THE PHOTOGRAPHIC EMULSION

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THE PHOTOGRAPHIC EMULSION

by

B. H. Carroll, D. Hubbard
and C. M. Kretschman

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[redacted]

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* The letter J. stands for Bureau of Standards Journal of Research (Washington, D.C.).

INTRODUCTION

Photographic-emulsion making is carried out commonly more as an art than as a technological process soundly based on science. The reasons for this situation are many. One is commercial secrecy. C. E. K. Mees, *in the introduction to his Theory of the Photographic Process, writes "A book on the theory of photography should contain a chapter on emulsion making,... The author's knowledge of this subject has been acquired in confidence, however, and he is not entitled to publish the material with the frankness, which alone would justify any publication". This statement, made in 1942, characterizes the attitude of the photographic industry to this day.*

Very few institutions exist at which photographic science is studied independently, and in these, for very good reasons, emulsion technology is, as a rule, neglected, preference being given to areas more suitable for academic research. For some years, however, emulsion work was done systematically at the National Bureau of Standards, under the guidance of the Senior Author of the papers in this book, Dr. B. H. Carroll. *The value of the series of papers produced during the years 1927 to 1934 is undisputed to this day, and they are widely quoted; indeed they should be regarded as classics.*

Access to the original papers is decidedly difficult, since the National Bureau of Standards Journal of Research *is not freely available everywhere. Hence it has seemed well worthwhile and a service to the photographic community to present these papers anew between two covers. The careful planning of the research will thus become apparent to the critical student and is well reflected by their order of publication.*

One wishes to acknowledge with gratitude the generosity of the National Bureau of Standards, whose regulations allow free reprinting of material published by them.

The papers fall into two main classes: chemical sensitization, and spectral sensitization. All of them will repay close study; it is perhaps just personal preference that causes the writer to single out two for special attention: that on Silver Ion-Gelatin Equilibrium *(No. 4) and that on the* Mechanism of Hypersensitization *(No. 12). In spite of the volume of research devoted to this question, the precise function of gelatine in our emulsions is not clear to this day, and these two papers form the backdrop to any research done, or to be done, on this subject. Furthermore, they lay the basis for the modern methods of control of emulsions by the measurement of pH and pAg by means of electrodes, and by an understanding of the processes involved.*

Photographic research at the Bureau of Standards did not start with the authors of the present papers. During the first World War Dr. W. F. Meggers, *the spectroscopist, worked on hypersensitization and was responsible, in 1922, for the establishment of an emulsion laboratory by* Drs. F. W.

Walters *and* B. H. Carroll *who took charge of it that year. One can well imagine these young men finding their feet and establishing their methods, leading to that most fruitful period of some 5 years reflected in this volume. Unfortunately, work came to an end in 1933 when the photographic laboratory was closed as an economy measure.*

Burt H. Carroll *was born on March 20, 1896 at Tenafly, N.J., and graduated to B.Chem. at Cornell University in 1917. After a few months in the consulting organization of Arthur D. Little Inc. he joined the Chemical Warfare Dept. of the US Army in Dec. 1917 and left in Feb. 1919 to work for his Ph.D. degree which he obtained at the University of Wisconsin in June 1922, on a thesis on the properties of solutions in mixed solvents and from Wisconsin went to the Bureau of Standards.*

In 1933, Dr. Carroll joined the Kodak Research Laboratories at Kodak Park, where he became Senior Research Associate in 1945. Most of his work was in the Emulsion Research Division, on sensitization and addenda; for some 10 years he was in charge of Scientific Plates. In 1962 he retired to a consultant's position with Kodak as well as the Rochester Institute of Technology where he was appointed as Professor in Photographic Science in 1963, a post he still holds, and in which he directs thesis problems for the BS and MS degrees in photographic science and teaches theory of photographic process.

He is Fellow of the SPSE and the OSA, member of the ACS and RPS; and elected corresponding member of the DGPh. He was honoured by the Société Française de Photographie with the Niépce-Daguerre medal and by the Royal Photographic Society with the Henderson Award.

Donald Hubbard *was born on Terra Ceia Island, Florida, Oct. 4, 1900. He obtained his B.S., and the MS degree from the University of Florida. In 1925, he joined* Drs. Meggers *and* Carroll *at the National Bureau of Standards. The work for his Ph.D. thesis on "Membrane Equilibria in Photographic Emulsions" is reported in abbreviated form as No. 12. After the photographic work at the Bureau was abandoned, he remained, being able to apply the fundamental understanding gained in the photographic work to a multitude of problems: chemical activity at liquid-glass interfaces; chemical durability of all kinds of glasses; interpretation of the potential on a glass electrode; and in particular, voltage anomalies; dispersion of glass fibres in the production of silicate papers; problems in the preparation and stress behaviour of concrete; coagulation of blood and the causes of circulatory occlusions and on the other end of the scale, a study of the sizes and shapes of tektites, those showers of interplanetary glass pellets, from which stems a life-long interest in space and space travel.*

Dr. Hubbard *is a Fellow of the Washington Academy of Science, member of the American Chemical and Optical Societies, and of the Association for the Advancement of Science. He was honoured by the American Department of Commerce with a Silver Medal for Scientific Attainment, and by the Société Française de Photographie with the Niépce-Daguerre Medal.*

Charles M. Kretschman *was born at Salisbury, Pennsylvania, on August 14, 1912, took his B.S. in Chemistry at George Washington University in 1934 and the M.S. in Organic Chemistry at Rochester (N.Y.) University in 1939. He did his studying whilst at work as Laboratory Assistant at the Bureau of Standards, joined the Eastman Kodak Co. in 1934 and is now a Technical Supervisor in production of photographic emulsions for infrared, documentary, recording and cine films.*

It will be clear that a well-qualified, competent team was at work during those fruitful years. One wishes this belated collection of their papers the success and recognition it so well deserves.

W. F. Berg

All articles, except the initial one, have been reproduced facsimile from the original papers published between 1928 and 1934 by the National Bureau of Standards at the United States Department of Commerce, as reprints from the Bureau of Standards Journal of Research, printed by the U.S. Government Printing Office.

THE PHOTOGRAPHIC EMULSION. I. THE COMPARISON OF EMULSIONS MADE WITH DIFFERENT BROMIDES*

BY BURT H. CARROLL AND DONALD HUBBARD

INTRODUCTION

The recent rapid progress of photographic science has been largely through study of completed materials, and there can be little doubt of the value of studying photographic sensitivity from the standpoint of the conditions under which it originates—a subject which, for commercial reasons, has been almost entirely a secret for a generation. The Bureau of Standards has accordingly undertaken an investigation of fundamental factors in emulsion making.[1] While much of the material presented here may be common knowledge to emulsion makers, it has never been published in quantitative form, and it is a fact that the literature, and also the verbal opinions which the writers have been able to obtain from various sources, are both filled with contradictions regarding the most elementary points of emulsion making. These contradictions probably arise from the widely varying conditions under which emulsions may be made and the rapid variations in the influence of any given factor as the type of emulsion is changed. Though the problem of securing systematic knowledge of the subject is in many quarters considered hopeless of solution, and though indirect methods have accomplished much, we believe in the possibilities of a frontal attack, provided that all information of possible significance be reported.

As a means of outlining the variables which need to be studied, a very brief description of emulsion making will be given. So far as we know, the only process to be considered for fast emulsions is the addition of a silver salt solution, either neutral or ammoniacal, to a solution of bromide or mixed bromide and iodide containing gelatin. The bromide is invariably in excess. The known variables in this first and most important step are numerous. Enumerating them without specifying their particular importance, they are: the other ions of the silver and halogen compounds; the absolute concentrations; the relative excess bromide; the relative percentage of iodide; the temperature; the method and rate of mixing; the hydrogen ion concentration

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* Published by Permission of the Director of the National Bureau of Standards of the U.S. Department of Commerce.

[1] The investigation was originally carried on by Dr. F. M. Walters, now of the Carnegie Institute of Technology, and the senior author. The equipment of the laboratory, and development of much of our present technique of emulsion-making, date from this period, and the data on emulsions 6–4 and 6–5, quoted in this paper, were obtained while Dr. Walters was associated with the project.

(pH); the presence of ammonia; the quality of gelatin.[1] After mixing (or "emulsification") the emulsion is commonly "ripened" for a time by digestion in the presence of the excess bromide and the by-products of the reaction; more gelatin is commonly added towards the end of the ripening. Ammonia is introduced at some point into almost all fast emulsions; in this country at least, more frequently during the ripening of an emulsion mixed in neutral solution than in the silver solution. Many other materials have been added to emulsions; citric acid and alcohol are frequently mentioned.

The most important variables in the ripening process appear to be the temperature and concentrations with special reference to soluble bromide and ammonia; the extent to which ripening can profitably be carried is controlled by the original conditions of emulsification.

Having obtained the desired degree of ripening, the usual practice is to chill the emulsion to a firm jelly, then shred, and wash in cold water to remove soluble salts. The pH and dissolved salts in the wash water have considerable influence by their effect on the swelling. An alternative procedure, which we have found useful in experimental work, is to centrifuge the silver halide out and re-emulsify in pure gelatin solution. After washing, the emulsion is remelted, commonly with the addition of more gelatin, and usually digested for some time at a moderate temperature. This step is omitted in the old emulsion formulae found in the literature; in fact it is usually recommended to melt with the minimum possible heating. The apparent variables in this step are temperature, pH[2] and the amount of gelatin added after melting. Before coating, chrome alum in quantities said to be photographically inert, is commonly added to harden the gelatin. Addition of small amounts of soluble bromide is recommended in the old formulae. Sensitizing dyes, with the exception of the eosins, which may be introduced into the original mix, are always added after washing. The concentration of dye and of soluble bromide are of considered importance as well as the individual characteristics of the dye.

THE COMPARISON OF EMULSIONS MADE WITH DIFFERENT BROMIDES

Eder[3] states that only potassium and ammonium bromides are to be considered for emulsion making and our original program was

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[1] Assuming for the gelatin good physical properties and the absence of such impurities as salts of heavy metals and reducing agents, the concentration of sensitizers such as thiocarbamides appears to be the major factor in determining its photographic quality.

[2] Rawlings and Glassett, Phot. J., **66**, 495 (1926).

[3] "Ausführliches Handbuch der Photographie", **3**, 19.

limited to a comparison of these two salts. Having detected differences between emulsions made with them, the experiments were extended to include sodium, calcium, cadmium, and zinc bromides.

Lüppo-Cramer[1] states as a result of his general experience that potassium bromide is better for some types of emulsions, and ammonium bromide for others. Eder suggests that because of its more acid reaction, the latter may give less fog in cooked emulsions. Lüppo-Cramer has published a recent paper on the ripening process,[2] in which he notes the very fine grain and slow speed of a cooked emulsion made with $CdBr_2$; this he attributes to retardation of the ripening by formation of a double salt with the AgBr, but we are unable to find any evidence for the existence of such a compound. He found sodium and potassium bromides to be equivalent. Lithium bromide caused faster ripening and more fog, while barium, strontium, and magnesium bromides were approximately equivalent to potassium bromide. No quantitative data are given.

Eder and Pizzighelli[3] compared silver chloride–gelatin emulsions made with various chlorides, finding that the chlorides of the alkali metals gave faster and softer emulsions than those of the alkaline earths, while emulsions made with zinc and cadmium chlorides were very slow, clear and "hard".

Schweitzer[4] reports that infra-red sensitive emulsions may be made by the use of mixtures of NH_4Br and $ZnBr_2$, and the famous infra-red sensitive collodion emulsions of Abney[5] were made with $ZnBr_2$. These are probably cases of sensitization by colloidal silver, from the fog readily produced under these conditions.

Suggestions as to the mechanism of the differences between the bromides are even rarer than experimental results. Differences in solubility of the silver halide have been suggested by Lüppo-Cramer and by Eder. Slater-Price[6] postulates that adsorbed bromide may be built into the crystal lattice of the grain, introducing strains depending on the dimensions of the cation.

We believe the most probable mechanisms to be as follows; one or more of these being operative when a given change in cation is made:

1. Adsorption on the silver bromide grains, affecting the crystal habit and recrystallization; the ripening is normally controlled more by the rate of recrystallization than by the rate of solution.

2. Alteration of the pH by hydrolysis of the bromide or by

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[1] Z. wiss. Phot., **23**, 290 (1925).
[2] Z. wiss. Phot., **24**, 291 (1926).
[3] "Ausführliches Handbuch der Photographie", **3**, 919.
[4] Phot. Abs., **6**, No. 408.
[5] Phil. Trans., **171** II, 655 (1880); **177** II, 547 (1886).
[6] Phot. J., **65**, 303 (1925).

repression of the dissociation of ammonia.

3. Alteration of the solubility of the silver bromide in the emulsion.
4. The removal of ammonia as complex cation, affecting solubility, pH, or crystal habit of the grain.
5. Changes in the viscosity and protective action of the gelatin.

In the following ammonia process formula, we have a type of emulsion in which a considerable amount of ripening from the standpoint of both speed and grain size, occurs after the mixing ("emulsification") is complete; in this case it may be possible to distinguish between effects on the formation of the grains and on the ripening. It is obviously impossible to precipitate crystals of the size and perfection characteristic of the grains of modern fast emulsion; they must be grown from their original ultramicroscopic beginnings. But we have evidence[1] that all the processes commonly associated with ripening go on at a greatly accelerated rate during the mixing, so that, as in the case of the following neutral formula, the grains may be well formed at the end of a gradual emulsification, and the emulsion is comparatively little changed by subsequent "ripening". Even with the ammonia process formula, the growth of grains and nuclei during mixing is far from negligible, and it will be difficult to say definitely that a given one of the factors just mentioned influences ripening or influences the formation of the grain.

1. EXPERIMENTAL

Materials

The *alkali bromides* were commercial "c.p." salts free from heavy metal and iron, and contained less than one-half per cent chloride. NaBr, because of its variable water content was used in solution.

Calcium bromide was purified by treating the solution with H_2S, filtering, making barely acid with HBr, and removing H_2S by prolonged bubbling with filtered air. It was used in solution without recrystallization.

Cadmium bromide was freed from bromate by treatment with HBr, and recrystallized from water and alcohol.

Zinc bromide was prepared by saturating redistilled HBr with analyzed zinc, free from heavy metals and iron. The solution was used without recrystallization.

Silver nitrate was spectroscopically free from other heavy metals

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[1] For example, emulsions 6–4 and 6–5 were made with the proportions given later as the neutral formula, but with different gelatin. 6–4 was mixed comparatively rapidly (5 minutes); initial speed 90, γ_6 0.92, average grain area 0.33 μ^2; after 80 minutes ripening at 75°, the speed was 200, γ_6 0.77, average grain area 1.38 μ^2. The mixing of 6–5 was extended over a period of 40 minutes; speed directly after completion of mixing 230, γ_6 0.55, average grain area, 1.89 μ^2, indicating much more ripening than 6–4 after 80 minutes.

and iron, and contained 0.05 per cent material not precipitated by HCl.

Gelatin.—Emulsions were made from all the bromides with two makes of gelatin of different types: Koepf "3738 hard" and Nelson No. 1.

Water.—Distilled water was used throughout.

Ammoniacal Emulsion Formula

The larger number of tests were made with an ammonia process formula, washing by centrifuge. The centrifuge was used primarily because of the possibility of following the ripening process in a single batch of emulsion, but also because it greatly improves the keeping qualities of ammoniacal emulsions.

The ammonia process formula was as follows:

A.	Water	125 cc.
	$AgNO_3$	0.1765 gram equivalent (30.0 gm.)
	NH_4OH	0.353 gram equivalent —(28–30 cc. concentrated ammonia solution)
B.	Water	250 cc.
	Gelatin	12.5 gm.
	Bromide	0.218 gm. equivalent (for example, 26.0 gm. KBr)
	KI	0.0015 gm. equivalent (0.25 gm.)

The ammonia necessary to redissolve the silver (2 mols per mol $AgNO_3$) is found to be reproducible to 1 per cent. The excess halide is 25 per cent; assuming complete precipitation of the iodide, the mol fraction AgI is 0.0085 (1.06 per cent by weight).

The emulsion is mixed in conventional fashion. The gelatin is soaked in the bromide solution for 15–25 minutes at room temperature, then placed in a thermostat at $45° \pm 0.5°$ and stirred about 15 minutes until the gelatin is dissolved and the solution is at thermostat temperature. A standard size Pyrex beaker (1.5 liter) and glass stirrer at 250 r.p.m. are used; the silver solution at 25°–30° is added from a separatory funnel in 2.5 minutes.

Within 2 minutes after the completion of mixing, one quarter of the emulsion is removed, the rest continuing to ripen at a constant temperature of 45°, with stirring. The sample is centrifuged at 3000 r.p.m. in a 5-inch hard rubber bowl. The time required for separation of at least 95 per cent of the silver bromide varies from 8 minutes with certain of the unripened emulsions to 2 minutes after long ripening. When separation is complete, the bowl is drained, the silver bromide re-suspended in 100 cc. of 1 per cent gelatin solution and the centrifuging repeated. Gelatin solution has been found preferable to water for washing, as when much of the gelatin is washed from the precipitate it no longer adheres properly to the walls of the bowl. Two separations have been found to give sufficient washing, the soluble bromide and ammonia being eliminated as completely as by ordinary washing. After the second separation, the silver bromide is suspended for coating in a solution of 12.5 gm. of gelatin in 175 cc. of water. After warming to 45°, it is filtered through an open (Whatman No. 41) paper and 10 cc. of 60 per cent alcohol is added to break foam and assist in setting.

