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THE PHOTOGRAPHIC EMULSION: NOTES ON STABILITY OF FINISHED PLATES

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ABSTRACT

The changes occurring in finished photographic plates on storage appear to be the result of continued after-ripening. The results are discussed with respect to variables known to affect this process. Existence of a critical region of bromide ion concentration was demonstrated and shown to be consistent with predictions from the silver ion-gelatin equilibrium. Formation of fog by adding acid to ammonia-process emulsions was confirmed and given a new explanation.

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I. INTRODUCTION

It is generally known that photographic sensitive materials gradually become developable without exposure ("chemical fog") and decrease in sensitivity; stability against these changes is an important property, which varies considerably with the type of material, and to a less extent with the make. Literature on the subject is scanty and qualitative; a good summary of the available information is given by Wentzel.[1] The data in this paper are not the result of a specific investigation of stability, but are rather an accumulation of tests on a considerable variety of experimental emulsions which were made under known conditions and stored together. The results, although incomplete, are at least an addition to the available literature.

The deterioration on storage appears to be primarily a continuation of the "after-ripening" process, going on at a much reduced rate because of drying and reduced temperature, and leading to practically the same consequences as excessive after-ripening by digestion. We have already [2] given data to show that unripened emulsions may undergo pronounced after-ripening on storage of the finished plates. If they have been thoroughly washed and coated without addition of soluble bromide the process is quite rapid; a great increase in sensitivity during the first 4 to 6 months is followed by deterioration which is under way within a year. The existence of this series of changes is

[1] Wentzel, Die Fabrikation der photographischen Platten, Filme und Papiere und ihre maschinelle Verarbeitung, vol 3, pt. 1, of Eder's Handbuch der Photographie 1930.
[2] Carroll and Hubbard, B.S. Jour. Research, vol. 7, (RP340), p. 219, 1931.

readily understood, as emulsion gelatins contain labile sulphur considerably in excess of the amount necessary to produce maximum sensitivity.[3] This gradually brings about excessive reaction of the silver bromide and the sensitizing compounds, with consequent fog and loss of sensitivity,[4 5] exactly as is observed from excessive after-ripening.

Deterioration on storage may have certain characteristics which are distinct from those of excessive after-ripening. Fog and desensitization may be caused by absorption of gases from the atmosphere, and by contact with the packing material; interference by either of these factors could readily invalidate experiments on other variables if storage conditions were not comparable. The fog on storage normally begins at the edges of the plates, and may be quite high for a few millimeters when the change in the center of the plate can barely be detected. This was first explained by Homolka,[6] by the migration of the soluble bromide in the emulsion during the drying process which normally begins at the edges. In case the drying is irregular, from badly designed plate racks or other causes of uneven air circulation, definite patterns may be formed on plates showing the positions of the eddies where drying was slowest.

In the last few years a number of organic compounds have been described [7] as preservatives for photographic materials. They are all of such character that complex formation with silver salts is probable, but experiments with nitrobenziminazol [8] have indicated that its effect on after-ripening is more than can be explained solely by the decrease in silver ion concentration which it produces.

II. EXPERIMENTAL

1. PROCEDURE

The experimental emulsions were all coated on glass, so that the effect of the support was reduced to a minimum. When old glass was used, the previous emulsion was removed by soaking in caustic-soda solution and scrubbing, and the plates were then soaked for at least a day in dilute chromic-acid solution before washing again and applying the substratum. The substratum consisted of emulsion gelatin 3.5 g per liter, hardened with chrome alum 0.3 g per liter; the plates were dipped in this solution and allowed to drain while drying. The finished plates were dried in a current of filtered air at 28 to 30 C, the humidity being kept down by recirculating it over ammonia coils, followed by electrical heating. The racks hold the plate only at the corners, slightly inclined to the vertical air stream; drying is quite uniform and usually complete in less than 3 hours.

