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

THE PHOTOGRAPHIC SENSITIVENESS OF SILVER IODIDE

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Introduction

It has long been known that photographic emulsions containing silver iodide appear to be much less sensitive than do silver bromide emulsions. Should we expect this from purely theoretical considerations?

The photographic process may be roughly divided into two parts, (a) the photochemical effect of light upon the plate, and (b) rendering this effect visible by the process of development. It is with the first of these that we are concerned. There are at present several theories as to the exact nature of the action of light upon the plate, of which probably the most acceptable are the "nuclear" theory and the "sub-halide" theory.

Luther[2] claims that when a pure silver halide is exposed to light it undergoes reduction according to the equation, $2AgX \xrightarrow{\text{light}} Ag_2X + X$. When the light is removed the sub-halide recombines with the free halogen according to the equation, $AgX + X \xrightarrow{\text{dark}} 2AgX$. Trivelli[3] represents the photochemical action by a series of steps, with the formation of several sub-halides; in each step halogen is liberated. The original and final stages may be represented as follows, $Ag_nX_n \rightleftharpoons nAg + \frac{n}{2}X_2$.

Lüppo-Cramer[4] is an exponent of the nuclear theory which according to Lorenz[5] may be expressed approximately by the equation, $nAgX + \text{light} \longrightarrow (n-1)AgX + Ag + X$. The silver particles liberated act as nuclei for the condensation of more silver during development.

It is to be noted that by each of these theories halogen is liberated, and from the law of mass action the reaction should proceed with greater velocity and more nearly to completion if this halogen were removed. So to represent the reaction more accurately, the equation (taking only the first one given above) should be written, $2AgX + \text{gelatin} \xrightarrow{\text{light}} Ag_2X + \text{halogenated gelatin}$.

The relative sensitivity of silver bromide and silver iodide must depend, in part at least, upon the speeds of their corresponding reactions. From the above equation we can see two factors which affect the speed of the reaction. The first of these is the stability of the silver halide. It is well known that bromine is more active than iodine, and has a greater affinity

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[1] Extract from a thesis submitted by Malcolm C. Hylan in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Luther, *Z. physik. Chem.*, **30**, 628 (1899).

[3] Trivelli, *Jahrb. Radioakt. Elektronik*, **8**, 334 (1911).

[4] Lüppo-Cramer, "Kolloidchemie und Photographie," Steinkopf, **1921**.

[5] Lorenz, *Z. Elektrochem.*, **7**, 277 (1900-1901).

for metals. This is evidenced by the fact that bromine will displace iodine from its salts. Silver and bromine, then, in silver bromide should be more strongly bound together than silver and iodine in silver iodide. Conversely, silver iodide should be more easily broken down by the action of light. This factor would seem to favor the greater speed or sensitiveness of silver iodide.

The second factor is the combining power of halogen and gelatin. Here, bromine, being the more active, would be expected to combine more readily. We shall show later that this is actually the case. This factor would seem to favor the greater speed of silver bromide. We have, then, our two factors opposed, and the relative speeds of bromide and iodide must depend, in part, upon the relative magnitudes of the two factors. Other factors, as we shall show, may also enter to affect the relative speeds of the two reactions.

J. A. Johnson[6] has recently discovered a method for making iodide emulsions as sensitive as bromide emulsions. His patent is described as follows.

"For the production of high-speed print-out papers, plates, films, etc., coated with a light sensitive silver iodide emulsion. The emulsion may be produced by treating paper coated with silver chloride, bromide, or bromo-chloride emulsions with a soluble iodide, or by coating the paper directly with a gelatin or collodion emulsion, and sensitizing the emulsion after drying with a solution containing an organic sensitizer such as 'monomethyl*para*amidophenol sulfate' and an inorganic accelerator such as sodium sulfite. The sensitizing operation may be performed in daylight, since the sensitized emulsion does not become light sensitive until it is dried. The visible image produced on printing may be fixed by merely washing in water to remove the sensitizer; the unchanged silver iodide remains in the emulsion but is light insensitive."