Samples are again taken at approximately 30, 60, and 120 minutes from the end of the mix, and treated like the first. This gives four stages of ripening, from the practicable minimum to over-ripening. The progress of the ripening can be followed by the texture of the silver bromide on the wall of the centrifuge bowl, which becomes very distinctly rougher with each successive sample.

The plates are machine-coated, with 9–10 cc. emulsion per 100 cm^2 (4 mg. AgBr per cm^2), a thickness which experiment has shown to be sufficient to elimiate the effect of coating thickness on gamma. They are dried at 17–19° C. The air after leaving the plates passes over ammonia coils which keep the humidity in the room at approximately 60 per cent.

Neutral Emulsion Formula

The "cooked" emulsion formula which was used was much less satisfactory, but the results obtained with it were parallel with the others. The solutions were as follows:

A.	Water	225 cc.
	Gelatin (Koepf)	10 gm.
	Bromide	0.265 gm. equivalent (50% excess halide, for example, 31.5 gm. KBr)
	KI	0.0015 gm. equivalent (0.25 gm.)
B.	Water	100 cc.
	$AgNO_3$	0.1765 gm. equivalent (30.0 gm.)

The emulsion was mixed at 75° C, in the same apparatus, with the important exception that the silver nitrate solution was delivered from a capillary stem funnel which increased the mixing time to 27 minutes, the idea being to secure a better range in grain size. Samples were taken 30, 60, and 105 minutes from the start of the mix. The results suggest that the grains first formed were over-ripened before the mixing was completed.

The emulsion was washed in the centrifuge and otherwise treated the same as the ammonia emulsion.

Methods of Testing

The standard sensitometric methods of the Bureau were used. Backed test strips were given a non-intermittent sector wheel exposure at an intensity of one candle meter, color temperature 5325° K; brush developed in unbromided pyro-soda,* and densities measured in diffuse light with a Martens photometer. Fog densities are automatically subtracted by the photometer as used; with backed plates, the fog strip is uniform within the limits of error of development for the entire length.

The grain of all experimental emulsions was photographed at 1500 diameters, using a Bausch and Lomb 2 mm. apochromatic objective N. A. 1.3, and Zeiss Homal IV ocular. The illuminating system consists of a Point-o-lite lamp, condenser to give approximately a parallel beam, Wratten "C" filter, and aplanat substage condenser N. A. 1.4. Measurements of grain size were made from enlargements to 5000 diameters. Circles of the proper diameter have been found more convenient than linear rules. The size classes differed by $0.2\ \mu^2$.

Reproducibility of Emulsions

The parallel results from the emulsions made in the two different gelatins are perhaps the best proof that the effects observed are correctly attributed to the cation of the bromide in question. But direct tests of the reproducibility of our emulsions indicate that it approaches that of the sensitometric methods.[1] Fig. 1 gives the data on two emulsions made by the same formula, comparing speed and gamma at all stages of ripening; 8–33 was made by one of the writers, and 8–58 by the other, a year later. Similar results have been obtained in other cases.

These results will be considered in detail after taking up the determination of conditions in the emulsion which might be expected to influence the photographic properties.

The centrifuged emulsions have an unusual tendency to increase in speed on storage, which introduces some uncertainty as to what is to be taken as the true value. The general question of ripening after washing will be taken up in a later communication. We may state with confidence, however, that the changes in the emulsions in question, while rapid for the first two to three months, become progressively slower, so that the changes between three and twelve

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* Solutions:

A. Water	1000 cc.	B. Water	1000 cc.	C. Water	1000 cc.
Pyro	60 gm.	Na_2SO_3	95 gm.	Na_2CO_3 (c.p.)	70 gm.
$K_2S_2O_5$	12 gm.	(Actual Na_2SO_3 determined by analysis)			

1 part each A, B and C to 7 of water; developed 3, 6, and 12 minutes at 20° C.

[1] We have so far had no experiences with inexplicable mutations such as the case given by Renwick, Phot. J., **61**, 333 (1921).

months are a small fraction of those in the first three. The tests in all cases were made between eight and nine months after coating, so that the difference in age, between any emulsions compared, becomes negligible. This storage ripening may apparently be eliminated by the proper amount of digestion before coating, but the correct amount varies with the emulsion and it was very desirable to avoid introducing another variable. We should, perhaps, mention that the storage ripening is equally marked in neutral and ammoniacal emulsions, and is prevented rather than accelerated by the addition of soluble bromides before coating.

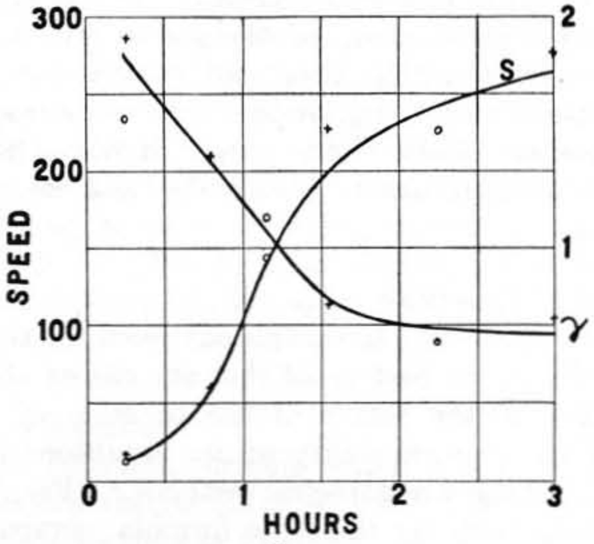

FIG. 1

The sensitometric data are presented in Tables 1 and 2. Average grain size of some of the emulsions is included.

Solubility of AgBr in the emulsion, and pH

The solubility of the silver halide in the (unwashed) emulsion has already been mentioned as of possible influence on the precipitation and ripening. Other conditions being the same, an increase in solubility would, by von Weimarn's theory, decrease the initial velocity of crystallization and, therefore, increase the average grain size. It would also increase the velocity of the Ostwald ripening. The solubility of silver bromide was determined under conditions approaching those of the (unwashed) emulsion as closely as practicable. As the separation of silver bromide from the solution could not be made quantitative in the presence of the gelatin, this was necessarily omitted, as was also the iodide. The ammonia was placed in the bromide solution to reduce changes in solubility during precipitation, and the silver bromide precipitated as in making an emulsion, temperature

TABLE 1.—*Ammonia Process Emulsions*

	Koepf Gelatin										Nelson Gelatin								
Bromide	Emulsion Number	Ripening Time	Speed	γ_3	γ_6	γ_{12}	Fog$_3$	Fog$_6$	Fog$_{12}$	Average Grain size μ^2	Emulsion Number	Ripening Time	Speed	γ_3	γ_6	γ_{12}	Fog$_3$	Fog$_6$	Fog$_{12}$
NH_4Br	8–63–1	4 min.	26	1.62	2.42	3.3	0.02	0.09	0.18	0.16	8–61–1	4 min.	50	2.1	3.1	3.6	0.05	0.13	0.26
	2	31 ,,	160	0.88	1.50	2.22	.12	.20	.38	0.35	2	32 ,,	100	1.40	2.15	3.2	.12	.22	.41
	3	63 ,,	340	0.58	0.97	1.50	.09	.24	.56	0.99	3	62 ,,	190	0.95	1.47	—	.14	.26	.51
	4	125 ,,	450	0.53	0.89	1.44	0.07	.26	.58	1.46	4	121 ,,	350	0.72	1.08	1.54	.21	.47	.65
KBr	8–64–1	4 ,,	35	1.26	1.93	2.63	0.02	0.07	0.13	0.16	8–62–1	4 ,,	67	1.28	2.46	3.3	0.04	0.11	0.26
	2	35 ,,	160	0.76	1.24	1.92	.11	.33	.68	0.87	2	31 ,,	590	0.65	1.01	1.51	.32	.56	1.00
	3	61 ,,	335	0.54	0.88	1.49	.09	.25	.42	1.05	3	61 ,,	780	0.61	0 98	1.51	.25	.55	1.10
	4	121 ,,	500	0·57	1.04	1.75	.07	.24	.49	1.40	4	121 ,,	950	0.62	0.94	1.29	.23	.48	0.92
NaBr	8–67–1	4 ,,	26	1.55	2.11	2.67	0.04	0.08	0.13		8–73–1	3 ,,	45	1.70	2.20	3.1	0.01	0.05	0.14
	2	33 ,,	370	0.57	0.97	1.35	.23	.35	.60		2	32 ,,	680	0.52	1.06	1.69	.15	.31	.68
	3	63 ,,	460	0.43	0.77	1.05	.22	.34	.54		3	63 ,,	790	0.62	0.95	1.45	.20	.37	.77
	4	121 ,,	430	0.74	0.97	1.63	.15	.33	.57		4	119 ,,	800	0.66	1.09	1.63	.14	.28	.59
$CaBr_2$	8–65–1	4 ,,	12	1.53	2.50	3.2	0.02	0.06	0.17	.12	8–74–1	4 ,,	23	2.35	3.2	4.2	0.01	0.03	0.11
	2	33 ,,	35	2.13	2.88	3.6	.06	.15	.37	.25	2	31 ,,	68	1.78	2.56	3.2	.05	.09	.20
	3	62 ,,	57	1.90	2.37	3.4	.08	.17	.34	.33	3	61 ,,	85	1.59	2.63	3.4	.08	.15	.29
	4	112 ,,	105	1.15	1.65	2.56	.08	.13	.34	.40	4	120 ,,	110 575*	1.36 0.54	2.16 0.80	2.90 1.20	.13	.21	.45
$CdBr_2$	8–66–1	4 ,,	2	0.24	0.40	0.53	0.01	0.05	0.13	.11									
	2	39 ,,	37	0.38	0.54	1.00	0.16	0.41	1.12	1.20									
	3	78 ,,	63	0.38	0.54	1.00	0.35	0.75	1.34	1.84									
	4	122 ,,	90	0.30	0.47	—	0.49	0.96	1.73	1.54									
25% Br as $CdBr_2$ 75% as KBr	8–70–1	3 ,,	5	1.15	1.95	2.13	0.03	0.09	0.19	.12	8–75–1	4 ,,	12	1.60	2.10	2.40	0.08	0.13	0.20
	2	36 ,,	300	0.43	0.74	1.07	.18	.30	.46	.20	2	31 ,,	410	0.60	0.90	1.20	.27	.37	.62
	3	67 ,,	240	0.55	0.88	1.28	.21	.48	.77	.81	3	61 ,,	575	0.56	0.87	1.23	22	.32	.57
	4	122 ,,	275	0.53	0.83	1.18	.16	.39	.67	1.17	4	121 ,,	715	0.44	0.66	1.00	.25	.51	.80
10% Br as $CdBr_2$ 90% as KBr	8–68–1	4 ,,	10	1.50	2.00	2.52	0.03	0.06	0.14	.13									
	2	31 ,,	110	1.23	1.88	2.50	.09	.18	.37	.33									
	3	61 ,,	450	0.51	0.87	1.42	.15	.28	.55	.53									
	4	124 ,,	530	0.56	0.74	1.14	.18	.45	.76	.87									
25% Br as ZnBr 75% as KBr	8–71–1	5 ,,	8	1.08	1.61	2.40	0.06	0.13	0.25	.15	8–76–1	4 ,,	21	1.73	2.44	2.96	0.09	0.15	0.36
	2	33 ,,	300	0.57	0.98	1.46	.16	.45	.74	.67	2	31 ,,	205	0.70	1.00	1.60	.26	.48	0.98
	3	61 ,,	155	0.53	0.84	1.26	.16	.43	.78	1.37	3	61 ,,	510	0.51	0.85	1.21	.28	.48	1.02
	4	118 ,,	150	0.45	0.79	1.04	.15	.45	.79	1.79	4	116 ,,	455	0.45	0.71	1.15	.35	.71	1.34

* The lower portion of this curve is effectively a second straight line, giving the speed and gammas indicated.

and concentrations, except as above noted, being the same. The mixture was stirred for an hour and sampled, with filtration, by the method of Walton and Judd.[1] Dissolved silver bromide was determined by diluting the sample with twenty times its volume of dilute HNO_3, digesting overnight, and weighing the precipitated AgBr in Gooch crucibles. The method was tested by adding a known small amount of nitrate, just sufficient to give a precipitate, to a sample of the ammoniacal bromide solution. 18.7 and 18.0 mg. AgBr were recovered from an amount corresponding to 18.8 mg.

TABLE 2.—*Neutral Emulsions* (*all with Koepf Gelatin*)

Emulsion	Ripening time from start of mix	Speed	γ_3	γ_6	γ_{12}	Fog_3	Fog_6	Fog_{12}	Average grain size μ^2
6–15–1	30 min.	130	0.82	0.84	1.57	0.13	0.42	.87	1.03
2	61 ,,	150	0.50	0.86	1.28	.24	.47	.93	1.65
NH_4Br									1.89
3	105 ,,	175	0.60	0.85	1.30	.19	.43	.83	
6– 8–1	33 ,,	225	0.68	0.96	1.40	.14	.41	.88	0.93
2	70 ,,	235	0.64	0.88	1.45	.13	.43	.87	1.15
KBr									
6–17–1	30 ,,	105	0.76	1.14	2.26	.17	.40	.71	1.06
2	60 ,,	110	0.64	1.00	2.08	.18	.42	.74	0.99
$CaBr_2$									
3	105 ,,	105	0.69	1.20	1.50	.21	.46	.74	1.67
6–16–1	30 ,,	15	0.78	1.34	2.18	.07	.18	.41	0.10
2	60 ,,	15	0.96	1.44	2.18	.05	.15	.29	0.12
$CdBr_2$									
3	105 ,,	18	1.31	2.06	3.3	.13	.29	.55	0.14

The pH of the solution was also determined by thymol blue, thymol-phthalein, alizarine yellow or tropaeolin O, comparing with glycocoll–NaOH or borax–boric acid buffer solutions, as recommended by Sörensen and Palitzsch respectively.

Solubilities in the ammoniacal emulsions are given in Table 3. The density of the solutions was not determined but the (volume) normality of the AgBr would be 0.00031 ± 0.00002 in the first case (KBr). The solubility of AgBr in NH_3, N 0.93 at 15° is 16 mg. per 100 cc. and at 25°, 52 mg.; extrapolating, it would be at least 100 at 45°.

The solubility of the silver bromide in the ammonia is thus seen to be greatly reduced by the presence of soluble bromide. The equilibrium in these solutions is too complex for calculation, but may be briefly discussed. Assuming that the solubility product $[Ag^+] \times [Br^-]$ remains approximately constant, the silver ion concentration must be greatly reduced by N 0.1 bromide, both by mass action and possible formation of complex anions such as $AgBr_2^-$. The concentration of the complex cation $Ag(2NH_3)^+$, dependent on Ag^+ and NH_3 concentrations, must be correspondingly reduced. Thus the further complication of the complex cadmium– or zinc–ammonia cation produces comparatively little effect on the solubility.

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[1] J. Am. Chem. Soc., **33**, 1036 (1911).

Table 3.—*Solubility of AgBr at 45° in solutions of the composition of unwashed ammonia emulsions: NH_3, 0.93 N; soluble bromide, 0.108 N; soluble nitrate, 0.465 N*

Bromide	Milligrams AgBr per 100 grams solution	pH
KBr	5.4	11.8 ± 0.5
NH_4Br	6.7	9.7 ± 0.2
NaBr	9.1	11.8 ± 0.5
$CaBr_2$	6.5	11.8 ± 0.5
$CdBr_2$	1.9	9.4 ± 0.2
25% Br as $CdBr_2$ 75% Br as KBr	6.4	10.3 ± 0.2
25% Br as $ZnBr_2$ 75% Br as KBr	4.5	10.1 ± 0.2
NH_4Br—Pyridine, 1.4 N	(0.6)	7.5 ± 0.2
NH_4Br—NH_3, 0.47 N	2.5	9.4 ± 0.2

When pyridine (3 mols per mol AgBr) was substituted for ammonia, the solubility was too low for measurement by this method. This was also the case for the completed neutral emulsions. It was possible, however, to secure satisfactory data on the solubility in plain bromide solutions simply by addition of $AgNO_3$ of appropriate concentration until a permanent precipitate was formed. N 0.1 or N 0.01 $AgNO_3$ was used, the volumes being from 1 to 7 cc., to 100 cc. of normal bromide solution, so that there was little dilution of the latter. It will be noted that these solubilities given in Table 4 are higher than those in the completed ammonia emulsions. As the solubility of the AgBr varies roughly as the square of the soluble bromide concentration, it falls during the mixing of the neutral emulsion lower than it ever goes in the ammonia process.

Table 4.—*Solubility AgBr at 74° in normal solutions of bromides*

Soluble Bromide	Normality AgBr	Soluble Bromide	Normality AgBr
KBr	0.0013	$CaBr_2$	0.00115
NH_4Br	0.0014	$ZnBr_2$	0.00068
NaBr	0.00095	$CdBr_2$	0.00024

Effect of the Halides on the Gelatin

Any attempt to explain the behavior of the emulsions in this way meets with the usual difficulty of interpreting physical tests on gelatin. A determination of the effectiveness as a protective colloid is most likely what is wanted in this case, but no satisfactory method has been devised. Viscosity was chosen, as it could be determined under the conditions of emulsion making. Measurements were made on Koepf gelatin at 45°, with a burette consistometer.[1] Concentrations were the same as in an ammonia process emulsion. After soaking for 20 minutes at room temperature, the gelatin was dissolved by heating for 25 minutes at 60° and filtered through a loose plug of glass wool. The determination was started after 10 minutes in the 45° thermostat and viscosity burette. After measuring the viscosity of a "neutral" sample (pH 5.2–5.4) ammonia was added to the remaining solution and another determination made after 15 minutes. A third was

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[1] Herschel and Bulkley, Ind. Eng. Chem., **19**, **134** (**1927**).

made after 90 minutes at 45° with the ammonia. The observed viscosities in centipoises, are given in Table 5.