The plates were stored in the same room with the drying cabinets. It is a basement room of relatively uniform temperature. During the summer the extremes of temperature and humidity do not reach it, but the temperature is almost never below 27 C for at least 3 months and frequently reaches 30°; during the winter it is normally about 20°. The plates were packed in the usual 3-part boxes after wrapping in

[3] Sheppard and Hudson, Ind. Eng. Chem. (Analytical Edition), vol. 2, p. 73, 1930.
[4] Sheppard, Phot. Jour., vol. 66, p. 399, 1926.
[5] Carroll and Hubbard, B.S. Jour. Research, vol. 11 (RP622), 1933.
[6] Homolka, Phot. Korr., p. 550, 1905.
[7] U.S. Patents nos. 1,696,830, 1,725,934, 1,758,576, 1,758,577, 1,763,989, 1,763,990; German Patent no. 558,419; Seyewetz, Phot. Korr., vol. 69, p. 67, 1933.
[8] Carroll and Hubbard, B.S. Jour. Research, vol. 9 (RP488), p. 529, 1932.

black paper obtained from a photographic manufacturer; plates where the emulsion had come in contact with the paper were discarded.

Test plates were developed in unbromided pyrogallol at 20 C. Test strips from the sector wheel sensitometer were brush developed for 3, 6, and 12 minutes. Plates exposed behind the Eder-Hecht wedge were tank developed under conditions roughly equivalent to the 6-minute brush development, although the dilute developer was more affected by bromide in the plates. Edge fog has been disregarded in the numerical data; the test strips were cut from the center of the plate, discarding a margin of at least 1 cm. From the total density, read in diffuse illumination with a Martens photometer, 0.06 has been subtracted for reflection by the support.

2. SOLUBLE BROMIDE

The procedure for testing the effect of soluble bromide has been to wash the emulsion thoroughly and then add the bromide in known amounts. In all recent experiments, the process has been controlled by determination of the bromide ion concentrations with the silver-silver bromide electrode. This can be strongly recommended for the purpose. Readings can be obtained in a few minutes with small samples. While the apparatus is more expensive and somewhat more delicate than that required for the conductivity method recommended by Wentzel, it has the great advantage that the readings are direct, and that there is no loss of sensitivity at low concentrations; a change in bromide ion concentration from 1×10^{-5} to $2\times10^{-5}N$ produces the same change in voltage as the change in concentration from 1×10^{-3} to 2×10^{-3}. It is therefore possible to detect significant changes in emulsions which have been washed too thoroughly to test by ordinary chemical methods. The complications in the washing process which are introduced by the combination of silver ions with gelatin have been discussed in some detail in previous papers.[9] [10] When it is necessary to use chemical methods for control, we have found the Volhard method (addition of excess silver nitrate and back titration with thiocyanate solution in the presence of nitric acid) much more satisfactory than the titration in neutral solution with chromate as indicator which is usually recommended.

The data are given in terms of the bromide ion concentration of the liquid emulsion, at 30 C wherever possible. It was found on using the electrode that the limit of the titration test for bromide is about $1\times10^{-4}N$, but that emulsions may be washed to $3\times10^{-6}N$ without producing an appreciable difference in fog in the freshly melted emulsion; the fog on digestion or storage is considerably affected by differences of this order. If to such emulsions soluble bromide is added in amounts of the order of 10 ml of 0.10 N solution per liter, the resulting bromide ion concentration may vary ±20 percent from the calculated $1.0\times10^{-3}N$ because of the presence in the emulsion of soluble bromide or "silver gelatinate", depending on the previous washing as already stated. This is not enough to be important photographically, but with smaller amounts of bromide the variation is to be taken into account. Wentzel recommends the addition of 8 to 16 ml of 0.10 N bromide solution per liter of emulsion; in the 1903 edition of the

[9] Carroll and Hubbard, B.S. Jour. Research, vol. 7 (RP376), p. 811, 1931.
[10] Carroll and Hubbard, B.S. Jour. Research, vol. 8 (RP430), p. 481, 1932.

