and acids is probably formation of bromine from the soluble bromide in the plate, with which hypothesis Lüppo-Cramer is in disagreement. The hypothesis was originally based on the fact, discovered by Lüppo-Cramer himself, that very dilute bromine solution causes fog and on a previously proposed mechanism of latent image intensification and fog formation by hydrogen peroxide, further evidence for which is now presented.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS. XXX. STUDIES IN THE ABSORPTION SPECTRA[1]

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The purpose of this investigation was to make a careful examination of the effects of a common ion on the absorption spectra of solutions of certain rare earth salts. The spectra of the colored rare earths are an invaluable aid for the rapid estimation of these elements, and although there are several references in the literature to the fact that the absorption bands are displaced by the presence of other substances, yet there appears to be little definite information available as to the precise nature of the changes to be observed. These studies were therefore undertaken with the intention of determining the conditions under which the absorption spectra may be relied upon for the analysis of rare earth mixtures.

An extensive bibliography of the literature prior to 1920 is given by Yntema.[2] Since then methods of quantitative spectral analysis for the rare earths have been suggested by Inoue[3] and by Delauney.[4] Irregularities in the absorption spectrum of neodymium have been observed by Prandtl[5] as mentioned in his criticism of the discovery of illinium.

Delauney, on the assumption that Beer's Law is observed by rare earth salt solutions, has suggested a method of quantitative analysis based on the variation in the width of certain of the absorption bands with change in concentration. He made analyses of solutions of praseodymium and neodymium nitrates and his results were accurate to 5%, which is better

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[1] In memory of Ira Remsen.

[2] Yntema, THIS JOURNAL, **45**, 907 (1923).

[3] Inoue, *Bull. Chem. Soc., Japan*, **1**, 9 (1926).

[4] Delauney, *Compt. rend.*, **185**, 354 (1927).

[5] Prandtl, *Z. angew. Chem.*, **39**, 897 (1926).