TABLE 5.—3.6% *gelatin solutions at* 45.0°. *Bromide, N* 0.62; NH_3, *N* 0.94

Bromide	Neutral Viscosity	Viscosity with Ammonia After 15 min.	After 90 min.	pH with NH_3
None	0.0186	0.0229	0.0204	11.5
KBr	0.0230	0.0214	0.0181	11.3
NH_4Br	0.0222	0.0210	0.0195	9.8
NaBr	0.0234	0.0221	0.0194	11.3
$CaBr_2$	0.0234	0.0197	0.0177	11.2
10% Br as $CdBr_2$ 90% as KBr	0.0197	0.0197	0.0175	11.3
25% Br as $CdBr_2$ 75% as KBr	0.0178	0.0199	—	11.0
25% Br as $ZnBr_2$ 75% as KBr	0.0185	0.0200	0.0191	10.4

It is obvious that the alkali bromides and calcium bromide all increase the viscosity to the same extent, within the limits of experimental error and that the addition of the ammonia in the presence of the alkali bromides differs little in its effect from that of the same volume of water. The decrease in viscosity with calcium bromide is more marked. The effect of the cadmium and zinc bromides is opposite to that of the others, the viscosity being reduced. The increase in viscosity on adding ammonia may be ascribed to the elimination of the cadmium or zinc ion by formation of the ammonia complex. The rate of decrease in viscosity on long digestion of the mixtures increases with pH; no other influence can be detected.

It appears to be impossible to explain the differences between the emulsions in terms of the effects of the gelatin. The calcium and cadmium bromides alike give lower viscosities in the presence of the ammonia than do the alkali bromides, but the properties of the emulsions made with them differ in opposite directions from those made with alkali bromide.

Crystal Habit of Grains

One point of interest, which the writers have never seen explicitly mentioned, is the influence of materials present in the original mix, on the crystal habit of the silver halide grains. This is illustrated by the photomicrographs of Fig. 2. When an ammoniacal mix is used, the ammonia being in either the silver or bromide solutions, the grains take a characteristic rounded form instead of the flat plates typical of the neutral emulsions. The spherical appearance of the grains is more apparent than real; it is largely due to their greater thickness and the very limited depth of focus of a high power microscope objective. On careful visual focussing, sharp angles, successively appear on one side or the other of the grain, but the whole grain can never be sharply focussed at once. As the ripening goes on, the grains become more distinctly hexagonal or triangular in shape, but the general shape is very persistent. The use of ammonia for ripening of emulsions mixed without it has no tendency to produce this form.

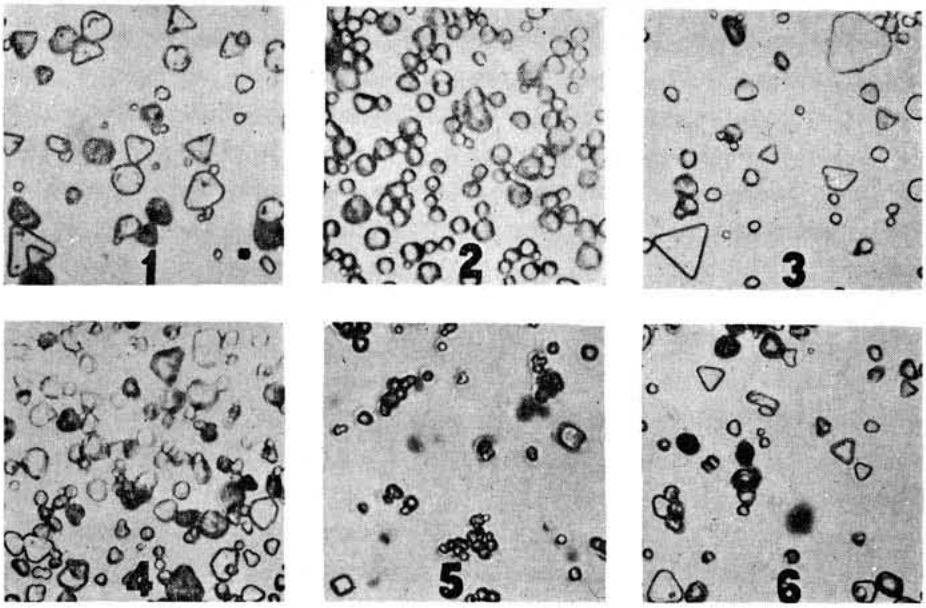

FIG. 2.—*Crystal habit of grains from emulsions made by different processes*
(1) Grains from neutral emulsion, made by mixing silver nitrate with mixed bromide–iodide solutions; (2) Ammonia in mix; (3) Ammonia and cadmium salts in mix; (4) Potassium cyanide in mix; (5) Pyridine in mix; (6) Diethylamine in mix. All at 3000 diameters.

When cadmium or zinc was used in ammoniacal emulsions, the removal of the ammonia as complex cation caused the silver bromide grains to take the characteristic form of neutral emulsions. The influence of the ammonia on the crystal habit of the silver bromide is apparently due to complex formation. It is not due to the alkalinity, since the addition of NaOH to emulsions to give the same pH as "full ammonia" had no influence on the habit of the grains; neither is it due to increased solubility, since emulsions made with KCN had flat hexagonal grains. Substitution of pyridine for ammonia gave fine grains with a strong tendency to coagulate, behaving somewhat like silver bromide without a protective colloid, so that it was difficult to secure a photomicrograph. The thickness of the grains is of the same order as their other dimensions; the larger ones are apparently tetrahedral. Diethylamine, on the other hand, gave flat plates, so the rounded grains are not characteristic of all nitrogen bases.

Under the same conditions of solubility and temperature, the flat plates would be expected to increase in area faster than the rounded grains, since the same change in mass produces a larger change in area, and since their shape is prsumably due to more rapid growth at the edges. This is fulfilled in the case of the ammoniacal emulsions containing cadmium or zinc.

2. GENERAL DISCUSSION

The left-hand set of curves in Fig. 3 (Emulsion 8–64) illustrate very well the general behavior of the ammonia process emulsions. The characteristic curve for the six-minute development, and the distribution of the projected area among the different class sizes of grains, are plotted on the same sheet. The unripened emulsion has a small grain and high gamma, but there is much more "toe" to the characteristic curve than in a good contrast emulsion. As the ripening progresses, there is a marked decrease in gamma and increase in speed; the straight line portion of the curve shortens more and more from the region of higher densities, and there is finally a decrease in speed. The average grain size steadily increases. The size–area curve broadens and flattens, so that the decrease in gamma is to be expected. One would, however, expect an increase in scale, which is not found, because the density for long exposures actually falls off with longer ripening. Part of this is due to the excessive fog on ripening for the longer times, but when the characteristic curves are plotted with fog included, there is still a marked loss of density at values of E greater than 1 c.m.s. This effect would be explained if there were a change with ripening in the photometric constant of the developed image. We have as yet no experimental evidence on this point. The other alternative is that a considerable portion of the grains have become undevelopable. The work of Svedberg, Schunk and Anderson[1] indicates that in an emulsion with wide range of grain sensitivity, some of the more sensitive grains are solarized before the least sensitive are developable, but the percentage is too small to account for the results here. Furthermore, this loss of density never occurs when the emulsion is increased in sensitivity without change in grain size, by digestion after washing, or by storage. The preliminary results reported by Sheppard[2] show that variations in the photometric "constant" may be much larger than had previously been reported. Assuming that the developed grains of the ripened and unripened emulsions have very roughly the same proportions, the larger grains should give the lower density, since the same mass of silver would have a smaller projected area, and the minimum thickness of metal encountered in a developed grain is completely opaque to visible light.

The emulsions made with Nelson gelatin invariably show more speed and generally worse fog than those made with Koepf, and the difference appears in the unripened stage; the former always have not only higher speed but higher gamma. Our experience in comparing different makes of gelatin in the same formula confirms the general rule that potential speed is always evident in the unripened state.

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[1] Phot. J., **64**, 272 (1924).

[2] Phot. J., **66**, 470 (1926).

This cannot be applied too freely in comparing the emulsions made with different bromides, since the ripening may proceed so differently.

Comparing the emulsions made with the alkali bromides, we find no certain differences between the sodium and potassium salts. The ripening of 8–61 with NH_4Br and Nelson gelatin is much slower than that of the corresponding 8–62 and 8–73 and 6–15 is slower than 6–8, but the differences between 8–63, 8–64, and 8–67, are within the limits of error. The pH of the ammoniacal emulsions containing NH_4Br is lower by 1.5 unit (Table 5) than those with KBr, owing to repression of the dissociation of NH_4OH by mass action of the NH_4 ion. The other conditions being almost identical, this should be sufficient to account for the difference in rate of ripening.

The emulsions made with calcium bromide are consistently slower and cleaner. The difference is less marked in the case of the neutral emulsion (6–17), which, as would be expected from the solubility, has a grain size about the same as that of the corresponding emulsions made with ammonium and potassium bromides. The very slow ripening of the ammoniacal emulsions (8–65 and 8–74) we can explain only by adsorption of $Ca(OH)_2$ on the grains. The pH of these is close to that of saturated $Ca(OH)_2$ solution, and the turbidity of the viscosity samples was distinctly higher as determined by nephelometry, than that of the other bromides. As the ammonia was added with the silver solution, there might be momentary precipitation of $Ca(OH)_2$, and if this were adsorbed, the growth of the grain would certainly be retarded, and probably reaction with thiocarbamides as well. The photographic difference in the neutral emulsions is not to be explained in this way, however, and we are obliged to admit that there is a specific difference in behavior, still to be explained.

The emulsions containing cadmium or zinc bromide have a very fine grain in the unripened state. Even in the case of the ammonia process emulsions, the precipitation begins in the practically neutral bromide solution, the ammonia being added with the silver. The solubility of the silver halide in the bromide solution is, therefore, one of the factors determining grain size. By von Weimarn's theory, the grain should be smaller because of the lesser solubility in cadmium or zinc bromide. The neutral emulsion with cadmium bromide remained very fine-grained and slow, the low solubility resulting in slow ripening. The ripening of the ammoniacal emulsions was much affected by the change in crystal habit of the grains, the flat plates being formed under conditions of comparatively high solubility with consequent very rapid change in area. The ripening becomes progressively more rapid with increasing proportions of cadmium in the series 8–68, 8–70 and 8–66. The great difference between the conditions under which the first and the last of the silver bromide is precipitated, in these emulsions, resulted in a peculiar distribution of grain size. Even the unripened emulsions contained some rather large grains, and 8–68–2, 3 and 4 (Fig. 3) show a distinct secondary "hump" in the size–frequency curve. Corresponding to this wide range in grain size, there is a scale extraordinarily long for these emulsions with their rapid mix and long ripening. All the ammonia

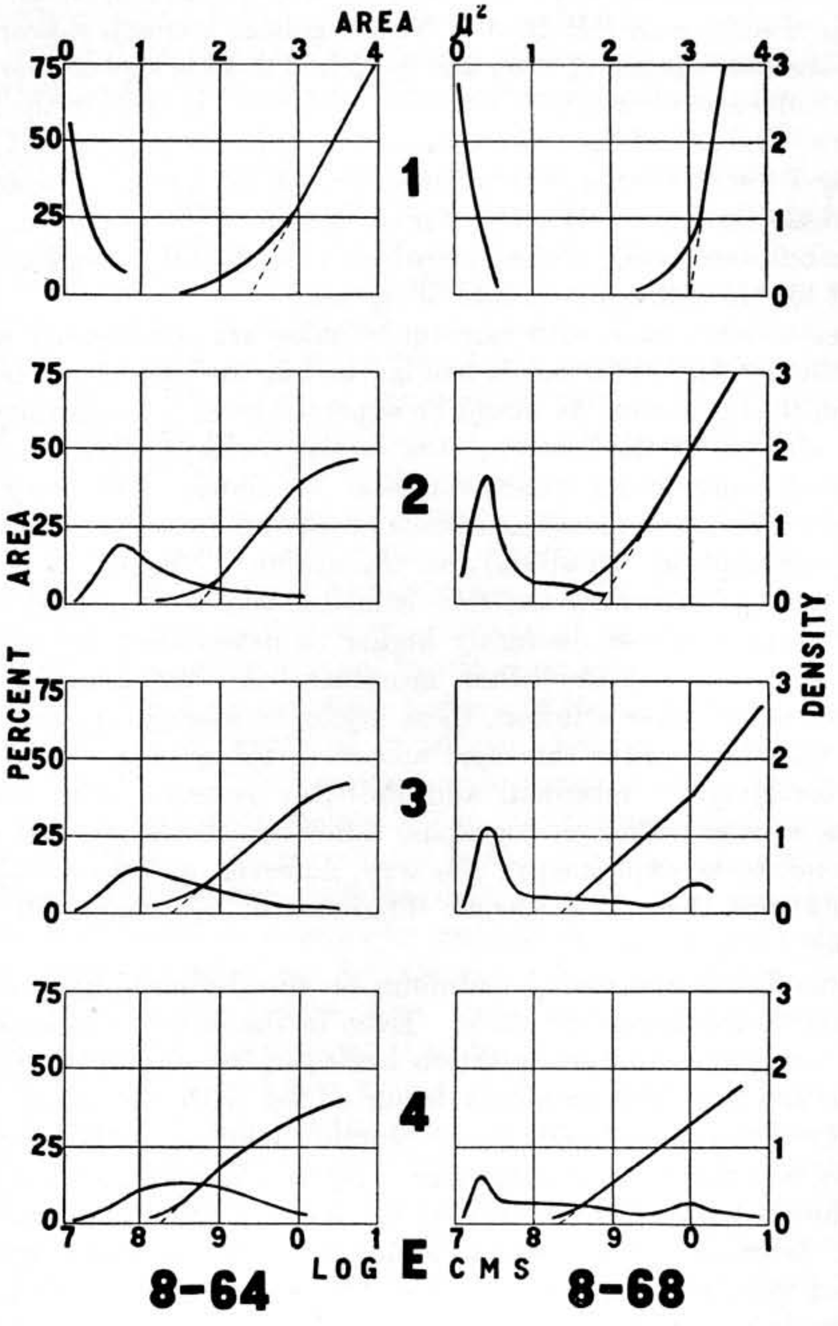

Fig. 3.—*Characteristic curve (for six-minute development) and distribution of total projected area between grains of different size classes, for two ammonia-process emulsions at four stages of ripening.* 8–64 *made with KBr,* 8–68 *with a mixture of KBr and CdBr*

emulsions with zinc and cadmium bromide show in an exaggerated way, the mechanism of ripening which we believe is generally characteristic of the formation of a fast emulsion. However, when the mixing is retarded, so that most of the ripening takes place by the time the addition of the silver is completed, great differences are introduced by the continual supply of freshly precipitated silver bromide. Referring to Fig. 3 the unripened 8–68–1 has a rather pronounced "toe" to its characteristic curve. After 30 minutes ripening, 8–68–2, the toe extends to higher densities, accompanied by a general displacement of the curve to the left. After 60 minutes, 8–68–3, the toe has continued its development to become a second straight line, encroaching still further on the original straight line portion of the characteristic curve, and finally (8–68–4) absorbing it entirely. The presence of the large number of small grains still remaining prevents the loss of density at large exposures such as occurs in 8–64. The emulsions with cadmium, and even more with zinc were of little value because of the excessive fog characteristic even of the fresh plates; if this can be eliminated, these salts may have considerable value. Calcium bromide, on the other hand, may have possibilities for process emulsions.

The neutral emulsions have been given less consideration, having been over-ripened by too high temperature and too large an excess of bromide. The range of grain size which was the object of the slow mixing was actually obtained, but the expected scale did not materialize for the reasons just mentioned.

3. SUMMARY

1. Emulsions of the rapid type have been prepared with potassium, ammonium, sodium, calcium, cadmium, and zinc bromides, or mixtures of the same, under otherwise identical conditions, and compared sensitometrically, and as to grain size.
2. Data on the solubility of silver bromide in the unwashed emulsions, on the pH, and on the viscosity of gelatin in the presence of the different bromides, have been obtained for their bearing on the mechanism of emulsion making.
3. The observed differences between the emulsions can, in most cases, be explained by simple chemical and physical principles.

SENSITIZATION OF PHOTOGRAPHIC EMULSIONS BY COLLOIDAL MATERIALS

By Burt H. Carroll and Donald Hubbard

ABSTRACT

Recent evidence indicates that photographic sensitivity is greatly increased by the presence of ultramicroscopic particles on the silver halide grains of an emulsion. Theories of this effect are discussed in some detail. Technique has been developed by which, without altering other variables, it is possible to introduce colloidal particles into the emulsion to test the possibility that these may be adsorbed by the grains and function as sensitivity nuclei. The experiments were carried out with a number of types of emulsion, including emulsions with the silver halide grains positively charged by adsorption of silver ions. Emulsions of this type were particularly adapted to sensitization by negatively charged metallic colloids; they were made stable enough for experimental purposes by new technique. The presence of the colloids interfered with after-ripening to such an extent that the ultimate effect was desensitization, but the direct result with colloidal gold and silver was an increase in speed at constant or decreased contrast. This may be explained, as proposed by Sheppard, by localization of the photochemical action in the grain around the nucleus, thus increasing developability. The theory that the sensitivity nucleus is a bromine acceptor does not apply to this case. Colloidal silver iodide produced a marked increase in contrast, on chemical development of the emulsion, and in total sensitivity, on physical development. The hypothesis of nucleus exposure which has been used to explain similar results on bathing in iodide solutions can not be applied here; both effects are explained by increased rate of development, probably caused by increased adsorption of the developer.