Handbuch, Eder suggests 6 ml as the normal amount, with a range of 3 to 20 ml. In an emulsion containing 0.2 mol of AgBr per liter, this is a range of 1.5 to 10 molecules of soluble bromide per 1,000 AgBr, which corresponds well with present practice as determined by analysis of commercial emulsions.[11] Calculation taking into account the combination of silver ion with gelatin shows that in an emulsion containing 0.2 mol (38 g) AgBr per liter and no excess of either silver or bromide at pH 7, the bromide ion concentration is $2\times10^{-5}N$; with 1 KBr per 1,000 AgBr it is $2\times10^{-4}N$; and with 5 KBr per 1,000 AgBr it is $1\times10^{-3}N$.

Figure 1 illustrates the dependence of fog after 7 to 13 months storage on the bromide ion concentration of 4 typical emulsions. The various portions of each emulsion were treated identically except for the adjustment of bromide ion concentration just before coating

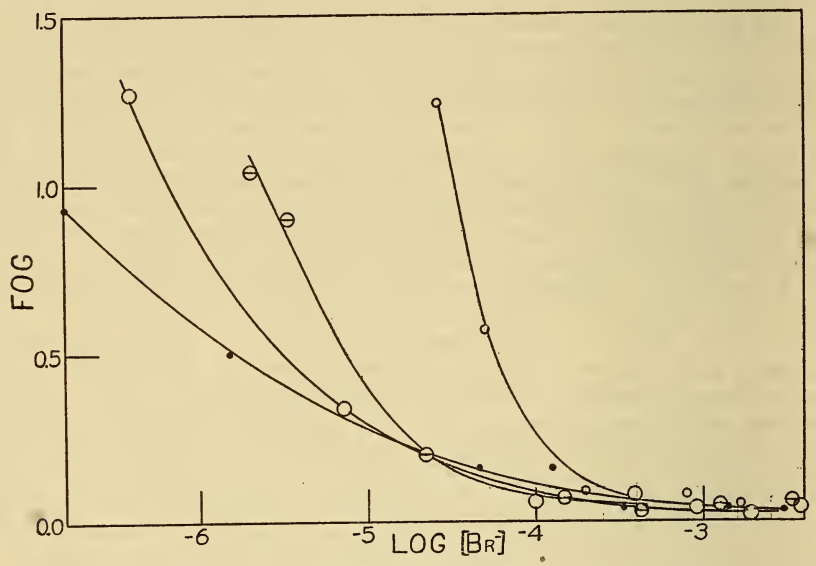

FIGURE 1.—*Stability of emulsions with varying bromide ion concentration.*

Fog, after 12-months storage, tank development, plotted against [Br−] measured in the liquid emulsion at 30.0 C. All emulsions of neutral type, 4 mol percent AgI. ○, 4–83, unsensitized, pH 6.4. ○, 4–108, pinaflavol sensitized pH 7.1. ⊖, 4–109, pinaverdol sensitized pH 7.1. •, 4–171, pH 6, sensitized with basic dye of unknown structure obtained by courtesy of Du Pont Film Mfg. Corp. (7 months storage only)

by addition of potassium bromide or silver sulphate solution. The data show clearly that a concentration of $2\times10^{-4}N$ bromide was sufficient to stabilize any of the emulsions. This is supported by the results of a number of earlier experiments, including ammonia-process emulsions with 0 to 2¼ percent AgI, in which it was found that the addition to the washed emulsion of 1 KBr per 1,000 AgBr was sufficient to prevent an increase in general fog of more than 0.05 in 6 months. This concentration does not prevent appreciable edge fog after 6 to 12 months. It is necessary to raise the bromide ion concentration to about $1\times10^{-3}N$ to avoid this; apparently the higher average concentration is necessary to maintain the first value out to the edges. If the emulsion is not sensitized by dyes, the sensitivity will not be appreciably affected by this increase,[12] and the higher

[11] Carroll and Hubbard, B.S. Jour. Research, vol. 10 (RP525), p. 211, 1933, table 1.
[12] Reference 10, (RP430), figure 7.