The details of the above were communicated to the former of us before the patents were issued, and the desire was expressed that the theoretical side might be investigated. A careful study of the process should disclose the true causes of the lack of sensitiveness of ordinary silver iodide, and in what manner they may be overcome.

Experimental Part

Relative Combining Power of Bromine and Iodine with Gelatin.—Experiments to determine the relative combining power of bromine and iodine with gelatin were performed as follows.

A solution of iodine in potassium iodide was titrated against sodium thiosulfate solution. Five cc. of iodine solution was found to be equivalent to 2.4 cc. of thiosulfate solution. A concentrated solution of potassium iodide was then prepared and bromine water was run in, liberating iodine according to the reaction $Br + KI \longrightarrow KBr + I$. The liberated iodine was titrated against sodium thiosulfate. In this way 5 cc. of bromine was found to be equivalent to 3 cc. of thiosulfate solution, or 4 cc. of the bromine solution was equivalent to 5 cc. of the iodine solution. About 4 g. of gelatin was dis-

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[6] Johnson, *C. A.*, **16**, 3270 (1922).

solved in 150 cc. of distilled water and divided into 4 equal parts. To each of two of these 8 cc. of the bromine solution was added; to each of the other two 10 cc. of iodine solution was added. To each of the gelatin-bromine solutions was added as much crystalline potassium iodide as a spatula blade would hold and the liberated iodine was titrated with thiosulfate. In both cases only 0.3 cc. of the thiosulfate was required, indicating that about 95% of the bromine had combined with the gelatin. Two gelatin-iodine solutions were then titrated with thiosulfate. In each case 5 cc. was required, indicating that practically none of the iodine had combined with the gelatin.

Experiments on Silver Iodide Emulsions.—Silver iodide emulsions were experimented upon directly in order to study their photosensitive characteristics and to determine the role played by Johnson's sensitizer. Excess of potassium iodide gave an emulsion that was not affected by light, was non-sensitive without treatment but was sensitized by bathing in Metol-sulfite solution, was not affected by light before sensitization and was accelerated by bathing in silver nitrate. Excess of silver nitrate, on the other hand, gave an emulsion that darkened on exposure to light, was sensitive without treatment, was unaffected by the Metol-sulfite solution, blackened when sensitized if previously exposed to light and was retarded by bathing in potassium iodide solution.

Johnson's emulsions contain an excess of potassium iodide. When they are washed for an hour in cold water an emulsion containing a large excess of potassium iodide is, after sensitizing, as fast as one containing much less potassium iodide, but when not so washed the greater the excess of potassium iodide the slower the paper. Furthermore, in this connection, small amounts of potassium iodide present in the developer bath act as very strong retarders or, if in sufficient amount, stop all action. It is well known that potassium bromide has a similar action in the development of bromide papers, although to a less degree.

Sensitizing Effect of Various Chemicals.—The effect of sensitizing with various developers was tried and a solution of monomethyl-*p*-amidophenol sulfate (Metol) with sodium sulfate was found to be the best. The sensitizing effect of several inorganic compounds was tried, a summary of which is given in Table I.

TABLE I

SENSITIZING EFFECT OF CHEMICAL SUBSTANCES

Sensitized with	Exposure	Treatment	Results
Dil. H_2S	5–20 sec.	Bathed in Metol, then in dil. alkaline Na_2SO_3	Fair image
Dil. $Na_2S_2O_3$	5–20 sec.		
5% $Na_2S_2O_3$	1 min.	Dil. alkaline Na_2SO_3	Faint image
Dil. NaOH	5–15 min.	Bathed in Metol	
Dil. KOH	3–5 min.	Bathed in Metol	
5% Na_2SO_3	3–5 min.	Metol, then alkaline sulfite	
5% $NaHSO_3$	3–5 min.	Metol, then alkaline sulfite	

Attention should be called to the fact that by sensitizing with 5% thiosulfate an image was obtained although no organic developer had been used at any stage of the process.

Properties of a "Neutral" Emulsion.—An emulsion having, within the limits of experimental error, no excess of either potassium iodide or silver nitrate was prepared as follows.