CONTENTS

I. INTRODUCTION

The sensitivity of a photographic emulsion is the resultant of its photochemical sensitivity, the chemical change produced by a given exposure, and of the developability of the photochemical change. Either or both of these may be affected by factors which are, over a limited range, nearly independent. These include, for example, the composition of the emulsion in terms of the percentages of the three silver halides, the size of the grains, the hydrogen ion concentration, and the presence of nuclei of ultramicroscopic dimensions adsorbed to the grains. The sensitivity as normally measured is a function of all these which defies exact formulation; but in the opinion of the writers, it approaches more nearly a product than a sum. In the case of the faster emulsions, the last-named factor, the nucleus, is perhaps the largest; it is the most generally accepted explanation of the large difference which may exist between emulsions identical except for the origin of the gelatin used in their preparation. This is the result of much indirect evidence,[1] culminating in the discovery by the Eastman Kodak Laboratories [2] of sensitizers in gelatin which almost certainly function by reaction with the silver halide to form nuclei of silver sulphide. Prior to Sheppard's publication, the nuclei were considered to be most probably metallic silver, and reasoning both from the conditions in the ripening emulsion and from the action of oxidizing agents on sensitivity, this still accounts for at least part of the nuclei.[3]

The mechanism by which the nucleus acts has been the subject of several hypotheses. In the opinion of the writers, the original mechanism suggested by Sheppard [4] is the most satisfactory. The essential feature of this is that the nucleus adsorbed to the surface of a silver halide grain produces what may be described as a weak spot in the crystal structure. The photolysis of the silver halide utilizes the entire energy absorbed by the grain, but is localized or oriented to this spot. As a fairly definite minimum size of latent image is required to start development, the efficiency of the primary photochemical process, from the standpoint of the resulting developed density, is greatly increased if the product is gathered into a single center instead of scattered through the grains in much smaller units. If the material of the sensitivity nucleus is silver, silver sulphide or other substance capable of acting as a development center, the silver from the photolysis of the silver halide will build around it to form the latent image, and the extent of photolysis necessary to produce a latent image of developable size may obviously be much reduced if the sensitivity nucleus was originally but little below this size. The orienting action would not necessarily depend on the composition of the sensitivity nucleus. It might be exerted by a material not in itself capable of acting as a development center. As Toy [5] has pointed out, the evidence is insufficient for Sheppard's statement that the

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[1] The following articles are of special importance: Svedberg, Phot. J., **62,** p. 186; 1922. Toy, Phil. Mag., **44,** p. 352; 1922. Clark, Phot. J., **64,** p. 91; 1924. Sheppard, Trivelli, and Loveland, J. Frank. Inst., **200,** p. 51; 1925.

[2] Sheppard, Phot. J., **65,** p. 380; 1925.

[3] Trivelli, J. Frank. Inst., **204,** p. 649; 1927. Lüppo-Cramer, Camera, p. 39; 1927. Weigert and Lühr, Naturwissenschaften, **15,** p. 788; 1927. Wightman and Quirk., J. Frank. Inst., **204,** p. 731; 1927.

[4] Sheppard, Trivelli, and Loveland, see footnote 1, above. Sheppard, Brit. J. Phot., **73,** p. 33; 1926.

[5] Toy, Brit. J. Phot., **73,** p. 295; 1926.

nucleus can not change the quantum efficiency of the primary photolysis.

Hickman [6] has suggested that silver sulphide may act as an acceptor for the bromine from the photolysis of the silver bromide. Lambert and Wightman [7] have examined the energy relations and found this possible, even when the reaction is postulated to go to sulphur bromide and metallic silver. On this theory, the failure of halogen absorbents, such as nitrite, to act as sensitizers may be due solely to the fact that they are not adsorbed by the silver halide, and an efficient sensitivity nucleus must be a bromine acceptor. The failure of the adsorption compounds of thiocarbamides and thioanilides [8] with silver halides to sensitize for anything but the print-out effect, although they are halogen acceptors, is an argument against this theory. This failure of known bromine absorbents to sensitize is supplemented by the success of materials which can not react with bromine during exposure, such as the metallic silver already mentioned. While it is possible for chemically inert nuclei to adsorb bromine, this is probably unimportant because of their insufficient capacity; the nuclei are of the same order of magnitude as the latent image, and it seems necessary to assume a chemical reaction between the nuclei and the bromine to account for the quantity of the latter which must be absorbed.

Most recently, Trivelli [9] has proposed a mechanism which combines some of the features of the others with an entirely new idea. He postulates a sensitivity nucleus containing both silver and silver sulphide, which on exposure sets up a photoelectric current from one to the other through the silver bromide, liberating silver from the silver sulphide by electrolysis. The theory derives support from the results of Toy [10] that the spectral sensitivity of silver bromide is the same for photoconductivity and photographic exposure, and from the improvement in sensitivity by the combined use of the sulphur sensitizers and reducing agents.[11] If correct, it follows directly that no single material can form an efficient sensitivity nucleus; although in practice silver will almost certainly be present to supplement a second substance. Silver sulphide would be expected to be an exceptionally good sensitizer, according to this theory, since according to Tubandt [12] it is by a very large factor the best conductor of the solid electrolytic type known. Silver iodide, which is one of the next best, has a conductivity not more than 10^{-3} that of the sulphide.

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[6] Hickman, Phot. J., **67**, p. 34; 1927.

[7] Lambert and Wightman, J. Phys. Chem., **31**, p. 1249; 1927.

[8] Sheppard and Hudson, Phot. J., **67**, p. 359; 1927.

[9] Trivelli, J. Frank. Inst., **204**, p. 849; 1927; **205**, p. 111; 1928.

[10] Toy, Nature, **120**, p. 441; 1927.

[11] Sheppard and Punnett, U. S. Patent 1623499.

[12] Tubandt and Reinhold, Zeit. anorg. Chem., **160**, p. 222; 1927.

Some experiments have already been reported on the effect of colloidal materials on sensitivity. Schwartz and Stock,[13] following the photolysis of silver bromide by the liberated bromine, found that it could be catalyzed by various colloids, and followed this up by introducing them into completed emulsions. They obtained some increase in sensitivity from Bredig method silver and from a proprietary silica sol (of unknown alkalinity). The metallic colloids in large amounts caused fog. Jenisch [14] added noble metal sols to the emulsion. Introduced after washing, small amounts had no effect and large amounts caused fog, but when colloidal gold was added to the bromide solution used in mixing the emulsion, the sensitivity was much improved by the use of 3 mg. per liter.

The primary object of this investigation was to determine the effect on sensitivity of nuclei adsorbed to the surface of the grains, the nuclei being prepared separately as a colloidal suspension, and introduced into an emulsion which should be reasonably free from ripening nuclei. To be certain that the presence of the nuclei should be the only new factor, they must be added to the emulsion after the end of the ripening, in the sense of change in grain size. Their presence during the mixing or ripening processes, especially the former, might very well change other variables, such as the structure or average size of the grains. An attempt to secure practical improvements in sensitivity by the use of colloids would be very seriously restricted by this condition. The greatest difficulty is the poor adsorptive capacity of the grains in a completed emulsion. Reinders [15] proved directly that the adsorption of gelatin by silver halides greatly reduces the adsorption of other materials. Some evidence of this had already been obtained from the behavior of emulsions. Lüppo-Cramer found that comparatively large amounts of colloid silver could be added to a completed emulsion with comparatively little effect, but if it were introduced into the original mix it produced intense fog. We succeeded in improving the adsorption, or at least the sensitization, by the use of opposite charges on the colloid particle and emulsion grain, as will be explained in more detail below; but at best only a small part of the colloid introduced is adsorbed. If the colloid used is such that its particles can act as precipitation centers for silver, the unadsorbed excess causes dichroic fog on development if allowed to remain in the emulsion; the dichroic nature of the fog indicates that it is the result of physical development on centers outside the grains. A means for avoiding this difficulty was at hand, in the centrifugal washing of the emulsions, which we [16] had already used for other purposes. The unadsorbed colloid re-

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[13] Schwartz and Stock, Berichte, **54**, p. 2111; 1921. Zeit. wiss. Phot., **22**, p. 26; 1922.

[14] Jenisch, Zeit, wiss. Phot., **24**, p. 248; 1926.

[15] Reinders, Zeit. Phys. Chem., **77**, p. 677; 1911.

[16] Carroll and Hubbard, J. Phys. Chem., **31**, p. 906; 1927.

mained in the gelatin when the silver halide was centrifuged out, only the portion adsorbed to the grains being carried with them.

The material of the nucleus must be insoluble and not reactive with silver bromide. Silver and silver sulphide are obviously suggested by their occurrence in normally ripened emulsions. Other silver salts less soluble than the bromide and metals more noble than silver also fulfill the necessary conditions. From these classes silver iodide and metallic gold were chosen for serious consideration.

II. EXPERIMENTAL METHODS

1. PREPARATION OF THE EMULSION

The emulsions were of both ammoniacal and neutral types. Those designated by the series No. 8 were made by the ammonia formula described in the first paper of this series,[17] using ammonium bromide. The ammoniacal type was found to be more readily sensitized with colloids, as with dyes. The neutral, centrifuged, emulsions have the series No. 6. Their formula was generally as follows, or in the same proportions with increased amounts:

Bromide solution		Silver solution	
Water ml	175	Water ml	225
Gelatin g	10	$AgNO_3$ g	30. 0
KBr g	23. 3		
KI g	0. 29		

The silver solution was added to the bromide solution very slowly, over a period of 10 to 15 minutes, both solutions being at 65° C. The emulsion was held at 65° with stirring until centrifuged, the last batch normally being separated within half an hour from the end of the mixing process. The emulsions of series 1 and 4 were made, respectively, by ammoniacal and neutral formulas identical with those of 8 and 6, but were washed after the usual chilling and shredding, instead of by the centrifuge. The ripening of these emulsions was limited to a few minutes after the completion of mixing. Swelled gelatin, sufficient to bring the total to 50 g in a batch of the above size, was then dissolved in the emulsion, which was rapidly chilled, and washed the next day after standing over night at 5 to 8° C. The pH, after washing 7 hours in Washington tap water, was from 7 to 8. Emulsions of all the series were also made with pure silver bromide, the formula being changed only by substitution of an equivalent amount of bromide for the iodide, without making any obvious difference in the effectiveness of the colloid sensitization, even by colloidal silver iodide.

All the later emulsions were made with deactivated gelatin, to reduce as far as possible the nucleation of the grains before addition

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[17] Carroll and Hubbard, J. Phys. Chem., **31**, p. 906; 1927.

of the colloid. The method of deactivation which we found most satisfactory for our purposes in these experiments is based on the conversion by ammonia of the isothiocyanates, and probably of more complex sulphur compounds, to the soluble thiocarbamides. After digestion with ammonia (approximately 20 minutes time at 45° with a normal solution), the gelatin was chilled, shredded, and washed for 24 hours in running water; 12 to 15 hours were necessary for removal of the ammonia so that no Nessler test could be obtained from the drainings. The final pH of the gelatin varied from 7 to 8. The physical properties were noticeably injured by the rather drastic ammonia treatment, but no serious difficulty was introduced. The emulsions made with it were slow and very free from fog, but the "after-ripening" (either by digestion or by storage) was not reduced as much as had been anticipated. Expressed in terms of the ratio of speed before and after digestion, it was of the same order as with untreated gelatin.

As a means of improving the adsorption of negatively charged colloids (such as the metals), a large proportion of the emulsions were prepared with the grains positively charged by adsorption of silver ions, instead of negatively charged by the normal excess of bromide ions. Gelatin emulsions with excess soluble silver salts were frequently prepared in the early stages of the development of dry plates,[18] and found to be highly sensitive but very instable, fogging completely in a few days. This is still not to be considered a practical type of emulsion, but we find that if the hydrogen ion concentration of the emulsion is increased well above the isoelectric point (pH preferably 3.5 or less), and deactivated gelatin is used, such emulsions may be kept for at least a month without noticeable increase in fog. It is impossible to ripen in the presence of soluble silver salts so the emulsions were made by one or the other of the usual formulas and after the first centrifugal separation, the silver bromide was suspended in acid gelatin, to which silver sulphate was added. After the second centrifuging, the silver bromide was suspended for coating in acid gelatin without further addition of silver sulphate, so that the final excess was limited to that adsorbed on the grains, and was of the same order as the excess soluble bromide in a normal emulsion. The quantities varied slightly, but the following figures are typical:

Excess bromide in the emulsion	g equivalent	0.044
Silver sulphate added to first suspension	g equivalent	.002
Silver sulphate found in clear gelatin from first resuspension after centrifuging out silver bromide	g equivalent	.001
Silver ion concentration in first resuspension	*N*	.0025

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[18] Eder, Ausführliches Handbuch der Photographie, 3d ed., **3**, p. 50.

No measurable amount of silver salts could be extracted from the plates coated with these emulsions. The traces of silver sulphate, which must have been present, were evidently adsorbed by the silver bromide. The above use of acid and silver sulphate is implied in the later references in this paper to "emulsions with excess silver." The sensitivity of portions so treated, when compared with other portions of the same emulsion which had been washed and coated at the same pH, but without the addition of silver sulphate, had been at least doubled. However, digestion was impracticable after washing and addition of the silver sulphate; accordingly, the sensitivity produced by the use of the soluble silver salt was less than could be obtained in the same emulsion by after-ripening (by digestion or storage after washing), at the normal pH of 6 to 8 and in the presence of the usual trace of soluble bromide. The characteristics of these emulsions will be described in more detail in a later paper.

Our regular procedure for washing by the centrifuge is to separate the silver halide from the ripening emulsion, resuspend in dilute gelatin (1½ per cent), separate again, and suspend in the gelatin used for coating. The quantity given in the formula is sufficient for coating four sets of test plates, and the division into the four batches was regularly made in the first resuspension. While both separations are necessary for adequate washing, the concentration of soluble materials in the first resuspension is less than 2 per cent of the value in the unwashed emulsion. The corresponding change in the solubility of silver bromide is still greater, so that ripening, in the sense of change in grain size and structure, may be considered negligible. After-ripening can not be eliminated, but the treatment of the different batches at this stage could be standardized, so that duplicate controls on both types of emulsions were found to check to 10 per cent; the uncertainty thus introduced is thus much smaller than the 50 to 200 per cent changes produced by colloidal sensitization. The capacity of our centrifuge is not sufficient for an entire emulsion at once, but the resuspensions of the two or more portions necessary were carefully mixed. As already mentioned, if the silver sulphate was used, it was added at this point. The emulsion could then be divided into batches identical in concentration, size, ripening, pH, and soluble bromide or silver, to be compared against each other for the sensitizing action of the colloids. The colloids were introduced at this stage of the process. Then, taking care to treat the control and sensitized batches the same, the centrifugal separation was repeated, eliminating the excess colloid. Adsorption of the colloid apparently reached its full value immediately. There was no improvement on allowing it to stand longer than a few minutes before centrifuging. Each batch was suspended for coating in 12.5 g gelatin in 180 to 220 ml volume, depending on the viscosity.

Unless stated to the contrary, all emulsions were coated without digestion after washing. After-ripening is very sensitive to materials adsorbed to the grain, such as color-sensitizing dyes or the colloids. Since digestion involved wide differences in the formation of sensitizing nuclei in the control and colloid-treated batches, it was eliminated as far as possible. The emulsions with excess silver were, of course, liable to fog under digestion treatment perfectly safe for normal emulsions, and could not be after-ripened on this account. The after-ripening in the presence of either dye or colloid is, to the best of our knowledge, invariably less; so much less, as a rule that the control ultimately becomes the faster either on digestion or storage ripening and any after-ripening which occurred before testing tended to subtract from the apparent sensitizing effect of the colloid. No method of sensitization by externally prepared nuclei which we have been able to devise is as efficient as the formation of the nuclei by reaction of the ripened silver halide grains with sensitizers, such as the thiocarbamides.

2. METHODS OF TESTING

The standard methods of the Bureau of Standards were used for testing, with modifications of the development to meet certain special cases. Exposure was in all cases on a nonintermittent time scale, at an intensity of one candle meter, of the spectral distribution of mean noon sunlight. The chemical development was by the brush method, at 20°. The appearance of three times of development (3, 6, and 12) indicates the usual pyro formula. As the emulsions with excess silver fogged excessively on prolonged development with unbromided pyrogallol, a metol-hydroquinone formula [19] was used for these. The acid emulsions were particularly sensitive to irregularity of coating. In cases of uncertainty, the 6-minute development was run in quadruplicate.

A considerable number of the emulsions were also compared by physical development,[20] before, and in some cases, after fixation.

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[19] Eastman D-61a. Stock solution, diluted with an equal volume of water for use:

Hot water	ml	500
Metol	g	3
Na_2SO_3	g	90
$NaHSO_3$	g	2
Hydroquinone	g	5.5
Na_2CO_3	g	10.5
KBr	g	1.5
Cold water to make	liter	1

[20] Stock solution; 50 ml mixed with 2 ml 10 per cent $AgNO_3$:

Water	ml	240
Metol	g	5
Citric acid	g	10
20 per cent gum arabic solution	ml	10

Six minutes development at 15° or less. Fixation before development in 25 per cent $Na_2S_2O_3$, 5 per cent Na_2SO_3, followed by 30 minutes washing in running tap water, pH 7 to 8.