concentration is certainly preferable. In the case of panchromatic emulsions, the risk of edge fog in 6 or more months may be outweighed by the desirability of maintaining the maximum sensitivity, since the spectral sensitivity may be decreased by 20 to 50 percent on increasing the bromide ion concentration from 2×10^{-4} to 1×10^{-3}.[13]

The plates have been considered stable when the fog was less than 0.2 after the indicated period of storage and the sensitivity had not decreased appreciably. On after-ripening the sensitivity passes through a maximum, and may begin to decrease before or after the

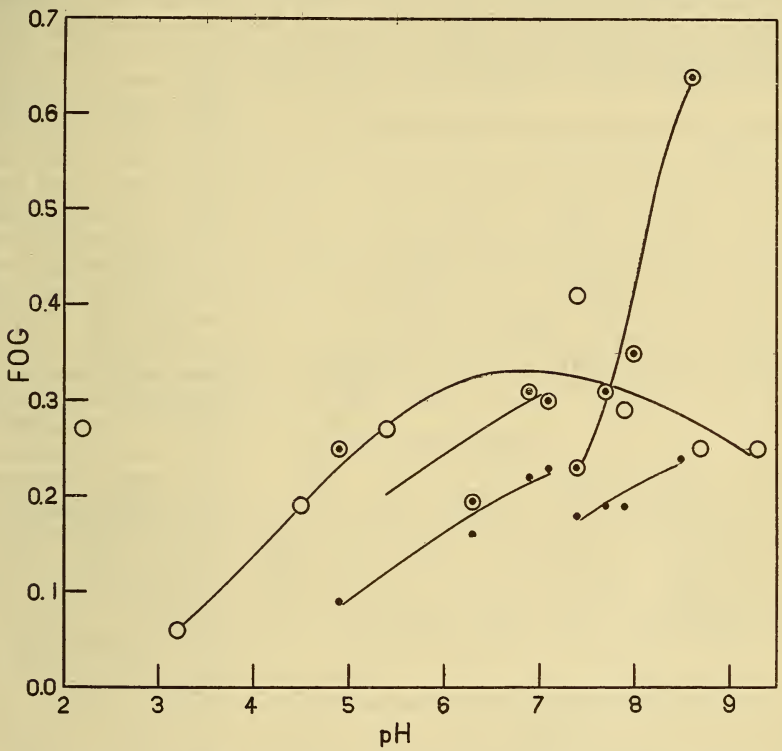

FIGURE 2.—*Stability of emulsions with varying hydrogen ion concentration.*

Fog after 12 months' storage, tank development, plotted against pH measured in the liquid emulsion. All emulsions of the neutral type. ○, 4-123, 4 mol percent AgI, pinaverdol sensitized [Br⁻] 8×10^{-5} at pH 7.4. •, unsensitized emulsions, 2¼ mol percent AgI; pH 7.1 and less, emulsion 4-99, [Br⁻] 1.0×10^{-4} at pH 7.1; pH 7.4 and over, emulsion 4-101, [Br⁻] 1.3×10^{-4} at pH 7.4. ⊙ emulsions 4-99 and 101, pinacyanol sensitized.

appearance of serious fog, but fog as high as 0.5 invariably corresponded to a considerable decrease (about 50 percent). The definition of sensitivity also must be considered, since some plates which are nearly useless from fog and loss of contrast may still show high speeds by the threshold method. The emulsions of figure 1 were practically constant in sensitivity as judged by the Eder-Hecht exposure, if the bromide ion concentration was $1\times10^{-3}N$ or greater. At anywhere from 5 to $1\times10^{-5}N$ [Br⁻] a decrease in sensitivity on storage set in, and the plates with the highest silver ion concentrations lost practically all sensitivity. Between these regions the

[13] Reference 8, (RP488), figure 6 to 9.

emulsions containing dyes were practically constant in sensitivity, while 4–83 doubled in speed at $10^{-4}N$ [Br^-]. In emulsions not thoroughly digested before coating there might have been much greater increases in sensitivity at about this point.