Ten g. of potassium iodide was dissolved in 100 cc. of distilled water (designated as Solution A). Ten g. of silver nitrate was dissolved in 40 cc. of distilled water and ammonium hydroxide added until the precipitate, at first formed, redissolved (designated as Solution B). Twenty-five cc. of Solution A was placed in a conductivity cell and the opposing resistance adjusted to give a reading near the center of the bridge. Solution B was added, 1 cc. at a time, the bridge reading being taken after each addition, until 20 cc. had been added. The experiment was then repeated, using 15 cc. of Solution A and adding 15 cc. of Solution B. Graphs were then made by plotting bridge readings against cc. added, and the volume of B corresponding to the break in the curve was determined. For the first titration 16.2 cc. of Solution B was equivalent to 25 cc. of Solution A. For the second titration 15.8 cc. of Solution B was equivalent to 25 cc. of Solution A. The average of the two is 16 cc.

From a buret, then, exactly 25 cc. of Solution A was run into a beaker, 5 g. of gelatin added, and the whole warmed until the gelatin had dissolved. Then exactly 16 cc. of Solution B was added.

The emulsion thus formed was painted on cards and dried. After about 4 hours, the cards, feeling dry to the touch, were exposed for 6 seconds, and bathed first in Metol, then in alkaline sulfite solution. A very good image was obtained.

Effect of Moisture.—Two or three days later some of these same cards were exposed and developed and the image found to be very much fainter than before. As the only difference between the cards at the two different times could be the amount of moisture in the emulsion, some of the cards were soaked in water for a minute and dried until they felt dry to the touch. Upon exposing and developing them very good images were again obtained.

To avoid the double bathing necessitated, in the case of iodide emulsions, by the use of the alkaline sulfite bath following bathing in the ordinary Metol developer, a developer was prepared by adding about 1% of sodium hydroxide to the Metol-sulfite solution, and was found to work well. Some of the cards covered with iodide emulsion, prepared according to Johnson, that is, with excess of potassium iodide, which had been coated several weeks previously, were exposed for 6 seconds and bathed for 10 minutes in this developer. A faint image was obtained. An iodide card covered with iodide emulsion prepared by converting a card covered with bromide emulsion, when exposed 6 seconds gave no image, even after 45 minutes' bathing in the developer. A "prepared" iodide card and a "converted" iodide card were then soaked in water for a minute and, after drying, exposed, the former for 6 seconds, the latter for 24 seconds. The former on 10 minutes' bathing in the developer gave a clear but light image; the latter, after 15 minutes' bathing, showed a faint trace of an image. The great difference between the "prepared" and "converted" cards is probably due to the fact that the latter have a surface coating of gelatin over the emulsion, put on to prevent abrasions, and to obtain results it is necessary to work down through this.

To compare the effect of moisture on bromide emulsions, a card covered with bromide emulsion was cut in two, and half soaked in water for a minute and dried. Both halves were then exposed for one second and bathed in developer for 15 seconds. At the end of that time the moistened card bore a good image, but the unmoistened card was still blank.

Comparison of Accelerating and Retarding Effects.—Three cards from the carefully prepared "neutral" emulsion, that is, having no excess of either potassium iodide or silver nitrate, were treated as follows. One was soaked in clear water, one in dil. potassium iodide solution, and one in dilute thiosulfate solution. After drying, each was exposed for 6 seconds and bathed in the alkaline developer for 15 minutes. The card treated with thiosulfate gave a very good image, the water-treated card a medium one, and the potassium iodide-treated card a poor one.

Discussion

The evidence of our experiments indicates that it is principally adsorbed potassium iodide which causes the apparent non-sensitiveness of silver iodide emulsions. That potassium iodide is adsorbed by silver iodide has been shown by Lottermosser and Rothe.[7] Theoretically, we should not expect potassium iodide to have any greater retarding effect on silver iodide than potassium bromide on silver bromide. The fact that its retarding action is much greater can be easily explained on the basis of adsorption. To quote Lüppo-Cramer,[8] "silver iodide in general possesses a higher degree of dispersity than the other silver halides." Consequently, a given weight of silver iodide has a much greater specific surface than the same weight of other silver halides, and therefore is capable of adsorbing much more soluble halide.