Physical development of gelatin emulsions is relatively unsatisfactory, but the acid emulsions in this case give less fog than the normal. By comparing only strips which had been developed together, and testing in duplicate or quadruplicate, the results were sufficiently reproducible.

Physical development is commonly regarded as a simple deposition of nascent silver on the nuclei provided by the latent image. It is at least true that the reduction of silver bromide, by a developer such as we used, is negligible, but the physical development is more sensitive than the chemical to adsorption effects which do not appear to involve a change in the amount of latent image. Physical development after fixation should be the most free from complications, but according to Lüppo-Cramer,[21] bathing with iodide can accelerate development even in this case, indicating that the remaining latent image is not entirely metallic silver. There is the further difficulty that the inertia is invariably much larger for development after fixation than for chemical development, so that it gives no information of conditions at small exposures. Bearing these limitations in mind, physical development is valuable for comparison with the normal method, as will be evident from the results on sensitized emulsions.

One of the principal difficulties of sensitometry became especially obvious in the course of this investigation. The colloid sensitization commonly changed the shape of the characteristic curve, and under these conditions the speed and gamma numbers alone are insufficient for comparison of the sensitivities. The characteristics of the underexposure period (the "toe") are also necessary, but in order to determine then accurately, one must locate more points in the underexposure region than is commonly done. Renwick [22] has shown that the equation, $D+c=u\,E$, for the underexposure region, accurately expresses the results up to the beginning of the straight-line portion of the characteristic curve, where it becomes $D=\gamma$ (log E–log i). Designating the exposure at this point by E_t, and that for zero density by E_0, he further derives the equations:

$$E_t=0.434\ \gamma/u$$

and

$$E_t/E_0=0.434\ \gamma/c^{23}$$

With the limited number of points available in the underexposure region, it is impossible to obtain from our curves the excellent verification of these equations which was found by Renwick. However, the data from the representative curves in Figure 1 will illustrate the points which we wish to make. Referring to Table 1 and the figure,

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[21] Lüppo-Cramer, Die Grundlagen der Photographischen Negativverfahren, p. 161.

[22] Renwick, Phot. J., **53**, p. 127; 1913.

[23] This becomes indeterminate for $c=0$, since E_0 then is also 0.

it is evident that curves 1 and 4 may be fairly compared on the basis of speed and gamma alone.

TABLE 1

Emulsion No.	Bureau of Standards speed	γ	Scale	c	u	E_o	E_t from D–log E curve	0.434 γ/u	E_t/E_o from D–log E curve	0.434 γ/c
6–65–1	33	0. 75	+10	0. 05	0. 66	0. 075	1. 0	0. 5	13	6. 5
6–65–3	11	2. 00	5	. 04	. 45	. 09	2. 5	1. 9	28	22. 0
6–65–4	36	1. 35	16	. 055	1. 02	. 05	. 8	. 6	16	11. 0

In the case of curves 1 and 3, while one may calculate from these quantities (and the definition, B. S. speed $= 10/i$) that the straight line portions of the curves must cross at log $E = 0.25$, $D = 0.58$, it is impossible to predict that they will practically coincide throughout the underexposure region. There is no theoretical reason why the speed and gamma derived from curve 3 might not be combined with a much larger value of c, with correspondingly decreased densities in most of the underexposure region.

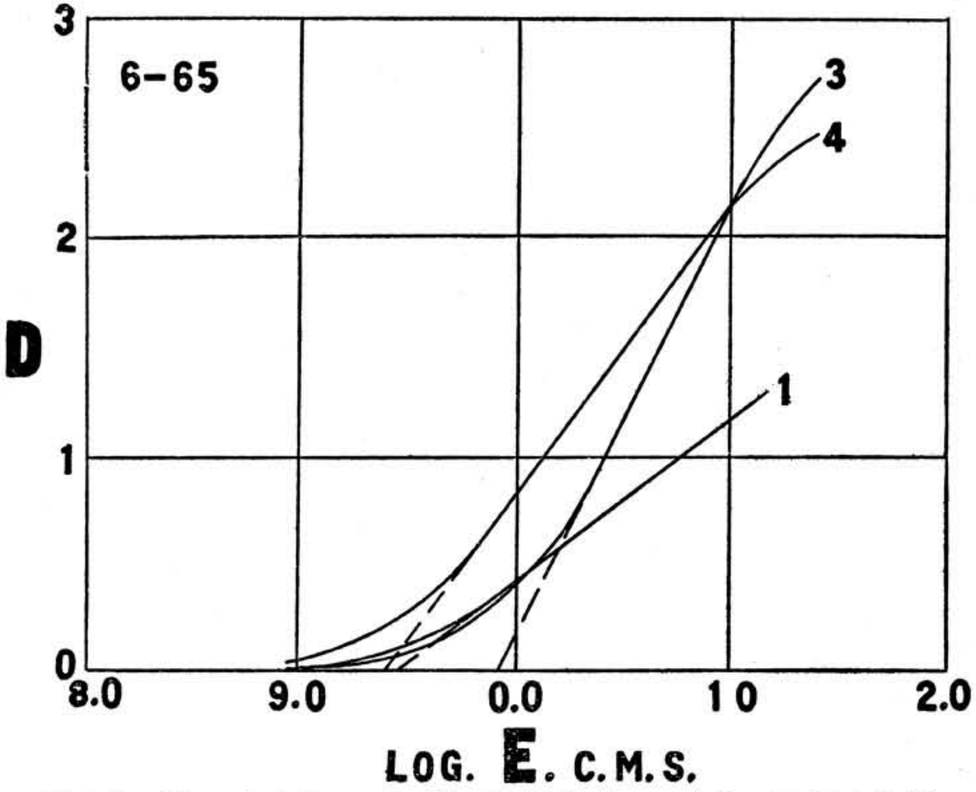

FIG. 1.—*Characteristic curves, 12-minute development, for emulsion 6–65*

(1) Control; (3) sensitized with colloidal silver iodide; (4) sensitized with colloidal silver

We have not made complete determinations of the underexposure characteristics. The characteristic curves, made with a sector wheel of the conventional H and D form, did not regularly include enough points in this region. Enough are given to illustrate the types of change in the underexposure region produced by colloid sensitization. In interpreting the value of c and u, it should be remembered that, while u corresponds exactly to γ in the equation for the straight line portion, it is c/u (or E_o), rather than c, which corresponds to log i. Those values of c and u which are given correspond to the longest time of development.

III. SENSITIZATION BY COLLOIDAL SILVER IODIDE

The data on this subject have been divided into four sections. Table 2 gives the results with normal emulsions (excess bromide), and Table 3 those with the acid emulsions, with excess silver. Both of these represent immediate tests, without digestion. As most of the emulsions with silver iodide were made before we decided to make use of physical development, some of those which appear for the second time in Table 5, on comparison of the effects with chemical and physical development, had changed considerably by storage ripening since the tests recorded in Table 2. Since silver iodide alone is not capable of acting as a development center, it may be left in the emulsion without causing fog. A number of such cases are given in Table 4. The iodide was added before digestion, but after the washing was complete, both centrifugal and normal washing having been used. The quantities of silver iodide are in all cases expressed as molar per cent of the total silver halide in the emulsion. The second column of Tables 2, 3, 4, and 5 gives the amount of iodide in the original mix of the emulsion, and, therefore, present before addition of the colloid; the amount of colloidal silver iodide is expressed as "AgI added."

TABLE 2.—*Normal emulsions, excess bromide; sensitized with colloidal silver iodide*

Emulsion No.	Mol per cent AgI	Type of colloid	Mol per cent AgI added	Bureau of Standards speed	γ			Fog			c	u
					3	6	12	3	6	12		
6-64-1	1.5	----------	0.0	56	0.30	0.45	0.50	0.12	0.22	0.28	0.04	0.86
2		3 per cent excess KI; undialyzed	1.0	27	.63	.80	.90	.31	.36	.44	.01	.42
3		3 per cent excess $AgNO_3$; undialyzed	1.0	26	.64	.72	.78	.21	.30	.34	.04	.38
4		None. Ag_2SO_4 greater than excess $AgNO_3$ in colloid	0	72	.20	.38	.44	.10	.18	.21	.03	.75
8-109-1	1.0	Excess $AgNO_3$; dialyzed	0	22	.67	.83	.88	.11	.15	.21	----	----
4			.4	19	1.10	1.42	1.60	.12	.19	.34	----	----
8-110-1	1.0	Equivalent; undialyzed	0	18	.80	1.00	1.10	.10	.12	.16	----	----
4			.8	20	1.33	1.85	2.13	.17	.22	.32	----	----
8-121-1	1.0	----------	0	17	.80	1.03	1.20	.13	.13	.23	.04	.52
2		3 per cent excess KI; undialyzed	1.0	17	1.37	1.60	1.87	.17	.18	.24	.10	.58
3		3 per cent excess $AgNO_3$; undialyzed	1.0	20	1.24	1.40	1.60	.15	.20	.25	.09	.70
4		Ag_2SO_4 equivalent to 4 times the excess $AgNO_3$ in colloid	0	27	.55	.70	.85	.09	.12	.16	.04	.55
8-123-1	1.0	----------	0	20	.70	.82	.96	.07	.08	.13	.03	.60
2		3 per cent excess KI; undialyzed	1.0	20	1.05	1.27	1.52	.15	.18	.25	.07	.56
3		3 per cent excess $AgNO_3$; undialyzed	1.0	16	1.25	1.50	1.65	.08	.10	.17	.11	.50
4		Colloidal AgI in the final suspension	.6	17	1.50	1.70	2.13	.11	.11	.20	.14	.66
8-125-4	0	Equivalent; undialyzed	0	20	----	2.15	----	----	.11	----	.09	.81
1			1.0	6	----	5.3	----	----	.36	----	.05	.24
8-96[1]-1	.8	----------	0	110	.72	1.35	2.10	.13	.25	.44	.04	3.6
3		5 per cent excess $AgNO_3$; dialyzed. Exposed to diffuse daylight	.8	142	1.20	1.82	2.55	.17	.27	.39	.13	5.4
6		5 per cent excess $AgNO_3$; dialyzed. Handled entirely under safe light	.8	147	1.18	1.81	----	.19	.27	----	.07	5.9

[1] All batches of 8-96 digested 30 minutes at 45° before coating.

TABLE 3.—*Acid emulsions, excess silver; sensitized with colloidal silver iodide*

Emulsion No.	Mol per cent AgI	Type of colloid	Mol per cent AgI added	Bureau of Standards speed	γ			Fog			c	u
					3	6	12	3	6	12		
6-60-1	1.0	----------	0.0	40	1.46	1.98	----	0.30	0.99	----	0.18	1.72
2		2 per cent excess $AgNO_3$; undialyzed	1.1	43	1.67	1.86	----	.22	.78	----	.14	1.70
3		2 per cent excess KI; undialyzed	1.1	34	1.85	2.35	----	.28	.90	----	.12	1.74
6-65-1	1.5	----------	0	28	.35	.63	0.75	.06	.11	0.22	.05	.68
2		3 per cent excess KI; undialyzed	1.0	11	.95	1.20	1.35	.06	.11	.24	.09	.27
3		3 per cent excess $AgNO_3$; undialyzed	1.0	13	.78	1.50	2.00	.08	.18	.37	.05	.46
8-111-1	1.0	----------	0	13	2.40	3.07	----	.07	.18	----	.23	.98
2		2 per cent excess $AgNO_3$; undialyzed	1.1	21	1.94	3.10	----	.07	.17	----	.23	1.24
3		2 per cent excess KI; undialyzed	1.1	12	2.35	3.20	----	.05	.18	----	.28	.81
8-113-1	1.0	----------	0	23	1.55	2.54	----	.11	.29	----	.26	1.10
6		1 per cent excess $AgNO_3$; undialyzed	.9	26	1.37	2.23	----	.17	.32	----	.19	1.18
8-122-1	1.0	----------	0	6.5	.57	1.38	1.98	.02	.11	.20	.02	.21
2		3 per cent excess KI; undialyzed	1.0	11	1.10	2.20	2.85	.11	.15	.26	.06	.27
3		3 per cent excess $AgNO_3$; undialyzed	1.0	9	1.15	2.30	3.05	.10	.14	.22	.03	.20

TABLE 4.—*Colloidal silver iodide in final suspension of normal emulsion*

Emulsion No.	Original AgI in mol	Added AgI in mol	After ripening	6-minute M-Q development			Physical development			Development after fixation		
				Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
	P. ct.	*P. ct.*										
8-123-1	1.0	0.0	2 months' storage	110	1.25	0.09	21	0.68	0.18	----	----	----
4		.6	do	47	1.65	.08	47	.95	.35	----	----	----
4-25-4	.0	.0	Digested 2 hours at 45°	50	2.07	.12	9	.55	.19	----	----	----
3		.5	do	27	2.70	.22	7	.95	.33	----	----	----
1-128-2	.0	.0	None	45	1.45	.02	7	.45	.04	----	----	----
5		.5	do	11	2.67	.05	15	.72	.15	----	----	----
1-128-6	.0	.0	Digested 2 hours at 45°	160	1.40	.08	10	.63	.05	----	----	----
8		.5	do	30	2.00	.19	17	.80	.16	----	----	----
1-129-1	.0	.0	do	30	2.15	.03	4.5	.68	.09	3.9	0.27	0.46
2		.5	do	18	3.30	.03	7.9	1.30	.20	1.8	.48	.48
1-130-1	.0	.0	do	138	2.10	.15	15	.98	.12	20	.28	.35
2		.5	do	132	2.50	.20	43	1.07	.27	17	.38	.34
1-133-1	.0	.0	do	174	1.33	.02	12	.60	.04	45	.15	.15
2		[1] .5	do	43	1.70	.02	43	.55	.16	11	.27	.21
3		.5	do	30	1.62	.02	22	.58	.13	22	.18	.49

[1] The silver iodide in this case was added after digestion was complete.

TABLE 5.—*Comparison of partial conversion to AgI, by bathing in soluble iodide,*[1] *with addition of colloidal AgI*

Emulsion No.	Original AgI in mol	Added AgI in mol	After ripening	Other treatment	6-minute M-Q development			Physical development			Development after fixation		
					Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
	P. ct.	*P. ct.*											
8–110–1	1.0	0.0	7 months storage.	Washed	166	1.30	0.16	31	0.61	0.22	39	0.25	0.43
1		.0	do	Bathed in KI solution and washed.	105	1.25	.15	43	.27	.23	------	----	----
4		.8	do	Washed	38	2.30	.25	31	.61	.35	39	.52	.37
8–109–1	1.0	.0	do	do	190	1.30	.18	25	.60	.21	------	----	----
1		.0	do	Bathed in KI solution and washed.	100	1.16	.17	110	.21	.18	------	----	----
4		.8	do	Washed	47	1.61	.20	43	.55	.27	------	----	----
8–125–4	.0	.0	None	None	20	2.15	.11	7	.78	.14	4	.23	.52
1		1.0	do	do	6	5.30	.36	9	1.04	.28	4	.50	.49
8–123–1	.0	.0	3 months' storage.	do	132	1.20	.08	26	.62	.13	25	.30	.44
2	.0	1.0	do	do	63	1.45	.18	39	.60	.29	17	.37	.47
6– 64–1	1.5	.0	do	do	145	.84	.25	5	.48	.17	26	.30	.42
3		1.0	do	do	34	1.00	.32	22	.45	.38	20	.36	.46
Cramer	-------	.0	----------	Washed	79	2.60	.10	22	1.45	.08	13	1.00	.08
Contrast	-------	.0	----------	Bathed in KI solution and washed.	52	3.05	.09	45	.67	:12	24	.74	.12

[1] Four minutes in N/400 KI, followed by 15 minutes washing in running water. The volume of KI solution was such that complete reaction would have converted about 10 per cent of the AgBr to AgI.

Silver iodide may readily be prepared in the colloidal state by reaction of dilute solutions of silver nitrate and potassium iodide. The charge on the particles is negative if an excess of iodide is used, positive if the silver is in excess.[24] We found it advisable to stabilize all our colloids with gelatin to avoid risk of coagulation on mixing with the emulsion. The silver iodide with excess iodide was made up at approximate neutrality, and that with excess silver at a pH less than 4.7, generally at 3.8, to reduce reaction of the excess silver with the gelatin. N/100 solutions, with 1 per cent gelatin, were rapidly mixed at about 30°. The excess Ag^+ or I^- in undialyzed sols never exceeded 3 per cent. In the absence of protective colloid, the sols with excess iodide are the more stable, corresponding to stronger adsorption of the iodide ion. We found that excess silver was liable to be completely removed by prolonged dialysis of the protected sols, reversing the charge on the silver iodide. Most of the sols were, accordingly, used without dialysis. In the case of the emulsions listed in Table 2, the soluble silver salt introduced along with those silver iodide sols containing excess silver nitrate, was never equivalent to the soluble bromide present in the emulsion at this point. All batches of emulsion listed in this table were coated with excess bromide, with the possible exceptions of 6–64–4 and 8–121–4. Silver

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[24] Lottermoser. J. pract. Chem. [2], 75, p. 293; 1907.

sulphate only was added to these, and it is evident that its effect was quite different from that of colloidal silver iodide.