3. HYDROGEN ION CONCENTRATION

Increasing alkalinity strongly accelerates after-ripening[14] and may be expected to decrease stability of the finished plates. The effect is not as simple as this would indicate, however. Results with some neutral-process emulsions are given in figure 2; these were digested at pH 7.0 ± 0.1 and acid or alkali was added just before coating. The emulsions without dye and those containing pinacyanol increased in fog with increasing pH, the rate of increase in the presence of this dye being very large above pH 7 where the sensitization by the dye[15] also rose rapidly. In the presence of pinaverdol there were indications of maximum of fog around pH 7, corresponding to the flat maximum of sensitization by the dye.[16] The sensitivity of these emulsions was nearly constant on storage, except for the portions of 4–99 without dye, which increased 50 to 100 percent. The ammonia-process emulsions represented in figure 3 show a peculiarity discovered by Lüppo-Cramer,[17] the increase in fog on adding acid.

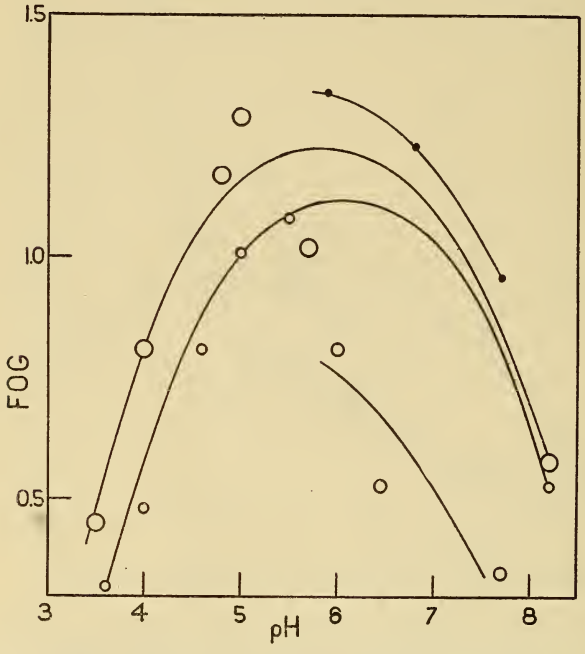

FIGURE 3.—*Stability of emulsions with varying hydrogen ion concentration.*

Fog after 6 months' storage, 6-minute brush development. All ammonia-process emulsions, 1 mol percent AgI, unsensitized. ○, 1–142, all portions digested at indicated pH. ○, 1–144, all portions digested at pH 8.2 and brought to indicated pH just before coating. ○, 1–124, undigested. •, 1–125, portions digested at indicated pH.

We believe that this is explained by the increase in silver ion concentration which accompanies increase in hydrogen ion concentration of such emulsions. These emulsions had been washed until they contained an excess of silver over halogen, which was present in the form of a silver ion-gelatin complex. On acidifying, some of the silver ions were liberated; for example, a decrease in pH from 7.1 to

[14] Rawling, Phot. Jour., vol. 66, p. 495, 1926; vol. 67, p. 42, 1927; vol. 69, p. 83, 1929; also Carroll and Hubbard, reference 10.
[15] Reference 8 (RP488), figure 5.
[16] Reference 8 (RP 488) figure 4.
[17] Lüppo-Cramer, Phot. Ind., vol. 22, p. 186, 1924.

5.7 produced an increase in silver ion concentration of 5 times. This decreased the stability by an amount much larger than the opposing effect of the change in hydrogen ion concentration. This explanation would apply not only to emulsions made by the ammonia process but also to plates made by the neural process and bathed in ammonia or other alkali as in Lüppo-Cramer's experiments. Below pH 6 the stabilizing effect of hydrogen ion concentration begins to become the more important. At a pH of 3 an emulsion may be stable in the presence of an appreciable excess of silver over halogen; as would be expected, this acidity decreases sensitivity by a serious amount. At the lowest values of pH (<4) the sensitivity of the emulsions represented in figure 3 was nearly constant on storage. At all higher values there was a decrease in contrast and effective sensitivity amounting to as much as one half.