The experimental evidence in support of the above hypothesis may be briefly summarized as follows, remembering that when emulsions are spoken of as sensitive and non-sensitive we refer to the ability to produce an image after exposures of, at most, but few minutes duration, followed by bathing in the common photographic developers. (1) Emulsions containing no excess of potassium iodide are sensitive. (2) Emulsions containing any excess of potassium iodide are non-sensitive. (3) Considerable washing of an emulsion containing an excess of potassium iodide will not render it sensitive. (4) The presence of mere traces of potassium iodide in the developer bath retards or, if in sufficient amount, stops all action. (5) Bathing the emulsion in dilute solutions of compounds which

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[7] Lottermosser and Rothe, *Z. physik. Chem.*, **62**, 377 (1908).

[8] Lüppo-Cramer, *Kolloid Z.*, **30**, 186 (1922).

would react with any adsorbed potassium iodide, thus removing it, renders the non-sensitive emulsion sensitive. This last point might easily be taken as due to the presence, in the emulsion, of reagents that combine with the liberated iodine. However, as they should react metathetically with any potassium iodide present long before exposure, it is likely that they function in both ways. In support of our hypothesis, and in harmony with (3) above, let us quote Trivelli and Sheppard[9]—"the separation (of adsorbed contaminants) by washing with pure solvent proceeds very slowly, adsorption being in most cases practically irreversible."

Our views find further confirmation in the work of Lüppo-Cramer[10] who found that a partial transformation of silver bromide or silver chloride into silver iodide is associated with a great increase in sensitivity, but that a complete transformation into silver iodide results in a marked decrease in sensitivity. He says, in explaining this fact, "It seems probable that in the case of a complete transformation, the hard-to-be-avoided excess of soluble iodide, which is held stubbornly adsorbed by the silver iodide, is the cause of the reversal of sensitiveness."

Renwick,[11] too, attributes the loss in sensitivity on converting bromide plates into iodide, in part "to the great capacity of silver iodide for adsorbing soluble iodides, which would very much increase the difficulty of reducing it to metallic silver by alkaline development."

In the light of our hypothesis we can easily explain why, with the washed emulsions, it makes no difference how much potassium iodide is in excess, while with the unwashed emulsions the excess of potassium iodide is measured by the retardation of development. In the first case the free or unadsorbed potassium iodide is washed out and only the adsorbed remains, while in the latter case both adsorbed and unadsorbed potassium iodide are present, and there is, therefore, much more chance that some will be left in to retard development.

Another cause of the apparent non-sensitiveness of ordinary silver iodide emulsions is the absence of a sensitizer, gelatin not combining with iodine sufficiently to play that role. The experimental evidence supporting this conclusion is (1) iodine has practically no power for combining with gelatin; (2) sensitization is effected by addition of hydrogen sulfide, sodium thiosulfate, various sulfites, potassium hydroxide and sodium hydroxide to ordinary iodide emulsions, and is increased by their addition to "neutral" emulsions. Each of these compounds has the power of combining with iodine. The reactions are: $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$; $H_2S + I_2 \longrightarrow 2HI + S$; $3I_2 + 6KOH \longrightarrow 5KI + KIO_3 +$

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[9] Trivelli and Sheppard, Eastman Kodak Co., "Monographs on the Theory of Photography," No. 1, p. 30.

[10] Lüppo-Cramer, *Phot. Korr.*, **50**, 561 (1913).

[11] Renwick, *J. Soc. Chem. Ind.*, **39**, 156T (1920).

$3H_2O$.[12] Iodine reacts similarly with sodium hydroxide: $SO_3^= + H_2O + I_2 \longrightarrow 2H^+ + 2I^+ + SO_4^=$.[13]

The catalytic effect of moisture is also an important factor in the sensitization of silver iodide emulsions. This probably does not affect the relative speeds of iodide and bromide emulsions, as our experiments indicate that the effect on the one is as great as the effect on the other. However, other factors lower the sensitivity of iodide emulsions to such a degree that it is likely that moisture is an important factor in raising the photochemical action above the "threshold value" of developability.