The characteristic effect of the colloidal silver iodide was an increase in contrast. Under practical conditions, with digestion of the emulsion after washing, the addition of silver iodide at any point after the original mix of the emulsion produces desensitization.[25] However, we found by testing the emulsions both with and without after-ripening, that this is explained by the marked tendency of the silver iodide to prevent after-ripening. The immediate effect was to increase the density over most or all of the straight-line portion of the characteristic curve, as compared to the control; the under-exposure region was slightly depressed, as a rule. When the iodide was added before the final centrifuging, the speed number was increased and decreased in an equal number of cases; if it was added to the final suspension (with either type of washing), there was an invariable decrease. Either on digestion or storage, the control batches reached higher sensitivities (by normal development), but the difference in gamma never disappeared.

Figure 1 shows the characteristic curves of three batches of 6–65: Control, silver iodide sensitized, and silver sensitized. These illustrate the typical effects of the iodide in increasing density only for the larger values of E, and of the metallic colloids, which were most effective at the "toe" of the curve.

All combinations of charge on the silver iodide particles and emulsion grains were tried out, without disclosing the expected improvement by opposite charges. In both types of emulsion the advantage was possibly with the colloid with the same charge as the grains, although the difference was not large enough to be determined with certainty. It is evident that the strong adsorption of silver iodide to silver bromide is specific and is not of the nature of a mutual coagulation of oppositely charged colloids.

The colloidal silver iodide was never exposed to full daylight. This might have affected it, but there was no difference evident between the results with preparations which had been handled only by a safe light, and those which were exposed to the artificial light or weak diffuse daylight of the laboratory. (8–96, Table 2.)

The most striking effect produced by the colloidal silver iodide was the apparent sensitization when the plates were physically developed (Tables 4 and 5). This was accompanied by an increase in fog, which was greater when the excess colloid was not removed by the centrifuge, the average increase being 215 per cent (Table 4) against 87 per cent (Table 5, excluding the bathed plates). The changes in sensitivity and fog both disappeared on development after fixation, within the large limits of error inherent in this method.

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[25] Renwick, Sease, and Baldsiefen, Photo. J., **66,** p. 163; 1926; also private communication.

With this evidence, it is possible to account for the results, and we believe that a similar method of attack will be useful in the study of the function of iodide introduced into the emulsion in the original mix.

The acceleration of development by bathing in solutions of soluble iodide, with partial conversion of the silver bromide to silver iodide, has been known for a long time. The results are discussed at length by Lüppo-Cramer.[26] His hypothesis of nucleus exposure ("Keimblosslegung") is the best known explanation of the phenomena connected with iodide bathing. It may be stated briefly as follows:

Only the nuclei on the surface of the grains are effective in promoting physical development. Those in the interior are relatively ineffective for chemical development, and totally so with the physical developers which do not reduce the grains but supply the silver of the developed image entirely from the solution. Conversion of silver bromide to iodide involves considerable change in volume and crystal structure, and, therefore, disintegrates the silver bromide grains, exposing the nuclei in the interior and making them available as development centers. This theory is apparently well substantiated where extensive conversion to iodide takes place, but Sheppard, Wightman, and Trivelli [27] have pointed out that the marked selective effects, which are found when very dilute solutions are used, are better explained by increased adsorption of the developer to the iodide. In our experiments, silver iodide was introduced into the emulsion after practically complete removal of soluble bromide, or other silver halide solvents. No replacement of bromine by iodine in the crystal lattice could take place, only adsorption of the silver iodide to the bromide, and the hypothesis of nucleus exposure is therefore inapplicable. The effects of the colloidal silver iodide may be attributed entirely to the acceleration of development. Speed increases even more than contrast, with increasing physical development, so that not only the increased contrast with chemical development, but the increased speed with physical, are accounted for in this way. The increased fog on physical development is logically explained by adsorption of silver nitrate (or a silver nitrate-metol complex). All the silver nitrate in the developer is ultimately reduced, and that adsorbed to the silver iodide in the emulsion produces fog instead of merely a suspension of silver in the developing solution. Fog and silver iodide present increase together in the order—development after fixation, development before fixation of emulsions with the unadsorbed silver iodide eliminated, development before fixation of emulsions with all the silver iodide present.

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[26] Lüppo-Cramer, Grundlagen der Photographische Negativverfahren, pp. 526–560.

[27] Sheppard, Wightman, and Trivelli, J. Frank. Inst., **196**, pp. 653, 779; 1923.

On the orientation theory of sensitivity nuclei, it might be possible for the adsorption of silver iodide to increase the primary photolysis of silver bromide; in other words, to increase the amount of latent image rather than its developability, but we have obtained no evidence to this effect.

It is not wise to attempt to draw analogies, from the results obtained either by bathing or by addition of colloidal silver iodide, to the use of iodide in the original mix of the emulsion. In the latter case the final product must be largely mixed crystals; while it has been suggested [28] that adsorption of the developer by iodide may account for the results obtained, there is evidence for a change in the primary sensitivity caused by distortion of the silver bromide crystal lattice on formation of mixed crystals with iodide.[29] Wilsey [30] has actually found, by X-ray measurements, the predicted change in the space lattice of (fused) silver bromiodide mixed crystals, and Huse and Meulendyke [31] find an analogous change in the spectral absorption of the fused salts and in the spectral sensitivity of emulsions of corresponding iodide content.

IV. SENSITIZATION BY COLLOIDAL SILVER

Metallic silver is one of the probable materials of the sensitivity nuclei, as already mentioned. It is of further interest because it can not be considered as a bromine acceptor. There is no evidence that the photolysis of silver bromide and the bromination of silver reach any equilibrium in light, so that the first process could not be accelerated by the second even in the earliest stages. Bromination after exposure but before development, by local differences of bromine pressure in the grain, would be expected to reduce rather than increase developability, since the bromine would tend to migrate from the interior of the grain to the vital development centers on the surface.

We were able to secure a very definite sensitization by colloidal silver of the acid emulsions with excess soluble silver salts. (Table 6.) The adsorption of the negatively charged metallic colloids on the negatively charged grains of the normal emulsions was apparently too poor for definite results. Gelatin-protected sols gave by far the best sensitization. It was apparently a question of protection rather than particle size, since dextrin-protected sols, which were practically ineffective, were converted by the addition of acidified gelatin into the equivalent of the sols reduced by hydrazine in the presence of gelatin, both in appearance and sensitizing action. The dextrin sols were prepared by the Carey Lea method, with a decreased amount of sodium hydroxide, as suggested by Wiegel.[32] They were purified by

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[28] Sheppard, Phot. J., **62**, p. 88; 1922.

[29] Trivelli, Rec. des Trav. Chem. [4], **3**, p. 714; 1923.

[30] Wilsey, J. Frank. Inst., **200**, p. 739; 1925.

[31] Huse and Meulendyke, Phot. J., **66**, p. 306; 1926.

[32] Wiegel, Zeit. wiss Phot., **24**, p. 316; 1927.

alcohol precipitation. No difference was apparent between those precipitated once and twice. A number of these sols were treated with hydrochloric acid or sodium chloride, with the idea that, if the adsorbed OH^- ions on the particles were replaced by Cl^-, the adsorption might be improved. There is no evidence that this was of any value. Commercial "argyrol," presumably reduced and protected by hydrolyzed albumen, produced only intense fog without sensitization.

The data in Table 6 are all without after-ripening. The retests in Table 7 were made after two months storage, using both chemical and physical development. The colloid for some reason retarded the reduction of soluble silver salt in the emulsion, since on chemical development the batch with colloid fogged less than the control. The much greater fog on physical development is probably explained by the presence of silver particles large enough to initiate deposition of silver, but not firmly enough adsorbed to accelerate reduction of the silver bromide grains.

There is no evidence in this case of a development effect. The change in sensitivity is primarily a decrease in inertia, with practically constant gamma. The indication is an actual increase in latent image, although it is impossible to decide whether there is a real increase in the photochemical process or only an orientation around silver nuclei.

TABLE 6.—*Sensitization with colloidal silver; acid emulsions with excess silver*

Emulsion No.	Preparation of colloid	Mg Ag per g AgBr	Speed	γ			c	u	Fog		
				3	6	12			3	6	12
6- 65-1		0. 0	28	0. 35	0. 63	0. 75	0. 05	0. 68	0. 06	0. 11	0. 22
4	Reduced by N_2H_4 from ammoniacal AgCl, in presence of gelatin	. 6	34	. 63	1. 18	1. 35	. 07	1. 10	. 19	. 56	1. 61
5	Dextrin; alcohol precipitated and dialyzed after adding NaCl	. 6	27	. 30	. 68	. 85	. 05	. 68	. 11	. 21	. 44
8-120-1		. 0	23	. 60	1. 85	2. 66	. 20	1. 27	. 12	. 29	. 55
2	Dextrin; twice precipitated by alcohol; added to final suspension	. 2	27	. 55	1. 60	2. 50	. 11	1. 24	. 15	. 44	. 73
8-122-1		. 0	6. 5	. 57	1. 38	1. 98	. 02	. 21	. 02	. 11	. 20
4	Dextrin, once precipitated by alcohol	. 6	10	. 80	1. 05	1. 82	. 07	. 40	. 08	. 13	. 16
5	Dextrin, twice precipitated by alcohol	. 6	8	. 70	1. 26	1. 60	. 02	. 23	. 07	. 11	. 16
6	Reduced by N_2H_4 in presence of gelatin	. 6	11	. 55	1. 24	1. 70	. 06	. 38	. 07	. 11	. 17
8-119-1		. 0	8	1. 05	1. 60	----	. 07	. 41	. 05	. 10	----
2	Dextrin; once precipitated by alcohol	. 26	8	1. 00	1. 70	----	. 06	. 40	. 09	. 14	----
3	Dextrin; twice precipitated by alcohol	. 26	8. 5	. 94	1. 55	----	. 06	. 34	. 05	. 12	----
8-124-1		. 0	14	1. 38	2. 13	----	. 03	. 52	. 08	. 11	----
2	Reduced by N_2H_4 from ammoniacal AgCl in presence of gelatin	. 6	31	1. 12	1. 75	----	. 06	. 99	. 10	. 14	----
3	As in (2), dialyzed	. 6	25	1. 22	1. 90	----	. 05	. 93	. 09	. 37	----
4	Dextrin; once precipitated by alcohol; plus gelatin and HCl to pH 4	. 6	25	1. 35	2. 20	----	. 12	1. 02	. 07	. 08	----
5	Dextrin; once precipitated by alcohol; dialyzed after adding 10^{-5} g equivalent HCl	. 6	15	1. 42	1. 83	----	. 04	. 50	. 20	. 28	----
6	Dextrin; once precipitated by alcohol; dialyzed after adding 10^{-4} g equivalent HCl	. 6	15	1. 22	2. 01	----	. 04	. 55	. 09	. 15	----

TABLE 7

Emulsion No.	Six minutes metol-hydroquinone development			Physical development		
	Speed	γ	Fog	Speed	γ	Fog
6- 65-1	100	1.05	0.78	10	0.73	0.12
4	33	1.52	.14	4	.57	.42
8-124-1	47	2.05	.41	9.7	1.02	.08
2	52	2.05	.17	10	.88	.59

V. SENSITIZATION BY SILVER SULPHIDE

We were unable to produce definite sensitization by colloidal silver sulphide in either type of emulsion. As the silver sulphide caused a considerable increase in fog, it is possible that the particles of the sol were too large. Our sols were prepared by two methods; first, by mixing 0.01 N solutions of silver nitrate and sodium sulphide, with 1 per cent gelatin in one or both solutions, and second, by the decomposition of silver thiosulphate in the presence of gelatin.

As we wished to compare the results of chemical and physical development on emulsions with silver sulphide nuclei, a number were sensitized with allyl thiocarbamide, 2 to 12×10^{-6} g/g of silver bromide. It is evident from the typical cases quoted in Table 8 that the percentage increase in sensitivity is nearly the same by both methods of development. The similarity is so great that a development effect becomes highly improbable. The thiocarbamide sensitization must increase the latent image formed.

TABLE 8.—*Comparison of chemical and physical development of emulsions sensitized with allyl thiocarbamide*

Emulsion No.		Six-minute development with metol-hydro-quinone			Physical development		
		Speed	γ	Fog	Speed	γ	Fog
1-129-1	Control	30	2.15	0.03	4.5	0.68	0.09
3	Sensitized	210	1.77	.08	13.0	.88	.09
1-131-6	Control	95	1.10	.17	27.0	.50	.16
4	Sensitized	380	1.32	.30	87.0	.57	.21
1-132-3	Control	125	1.60	.02	7.9	.52	.03
7	Sensitized	480	1.42	.16	16.0	.77	.06
1-133-1	Control	175	1.33	.02	12.0	.60	.04
6	Sensitized	410	1.47	.10	40.0	.58	.07

VI. SENSITIZATION WITH COLLOIDAL GOLD

Metallic gold was found to be, under proper conditions, the most effective of the colloidal sensitizers. The optimum conditions for its use are so restricted that erratic results were obtained for a considerable time. They may be summarized as follows:

The *gold sol* should be blue to purple in color (absorption maximum about 560 to 570 mμ); free from unreduced auric chloride; free from particles coarse enough to give a cloudy appearance; protected by gelatin.

The *emulsion* should contain excess silver in a concentration of the order of 2×10^{-3} N at the time the gold sol is added, and the pH at this time should be less than 3 (preferably not less than 2); the excess gold and soluble silver should be removed by centrifuging.

Some sensitization of normal emulsions, with excess bromide, is probable, but we were unable regularly to secure effects larger than the experimental error by adding the colloidal gold to the fully ripened and washed emulsion as already described with the other colloids. A number of experiments were also made under other conditions which appeared to have possibility of greater effectiveness. The work of Jenisch [33] on addition of the gold to the bromide solution used in making the emulsion, was repeated with completely negative results, although we tried both neutral and ammoniacal emulsions with varying degrees of ripening and with three different gold sols. When the gold was added after the mixing was complete, but before washing, it usually caused fog, but the sensitization was within the limits of error. As the presence of the gold under these conditions may alter variables, such as the ripening process, these experiments were discontinued when they did not show promise of practical results.

The necessity of a low pH was entirely unexpected. It is probably connected with the increase in sensitivity of emulsions with excess silver as the pH of their first resuspension is decreased, an equally unexplained effect, to be treated in a later publication. The data in Table 9 permit direct comparison of sensitization of the same emulsions by the same gold sols at different hydrogen ion concentrations, supported by results with comparable emulsions. The increase in sensitivity at pH 2.2 to 2.5 was 60 to 200 per cent, as compared to 10 per cent or less at pH 4.5 to 5.2. The figures for the underexposure region show that the sensitizing effect of the gold was strongest there; as there was usually a decrease in gamma, it tended to disappear with increasing exposure.

On any of the theories of sensitivity, there should be a minimum effective size for the sensitivity nucleus, and, assuming it to be either a portion of the subsequent development center or a bromine absorbent, the sensitization would, within limits, increase with the size. We made no direct determinations of particle size in the gold sols, but, at least in the case of sols prepared by the same general method, it seems safe to assume that the particle size increases as the spectral absorption shifts to the longer wave lengths. We found that a series of sols ranging in color from red through purple to blue may be prepared by reduction of auric chloride with hydrazine in the presence of gelatin, varying only the hydrogen ion concentration at the time of reduction. Our results were similar to the much more comprehensive work subsequently published by Beaver and Muller.[34] As will be evident from inspection of Table 10, the effectiveness of the gold sols increase from almost nothing with the red sols to a maximum with the blue. The regular change in the underexposure regions of 8–113 and 8–115 should be noted. It is peculiar that the neutral emulsions, 6–56 for example, were fogged by the gold more than were the ammoniacal type. The pH given in the "description of colloid," Table 10, is that at which reduction of the gold took place; the pH of the different batches of emulsion was independent of this, and was approximately 3.5.

All our sols were made up quantitatively with equivalent amounts of standard solutions of auric chloride and hydrazine sulphate, and were generally dialyzed for several days in collodion sacks against distilled water. Undialyzed sols with incomplete reduction (see 8–150–4, Table 11) were generally desensitizing, because of the auric chloride. However, the presence of the gelatin interfered with analysis for possible hydrazine in the sols. Accordingly, hydrazine sulphate was added to the emulsions under the same conditions used for the gold, and was mixed with gold sols on the possibility that the combination might be more effective than either one alone. Large quantities (0.001 mol per mol Ag Br) caused intense fog in the emulsions with excess silver. Smaller amounts, of the order used in preparation of the gold sols, were quite inert, as will be evident from Table 11.

As gold is attacked by the halogens, it might be considered an acceptor for bromine from the photolysis of silver bromide, provided that gold halides are inert to the latent image. Auric chloride solution was found to be destructive to the latent image in high dilutions, as is evident from Table 12. It is even more destructive to sensitivity. There remained the possibility that halogenation may go through the aurous state. Aurous chloride is decomposed by water to gold and auric chloride, and the bromide is less stable. This is, in itself, probably a sufficient argument. However, it is possible to prepare moderately stable solutions of aurous gold[35] by reduction of auric chloride with sulphite in the presence of soluble chloride. These solutions are almost as destructive to the latent image as those of auric chloride. Because of their unstable nature it was difficult to reproduce results. They occasionally produced heavy fog, accompanied by more than the usual destruction of the latent image, and it was difficult to correlate this with their stability. An illustration of this occurs in the last section of Table 12. These

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[34] Beaver and Muller, J. Am. Chem. Soc., **50**, p. 304; 1928.