The poorer stability of ammonia-process emulsions is not as marked as is to be anticipated from their reputations. When neutral and ammonia emulsions with the same iodide content are compared at the same pH and bromide ion concentration, the difference is apparently small. These conditions are seldom fulfilled in practice, since after normal washing in hard water the pH of an ammonia-process emulsion is likely to be 8.0 to 8.5, and that of the neutral-process emulsion 7.0 to 6.5. Further, because the combination of gelatin with silver ions increases with pH, the washing of the ammonia-process emulsion proceeds further in the same time; and in addition to this most formulas direct a more thorough washing to eliminate the ammonia.

4. OTHER VARIABLES

The entire ripening process under given conditions becomes more rapid with decreasing proportion of iodide; the difference is most marked when pure bromide emulsions are compared with those containing small amounts of iodide. Increase in fog on storage is, however, relatively independent of the amount of iodide; pure bromide emulsions were appreciably less stable than those containing 2 percent AgI, but there was no certain difference produced by further increases in iodide content.

Of the sensitizing dyes which were used, only pinacyanol at a pH above 7 tended to cause increase in fog on storage; erythrosin, pinaverdol, and pinaflavol had no effect or even tended to preserve the plates in spite of their tendency to cause fog directly after their addition. All the dyes stop storage ripening of undigested emulsions almost completely.

In general, the increase in fog on storage is less in emulsions which have been digested, provided the digestion was not carried past the optimum sensitivity. This is especially noticeable in emulsions digested and coated without addition of soluble bromide after washing. We have previously observed this [18] and offered a tentative explanation.

Emulsions prepared with deactivated gelatin and allyl thiocarbamide showed normal after-ripening on storage, if not digested to equilibrium. The fog was low (not over 0.1 on the tank development after 1 year) in emulsions with a ratio of 4×10^{-5} g equivalent of

[18] Reference 2 (RP340).

sensitizer per g equivalent of AgBr (or less), [Br^-] of emulsion 5×10^{-5}. With double this amount, the fog increased to about 0.2 and with 12 or 16×10^{-5} ratio, deterioration was serious.

III. DISCUSSION

The results are in accordance with the theory stated in the introduction, that deterioration on storage is the consequence of continued after-ripening; that is, of continued reaction between the silver halide and the sensitizing and fogging constituents of the gelatin. Some of its characteristics may be better understood by considering the probable changes on drying the emulsion. The water content is thereby reduced from about 15 times the weight of the gelatin to about one seventh of the latter, or a reduction to approximately 1 percent of its original amount. Materials in solution in the emulsion will thus be greatly increased in concentration. Acid or alkali in small amounts will be an exception to the expected result because gelatin has the characteristic common to good "buffers", that its pH is little affected by concentration. Soluble bromide must, however, be much more concentrated in the dried emulsion than in the state where its concentration was measured for these experiments. The adsorption of soluble bromide by silver bromide may be expected to reach a condition of practical saturation at some concentration of the former. The data suggest that this is something over 0.02 N, since the stability is little improved by further addition of bromide above that necessary to produce 0.0002 N in the liquid emulsion. With smaller amounts, the change in concentration on drying is considerably affected by the combination of silver ions with gelatin. At pH 7 and [Br^-] 2×10^{-5} N, the emulsion contains no excess of silver or halogen; in solution the free bromide ions are in excess of the free silver ions, but the silver ions conbined with the gelatin are equivalent to this excess. Therefore, on drying, the bromide ion concentration will remain practically unchanged, since there is essentially a solution of silver bromide in gelatin solution; the net effect will be crystallization of solid silver bromide from solution, since the gelatin will give up silver ions to a solution of higher bromide ion concentration. It is possible, then, that on drying an emulsion with an initial [Br^-] of 2×10^{-5} N, the final value shall be the same, while starting at [Br^-] 2×10^{-4} N it rises to 2×10^{-2}, so that this region is one of rapid change in stability.

Washington, September 16, 1933.