We conclude then, that silver iodide emulsions are not strictly non-sensitive, but that, quoting Bolas,[14] "whether exposed or unexposed they are almost unaffected by such weak alkaline developers as are used in ordinary photographic practice;" that their low sensitivity is due primarily to the adsorption of potassium iodide, together with its strong retarding effect, and secondarily to the inability of gelatin to act as a sensitizer; and that if a sufficiently strongly alkaline developer is used, in spite of their low sensitivity, fair results may be obtained.

Johnson's process of sensitization does two things: (1) it removes adsorbed potassium iodide, and (2) it leaves organic developer in the emulsion to act as sensitizer, and later as developer. Hence, the emulsion being light sensitive and organic developer being present, all that is necessary to obtain an image is to expose it and then bathe it in dilute alkali to make the developer active. Bathing the sensitized paper in distilled water does not, as Johnson claims, desensitize it. It merely removes the unadsorbed developer dissolved in the emulsion, so that after exposure it is necessary to bathe the paper in organic developer before the alkali bath in order to bring out the image.

Summary

1. It is shown that from purely theoretical considerations it is impossible to predict whether or not silver iodide should be photographically more sensitive than silver bromide.
2. Johnson's method of sensitizing the apparently non-sensitive silver iodide emulsions is described.
3. Experiments have been performed to determine the nature of this process of sensitization.
4. It is shown that gelatin, which has a sensitizing effect in bromide emulsions, has practically no sensitizing effect in iodide emulsions.
5. Potassium iodide is shown to have a powerful retarding effect, emulsions containing an excess of this reagent being non-sensitive.
6. A number of compounds, both organic and inorganic, which should

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[12] Thorpe, Longmans, **1912**, vol. III, p. 152.

[13] Treadwell and Hall, vol. I, p. 349.

[14] Bolas, *Brit. J. Phot.*, **68**, 532 (1921).

react with potassium iodide or with iodine have been shown to have sensitizing effects.

7. An emulsion having no excess of silver nitrate or potassium iodide has been prepared and found to be sensitive.

8. Washing to remove the excess of potassium iodide does not make the regular iodide emulsion sensitive.

9. The amount of moisture present in the emulsion has been shown to have considerable effect on the sensitiveness.

10. In general, sensitization has been effected by treatment with a chemical which would react with potassium iodide to remove it, or remain in the emulsion to combine with any iodine liberated.

11. The "non-sensitive" emulsions have been found to be sensitive when a strongly alkaline developer was employed.

12. It is concluded that the apparent non-sensitiveness of silver iodide emulsions is due primarily to adsorbed potassium iodide, secondarily to the absence of a sensitizer, gelatin not playing that role; and that ordinary, apparently non-sensitive, silver iodide emulsions are truly sensitive when a sufficiently strongly alkaline developer is used.

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY FERRIC SALTS. II

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It has been known for some time that the decomposition of hydrogen peroxide is accelerated by the presence of iron salts in solution. The most recent quantitative investigations are those which were made by von Bertalan,[1] by Duclaux,[2] by Mummery,[3] and by one of the writers of this paper.[4] The purpose of the present paper is to present the results of subsequent experiments which necessitate certain modifications in the conclusions reached by these investigators. The work already reported was done with very dilute solutions of the catalyzing salts (up to 5 millimoles per liter). More concentrated solutions than this could not conveniently be used by the two first-named writers, owing to the difficulty of following the more rapid reactions by the cumbersome method of titrating samples with permanganate. On the other hand, the gasometric method offers an accurate means of measuring the rate of a reaction so rapid as to be entirely completed in 5 minutes.

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[1] von Bertalan, *Z. physik. Chem.*, **95**, 328 (1920).

[2] Duclaux, *Bull. soc. chim.*, **31**, 961 (1922).

[3] Mummery, *J. Soc. Chem. Ind.*, **32**, 889 (1913).

[4] Bohnson, *J. Phys. Chem.*, **25**, 19 (1921).