[35] Lenher and Diemer, J. Am. Chem. Soc., **35**, pp. 546, 552, 733; 1913.

solutions evidently represent an equilibrium mixture. When sulphite sufficient to reduce the auric chloride to the aurous state is used in the presence of small amounts of soluble chlorides, the yellow color of the solution is not completely discharged, nor is the use of excess sulphite sufficient to do this, but it gradually fades out as the concentration of chloride is increased. It will be noted in the last section of Table 12 that as the molar ratio of NaCl to AuCl is raised from 1 to 100, the reduction in density is less, while the addition of more sulphite has no such effect. In fact, it increases the action on the latent image, corresponding possibly to the maximum increase in the electrode potential of gold found by Diemer at the concentration of sulphite corresponding to reduction to AuCl. The evidence is that the actual concentration of aurous ion in these solutions is infinitesimal, as a result of complex formation, and, altogether, that there is no possibility that the bromination of gold either to the aurous or the auric state could assist in the photolysis of silver bromide. We discovered a minor point which is not mentioned by Lenher and Diemer. The aurous solutions are much more stable if neutralized (pH 6 to 7) than if left at the naturally acid reaction of auric chloride solutions. The decomposition in the presence of low concentration of chloride becomes a matter of hours instead of minutes.

Using physical development, the colloidal gold has a marked tendency to cause fog. (Table 9.) Probably because of this there is more often a decrease than an increase in the sensitivity measured this way. With chemical development the unadsorbed gold may be left in the emulsion without causing fog. This is illustrated in Table 13. It is evident that the heavy fog of the gold-sensitized neutral emulsions is not due to unadsorbed excess colloid.

The sensitizing action of collodial gold can not be ascribed to its absorption of bromine or to its ability to act as a development center independent of connection with a silver bromide grain or to its ability to accelerate development. It is uncertain whether a silver-silver bromide-gold photoconductivity cell could be set up or whether its action would increase developability. The theory of an oriented photolysis caused by the adsorption of the gold to the surface of the silver bromide seems to fit the case better than any of the others.

TABLE 9.—*Effect of emulsion pH when colloidal gold was added, on the sensitization produced by the gold*

Emulsion No.		pH at addition of gold	Mg Au per g AgBr	Chemical development, 6 minutes metol-hydroquinone					Physical development		
				Speed	γ	Fog	c	u	Speed	γ	Fog
8-136-1	Control	5.0	0.0	4.5	2.07	0.05	0.00	0.32	2.6	0.73	0.02
2	Gold added to first resuspension	5.0	.06	5.0	2.35	.09	.00	.32	2.7	.72	.10
3	Control	2.5	.0	190.0	.83	.21	.00	2.3	12.0	.57	.02
4	Gold added to first resuspension	2.5	.06	350.0	.80	.48	.00	4.5	20.0	.50	.05
8-138-1	Control	5.2	.0	6.3	1.28	.03	.03	.48	6.3	.60	.03
2	Gold added to first resuspension	5.2	.06	6.9	1.30	.05	.04	.68	2.0	.61	.17
3	Control	2.2	.0	79.0	1.00	.48	.06	1.65	30.0	.51	.02
4	Gold added to first resuspension	2.2	.06	300.0	.79	.48	.02	4.4	14.0	.50	.17
8-140-3	Control	2.4	.0	230.0	1.00	.40	.01	4.1	27.0	.56	.02
4	Gold added to first resuspension	2.4	.06	380.0	.72	.67	.02	4.2	22.0	.48	.09
8-150-1	Control	2.5	.0	145.0	.92	.17	.07	2.55	11.5	.90	.09
2	Gold added to first resuspension	2.5	.12	230.0	.93	.31	.08	5.0	26.0	.53	.08
8-129-1	Control	4.5	.0	16.0	1.63	.05	.04	.48	5.7	.65	.04
2	Gold added to first resuspension	4.5	.12	15.0	1.80	.05	.05	.49	3.9	.69	.17
8-131-1	Control	5.0	.0	11.0	1.45	.05	.01	.52	3.3	.95	.05
3	Gold added to first resuspension	5.0	.09	10.5	1.42	.06	.02	.68	2.1	.96	.16

TABLE 10.—*Comparison of sensitization by gold sols of varying dispersion*

Emulsion No.	Description of colloid	Mg Au per g AgBr	Speed	γ		c	u	Fog	
				3	6			3	6
6-56-1	Control	0.0	64	0.20	0.80	0.09	1.06	0.03	0.35
4	Reduced by N_2H_4 in presence of gelatin. Blue	.2	103	.50	.83	.04	2.60	1.03	2.23
5	Reduced by HCHO, without protection. Red	.2	44	.92	1.37	.11	1.40	.28	.72
8-113-1	Control	.0	23	1.55	2.54	.25	1.10	.11	.29
2	Reduced by N_2H_4 in presence of 0.1 per cent gelatin; pH 3.5. Orange	.2	23	1.60	2.45	.23	1.18	.15	.34
3	Reduced by N_2H_4 in presence of 0.1 per cent gelatin; pH 8.2. Purple	.2	35	1.48	1.93	.20	1.50	.17	.40
4	Reduced by N_2H_4 in presence of 0.05 per cent gelatin; pH 8.5. Blue	.2	50	1.08	1.93	.20	2.00	.21	.45
5	Reduced by N_2H_4 in presence of 0.025 per cent gelatin; pH 8.5. Blue	.2	48	1.65	2.10	.28	2.55	.19	.50
8-115-1	Control	.0	21	1.62	2.37	.12	1.05	.10	.16
2	Reduced by N_2H_4 in presence of 0.1 per cent gelatin; pH 3.5. Orange	.2	14	1.70	2.60	.10	.72	.13	.23
3	Reduced by N_2H_4 in presence of 0.1 per cent gelatin; pH 8.2. Purple	.2	50	1.13	1.54	.06	.66	.41	.94

TABLE 11.—*Test for sensitization by hydrazine; comparison of dialyzed and undialyzed gold sols*

Emulsion No.	pH when N_2H_4-H_2SO_4 or gold was added		Mg Au per g AgBr	Mol N_2H_4-H_2SO_4 per mol AgBr	Chemical development 6-minute metol-hydroquinone			Physical development		
					Speed	γ	Fog	Speed	γ	Fog
8-128-1	4	Control	0.0	0.0	20.0	1.65	0.06	7.9	0.54	0.04
3	Same as (1)	Undialyzed blue gold by N_2H_4	.12	----------	25.0	1.53	.66	4.3	.82	.23
4	do	Same gold as in (3) dialyzed	.12	----------	25.0	1.85	.12	4.5	.78	.16
8-130-1	4	Control	.0	0.0	12.0	1.37	.09	4.5	.40	.03
2	Same as (1)	Hydrazine only	.0	1.6×10^{-5}	12.6	1.40	.09	5.0	.38	.03
3	do	Hydrazine only	.0	1.6×10^{-6}	12.6	1.43	.08	5.5	.31	.02
6	do	Dialyzed blue gold by N_2H_4	.12	0.0	17.4	1.30	.13	4.7	.28	.15
8-133-1	4	Control	.0	0.0	17.0	1.30	.08	2.5	.60	.04
2	Same as (1)	Dialyzed blue gold by N_2H_4	.06	0.0	20.0	1.23	.08	2.5	.58	.06
3	do	Hydrazine only	.0	3.3×10^{-5}	18.0	1.23	.07	2.5	.61	.04
4	do	Same gold as in (2), plus N_2H_4-H_2SO_4.	.06	3.3×10^{-5}	16.0	1.26	.08	2.4	.62	.08
8-138-3	2.2	Control	.0	0.0	79.0	1.00	.48	30.0	.51	.02
5	2.2	Hydrazine only	.0	8.2×10^{-5}	110.0	1.08	.43	8.0	.53	.04
4	2.2	Dialyzed purple gold by N_2H_4	.06	0.0	300.0	.79	.48	14.0	.50	.17
8-140-1	5.0	Control	.0	0.0	132.0	.36	.08	2.9	.38	.02
2	5.0	Hydrazine only	.0	1.6×10^{-4}	110.0	.36	.09	5.0	.26	.02
3	2.4	Control	.0	0.0	230.0	1.00	.40	27.0	.56	.02
4	2.4	Dialyzed purple gold by N_2H_4	.06	0.0	380.0	.72	.67	22.0	.48	.09
5	2.4	Hydrazine only	.0	1.6×10^{-4}	174.0	1.07	.48	25.0	.60	.02
8-150-1	2.5	Control	.0	0.0	145.0	.92	.17	11.5	.90	.07
2	2.5	Dialyzed blue gold by N_2H_4	.12	0.0	230.0	.93	.30	26.0	.53	.08
4	2.5	Undialyzed purple gold by N_2H_4; reaction between $AuCl_3$ and N_2H_4 incomplete.	.12	----------	75.0	.93	.18	14.5	.37	.21

TABLE 12.—*Effect of gold chlorides on latent image. Strips exposed in the sensitometer were bathed in gold chloride solutions, 0.100 g. Au per liter, washed thoroughly and developed without drying. All results average of two strips*

Emulsion No.	Solution	Total density at successive exposures—							Fog density
1-122-1	Water	0.46	0.63	0.80	0.93	1.09	1.30	------	0.41
	$AuCl_3$, + K_2CO_3 to pH 7	.33	.46	.63	.78	.96	1.13	------	.26
1-122-1	Water	.54	.66	.84	1.02	1.23	1.39	1.61	.51
	AuCl . 10 NaCl, pH 7	.38	.50	.61	.74	.88	1.05	1.23	.51
Eastman "36"	Water	.26	.43	.67	.95	1.28	1.57	1.97	.16
	AuCl. 25 NaCl, pH 7	.27	.40	.59	.83	1.11	1.45	1.78	.18
	$AuCl_3$, + K_2CO_3 to pH 7	.20	.28	.43	.61	.87	1.12	1.45	.17
Cramer "contrast."	Water	.11	.23	.51	1.00	1.75	2.9	------	.07
	AuCl . 10 NaCl, pH 6.5	.19	.26	.47	.85	1.46	2.2	------	.14
	$AuCl_3$. 10 NaCl, + K_2CO_3 to pH 7.5	.10	.15	.30	.56	1.01	1.6	------	.08
	Water	.05	.16	.38	.80	1.39	2.18	------	.02
	AuCl . 10 NaCl, pH 6.5 Na_2SO_3 to reduce to AuCl	.71	.77	.84	1.00	1.31	1.75	------	.74
	AuCl . 100 NaCl, pH 6.5 Na_2SO_3 to reduce to AuCl	.12	.19	.34	.62	1.02	1.55	------	.11
	AuCl . 1 NaCl, pH 6.5 Na_2SO_3 to reduce to AuCl	.12	.18	.32	.57	.96	1.45	------	.07
	AuCl . 10 NaCl, pH 6.5 Na_2SO_3 to reduce to Au	.05	.11	.25	.54	.98	1.54	------	.02
	AuCl . 10 NaCl, pH 6.5 Twice Na_2SO_3 to reduce to AuCl	.05	.07	.18	.42	.84	1.38	------	.03

TABLE 13.—*Colloidal gold added to final suspension of emulsions; blue sols, reduced by hydrazine and gelatin protected*

Emulsion No.	Mg Au per g AgBr		Speed	γ		Fog	
				3	6	3	6
6-60-1	0.0	Control	40	1.46	1.98	0.30	0.99
4	.2	Gold added to first resuspension	135	1.22	1.52	.55	1.28
5	.02	Gold added to final suspension	50	1.28	1.92	.31	.98
8-111-1	.0	Control	13	2.40	3.07	.07	.18
4	.2	Gold added to first resuspension	20	1.75	2.70	.08	.27
5	.06	Gold added to final suspension	14	1.70	3.00	.09	.26

VII. SUMMARY

1. Photographic emulsions, after ripening and washing, were treated with gelatin-protected sols of silver iodide, silver sulphide, metallic silver and metallic gold, under such conditions that the control and treated portions might be expected to differ only in the presence of particles of the colloid adsorbed to the silver halide grains of the latter, with the object of thus introducing sensitivity nuclei. Results were improved by the use of deactivated gelatin, to reduce nucleation prior to the addition of the colloid.

2. Gelatin emulsions with excess silver salts may be developed normally, if the excess silver is reduced to a concentration of the order of the excess bromide in a normal washed emulsion, and if the hydrogen ion concentration is maintained at a sufficiently high value after the introduction of the excess silver. The grains of these emulsions carry a positive charge, and they are particularly adapted to sensitization by the negatively charged metallic colloids.

3. The effects produced by the silver iodide, and by the two metallic colloids, differ in type and in probable cause. The results with colloidal silver sulphide were negative. All the colloids retarded after-ripening to such an extent that the practical effect, when the emulsion was digested after washing, was desensitization.

4. Colloidal silver iodide produced a marked increase in contrast with chemical development of the emulsion; the immediate effect, without after-ripening, was an increase in density for the longer exposures. Using physical development, there was a great increase in speed. Both these effects may be explained by acceleration of development, and this is most probably to be attributed to increased adsorption of the developer, since the conditions exclude the possibility of nucleus exposure.

5. Colloidal gold and silver increased the speed of emulsions with excess silver. The effect was most pronounced in the underexposure region, and bears no resemblance to an acceleration of development. The evidence is that these materials can not increase the photochemical sensitivity of the emulsions by reacting with bromine liberated in the photolysis of silver bromide. The results are readily explained in terms of orientation of the photolysis at the sensitivity nucleus formed by the colloidal particle.

WASHINGTON, May 29, 1928.

RP340

THE PHOTOGRAPHIC EMULSION: AFTER-RIPENING

By Burt H. Carroll and Donald Hubbard

ABSTRACT

After-ripening is defined as the increase in sensitivity of photographic emulsions after washing. Following a discussion of the process, and review of the literature, the experimental methods of the National Bureau of Standards photographic emulsion laboratory are described in detail. After-ripening by digestion was studied with respect to eight of the more important variables. The amount of after-ripening which is practicable is dependent on the extent to which sensitivity nuclei have been formed during ripening before washing. The influence of temperatures and of bromide, chloride, and hydrogen ion concentrations, is according to predictions on the basis of chemical reactions forming sensitivity nuclei. The effect of gelatin-silver halide ratio can be explained by its influence on rate of development. Variations between different samples or makes of gelatin are illustrated. The progress of after-ripening with inert gelatin plus known sensitizing materials is very similar to that under the usual conditions, but there are important quantitative differences. The increase in practicable after-ripening with increasing percentage of silver iodide is illustrated. After-ripening during storage of finished plates was found to be similar to that by digestion, but frequently more efficient. Changes in bromide ion concentration during digestion, and in nonhalide silver during digestion or storage, are further proof of reaction during after-ripening, but it is evident that most of the nonhalide silver is photographically inert.

CONTENTS

I. INTRODUCTION

This paper is to be considered as a survey of its limited field rather than a completed investigation. Publication of the material here presented is dictated not only by the considerable length of the article but because the existence of this very important process is apparently unknown to otherwise well-informed writers on photography. Recent literature has included specific if qualitative references (1), (2), (3), (4), (5) [1] to the fact that the sensitivity of an emulsion may be enormously increased by digestion *after washing*, but the general impression of the emulsion-making process is based on early literature (6) which cautions against such treatment.

We are unable to say how far our experiments correspond to commercial practice,[2] but some of the resulting emulsions are quite similar to very fast commercial products. We are also uncertain how much of the material presented may be common knowledge among emulsion makers, but it has never been published in quantitative form and it seem particularly unlikely that any information on this subject is to be expected from commercial sources.

The term "ripening" has been used to include any digestion or storage after mixing the emulsion, used to increase sensitivity. It is generally understood now, however, to mean digestion in the presence of excess soluble bromide, with or without the addition of ammonia. In the presence of these solvents for silver halide, there is a continuous increase in average size of the silver halide grains, with complicated changes in the size distribution. We will use "ripening" in this sense. "After-ripening" will be understood to mean changes in sensitivity after the silver halide solvents have been removed by washing; it is therefore associated with no appreciable change in grain size. After-ripening is normally carried on by digestion of the melted emulsion after washing; we shall use the term digestion to imply heat treatment of the washed emulsion, as distinct from the ripening by heat before washing. Marked after-ripening may also occur on storage of finished plates, especially if ripening and digestion have been limited; we shall refer to this as "storage ripening."

The impression which is given by the early literature is that the sensitivity of an emulsion is controlled almost entirely by the ripening and this is true of many of the older formulas.

Present procedure is apparently different; several authoritative statements to this effect have been published, for example, the following by Sheppard (Bogue, Colloidal Behavior II, p. 763):

> These relatively coarse-grained negative emulsions are not produced from fine-grained emulsions by ripening, but the grain size is determined by the conditions of initial precipitation. High concentration of the reactants ($AgNO_3$ and KBr), low concentration of gelatin, high temperature of mixing, and retarded addition permit the process of recrystallization to take place at once, with the formation of definite, coarse-grained suspensions.

Our own experience is in excellent agreement with this, but it may be amplified to advantage at one point. If the silver solution is added to the bromide, the first grains are formed in the presence of a high concentration of the latter. Now the solubility of silver bromide in a solution of potassium bromide increases very rapidly with increasing potassium bromide concentration [3] and the rate of ripening (or at least the rate of change in grain size) obviously will increase with the solubility (7) so that there is very rapid ripening during the mixing. If the addition of the silver solution is retarded, using either a

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[1] Numbers in parentheses here and elsewhere in the text refer to the bibliography at the end of the paper.

[2] Lüppo-Cramer (reference 1) states that, contrary to a common impression, he has found no significant difference between large and small batches of emulsion made by the same formula, provided that all variables, such as the rate of mixing, were actually kept constant.

[3] Approximately as the fifth power, Hellwig. Z. Anorg. Chem., **25**, p. 183; 1900.

slow continuous stream, or "double emulsification" (8), (9), the ripening of the silver halide first formed may be carried to its practical limit by the time the mixing is completed, and little or no more ripening in the usual sense is desirable.[4] Ripening is followed by washing the emulsion, removing the silver halide solvents, such as soluble bromide and ammonia, so that the grain size and distribution is fixed after washing. It is a common impression [5] that sensitivity is also practically fixed. The emulsions described in the early literature were generally low in iodide and ripened for a long time with ammonia. Emulsions of this type can not be after-ripened to any considerable extent. With other formulas capable of producing emulsions resembling modern commercial products, the sensitivity just after washing may not be more than 5 per cent of the final value which is reached by digestion at temperatures of 35° to 65° C. Our experience is that it is impossible to make a satisfactory fast emulsion of the neutral ("boiled") type without after-ripening, and that it is at least very difficult to do without it in ammonia-ripened emulsions.

In case the emulsion is coated without digestion, there will, in general, be an increase in sensitivity, on keeping the plates, which equals or exceeds the increase which could be produced by digestion This was frequently observed in the early days of dry plates; Eder (11) cited several conflicting observations on this point, and gave the weight of his opinion to the erroneous conclusion of Gaedicke that there was no increase in sensitivity on storage if no trace of ammonia remained in the emulsion. We have already commented briefly on this subject (7).

The number of variables in a photographic emulsion is such that a complete series of independent changes in each one is quite impracticable. We believe that we here present enough data to indicate the sign and order of magnitude of the effect which several of these variables have upon after-ripening, although the exact course of the process with a given formula must obviously always remain a matter for careful determination in each individual case.

The nature of the processes occurring during after-ripening will be discussed at more length in connection with the evidence offered in this paper. As already mentioned, the change in grain size is negligible, since the solubility of the silver halide is practically the same as in pure water. After-ripening is primarily the period of formation of sensitivity nuclei. Thiocarbamides and related sulphur compounds have formed insoluble molecular compounds (12) with the silver halide during the mixing and ripening, but in the absence of ammonia, there is little rearrangement of these to form silver sulphide until the bromide ion concentration has been reduced by washing. Reduction of silver bromide to metallic silver also leaves soluble bromides as a product of the reaction and, therefore, must be much more rapid after washing; to date, there is neither positive proof or dis-

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[4] We have already (7) mentioned the marked increase in speed and decrease in contrast produced by slow mixing of a neutral emulsion. Lüppo-Cramer (1) has recently given further illustrations of this, with characteristic curves. Conditions in an ammonia process emulsion are much more complicated because of the competing formation of two kinds of complex ions $(Ag(NH_3)_2)^+$ and $(AgBr_x)^-$, but the wider range in grain sensitivity is still observed, with similar changes in the characteristic curve. Wall (10) has also discussed some of the consequences if the method of mixing the emulsion is varied, for example by addition of the silver and bromide solutions simultaneously to the gelatin; but we doubt if the evidence supports his view that a "slow form" of silver bromide is formed in the presence of a high concentration of soluble bromide.

[5] For example, Neblette, "Principles and Practice of Photography" p. 162, 1926, says that after washing "The emulsion may be regarded as complete."

proof that this reaction is a source of sensitivity nuclei, but the writers agree with Lüppo-Cramer that it is very probably an important part of after-ripening.

II. EXPERIMENTAL METHODS

1. SENSITOMETRY

The usual methods of this bureau were employed—nonintermittent time scale exposure at an intensity of 1 meter-candle, brush development in unbromided pyrogallol at 20° for 3, 6, and 12 minutes, and measurement of density in diffuse illumination by a Martens photometer, the density of the fog strip being automatically subtracted. The illumination was the quality of mean noon sunlight; the more recent tests were obtained with a lamp of color temperature 2,360° and the Davis-Gibson filter tentatively adopted at the International Congress; the previous source was a lamp operated at a color temperature of 2,810° K. and a Corning "Daylite" glass filter giving photographically equivalent quality. The emulsions were machine coated on 5 by 7 inch (or in a few cases 4½ by 6½ inch) plates; three test strips 1⅛ by 5 inches cut from the center of the plate and backed with black shellac. The coating was somewhat heavier than commercial practice; this minimizes the photographic effect of irregularities incident to coating small experimental batches, but it obviously increases the fog density. Because of the very rapid storage ripening in the undigested emulsions, the tests were always made soon after coating (in 12 to 40 hours after drying was complete, unless stated to the contrary). Excepting in Table 1, the term "speed" in all our tables refers to the National Bureau of Standards speed number, $10/i$. The inertia (i) is expressed in candle-meter-seconds. Subscripts, or subheadings under γ and fog, indicate the time of development in minutes; six minutes is approximately the normal time for this developer.[6]

Sensitometry of experimental emulsions unfortunately is especially subject to difficulties in assigning numerical values to the data, as almost invariably some members of a series of emulsions fail to have characteristic curves with satisfactory straight line sections. Our conclusions are in all cases based on comparison of the complete characteristic curves, but by giving both speed and γ in the tables, a reasonably adequate idea of the changes in effective sensitivity has been presented.

A complete set of data illustrating change of sensitivity during after-ripening is given in Table 1 and Figures 1, 2, and 3. We are indebted to Messrs. Raymond Davis and G. K. Neeland for exposures of emulsion 4–68 with sector wheels giving steps on the log E scale of 0.15 and 0.20, as our wheel is of the conventional H and D pattern (nine steps, each twice the preceding one). The characteristic curves for 6 and 12 minute development are plotted in Figures 1 and 2; Figure 3 and Table 1 give the numerical constants assigned to these curves, including speed numbers both by the B. S. system

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[6] The order of sensitivity of the experimental emulsions may be judged by comparison with commercial emulsions tested under the same conditions. A moderate speed negative emulsion, Eastman roll film, has a B. S. speed of 220, γ_6 0.88; two very fast emulsions, the Hammer Press plate (emulsion 4063), and Eastman Hyper Press plate (emulsion 3082) have speed 660, γ_6 1.05 for the former, and speed 1250, γ_6 0.86 for the latter.

and by that proposed by Jones and Russell (13). In the latter system, the speed is taken as proportional to the reciprocal of the exposure (E_m) corresponding to the minimum useful gradient, which is taken as $G=0.20$. For purposes of comparison the maximum value of each of the curves in Figure 3 has been made equal to 1.00.

As in most of the other cases of after-ripening, the curves of 4–68 at various digestion times differ not only in speed but in contrast and shape. The variation in sensitivity can not be adequately expressed by any single constant, but the speed number based on minimum useful gradient is evidently the best approximation to such an expression. Speed numbers in both systems are found to be dependent on time of development, falling in line with the results obtained by Davis and Neeland (14) with commercial emulsions. The reader is referred to their paper for a more complete intercomparison of the systems. The speed numbers given in this paper are an average value for the three times of development.

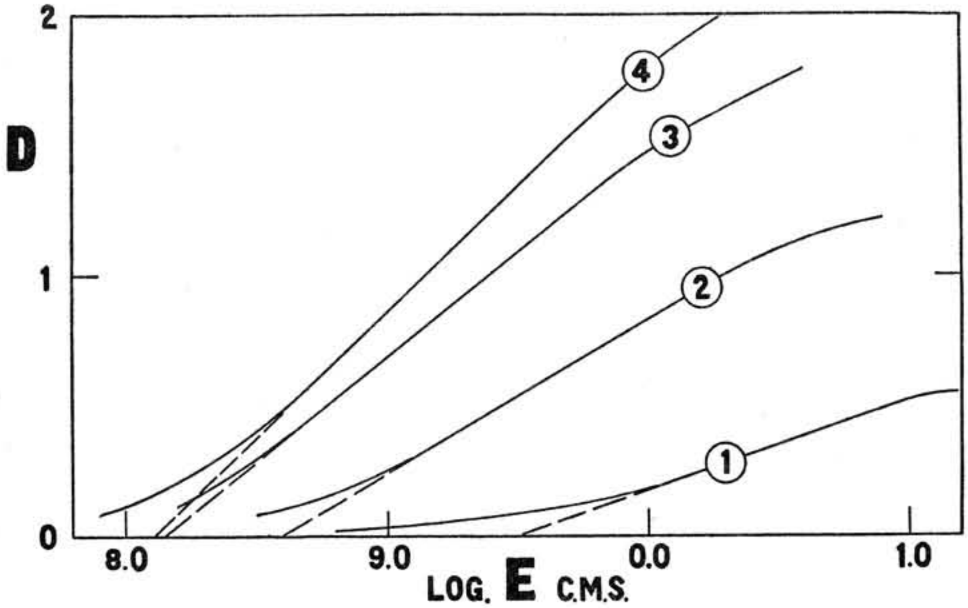

Figure 1.—*Characteristic curves, 6-minute development of emulsion 4–68 at four stages of after-ripening*

Digestion at 55°, pH 7 [Br^-] 5×10^{-3} *N*. Curve 1, minimum digestion; curve 2, 1.0 hour; curve 3, 2.0 hours; curve 4, 3.0 hours

Table 1.—*Comparison of methods of expressing sensitivity of emulsion 4–68 at different stages of after-ripening*

Time of digestion (in minutes at 55°)	6-minute development				12-minute development			
	B. S. speed number 10/i	γ	Jones and Russell speed number 10/E_m	Fog	B. S. speed number 10/i	γ	Jones and Russell speed number 10/E_m	Fog
5	31.6	0.35	22.4	0.03	45	0.40	38.9	0.10
60	275	.57	455	.03	182	.92	435	.13
120	710	.81	1,200	.06	505	1.25	1,230	.18
180	735	.99	1,380	.09	435	1.71	1,445	.24

2. APPARATUS AND PROCEDURE USED IN EMULSION MAKING

The emulsions were mixed in batches using 30 to 60 g of silver nitrate (0.176 to 0.35 mol), the final volume being 0.7 to 1.5 liters. These were subdivided into batches of 0.044 mol (equivalent to 7.5 g $AgNO_3$) for comparison of differences in times of digestion or other variables. In all cases, the silver solution was added in a continuous stream to the mixture of bromide, iodide, and gelatin; the rate was varied over a considerable range by the use of separatory funnels fitted with capillary stems of different bores. The mixing vessel was a 1.5 liter Pyrex beaker, with a mechanical stirrer running 200 to 300 r. p. m. Using a silver shaft running in a glass bearing in the glass cover plate over the beaker, neither the liquid emulsion nor the condensate from it could come into contact with any material except glass or silver. Silver in contact with liquid emulsion was found to blacken quite rapidly in use, apparently from formation of silver sulphide (see Lüppo-Cramer (15)), so the actual stirrer was made of glass.

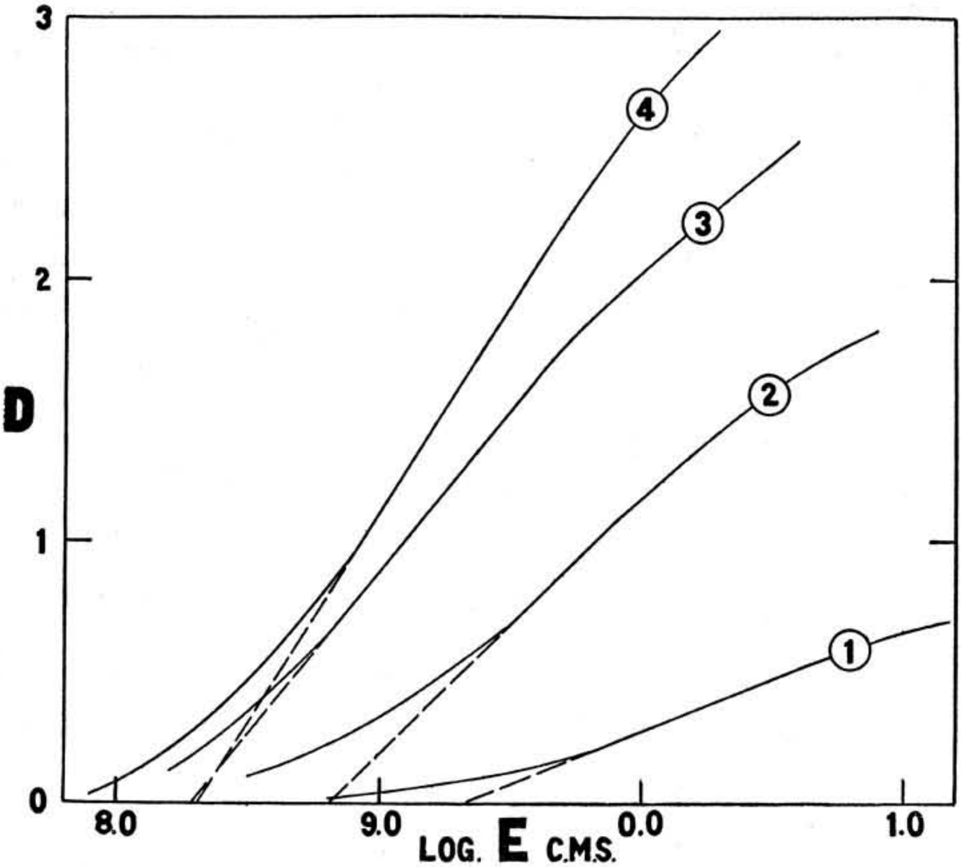

FIGURE 2.—*Characteristic curves, 12-minute development, of same emulsion as in Figure 1*

Both ordinary and centrifugal washing were used. For the ordinary method, the emulsions were rapidly chilled by pouring into a layer 1 to 2 cm thick in a clean enamelled tray floated on water at 5° to 8° C.; unless otherwise stated, they were left overnight at 5° to 8° C. before shredding and washing. Our shredding press forces the set jelly through a sieve built up from sharpened metal strips set on edge, cutting it into clean "noodles" 5 to 6 mm square in cross section; there is very little formation of fine material, and consequently good circulation of water through the mass of "noodles." Using these relatively large but clean-cut noodles, we find that washing is more rapid than when the emulsion is, for example, shredded through netting into "noodles" which have more tendency to pack into a tight mass. The shredded emulsions were placed in silver-plated cans with 20-mesh screens of pure nickel at the bottom; these rested in slightly larger crocks, and the water, at the rate of at least 0.5 liter per minute, passed down through the emulsion and out over the edge of the crocks. Washington city water was used without treatment other than filtering and cooling; the normal temperature was 7° to 8° C., average hardness of the water, calculated as $CaCO_3$, 80 mg per liter. The washing was very thorough, lasting 6 to 8 hours, with frequent hand stirring of the emulsion; for experimental purposes at least it is much more satisfactory to wash completely and add soluble bromides as desired, rather than to attempt to leave a definite amount. In the absence of ammonia in the emulsion, the pH after washing was 7 ± 0.5; if it was made with ammoniacal silver oxide, the pH might be as high as 8.5.

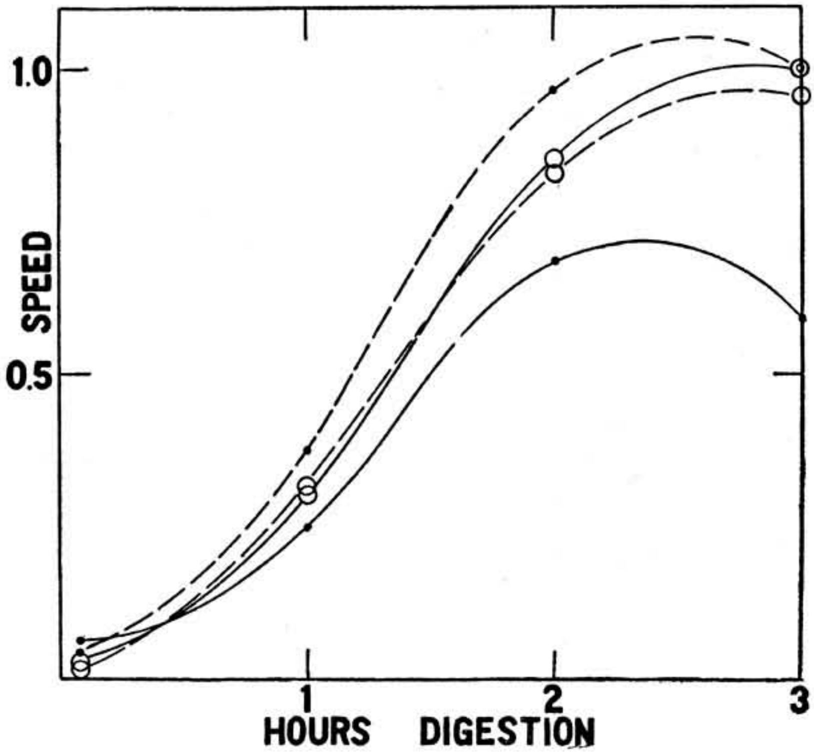

Figure 3.—*Speed numbers of emulsion 4–68 at four stages of after-ripening by National Bureau of Standards (.) and Jones and Russell (o) systems, plotted against time of digestion*

The maximum in each system has been made equal to 1. Dashed lines 6-minute development; solid lines, 12-minute development.

Our methods of centrifugal washing have already been described (7) (16); briefly, at the end of the desired ripening time, the silver halide is separated from the liquid emulsion, using a 5-inch imperforate bowl at 3,000 r. p. m. The silver halide collects on the walls of the bowl in an adherent layer carrying considerable adsorbed gelatin, but is readily reemulsified by covering with 1.5 per cent gelatin solution and rubbing gently. This "wash suspension" is again centrifuged, and the silver halide suspended in the more concentrated gelatin (about 60 g per liter) used for coating; two separations reduce the bromide ion concentration to a value comparable with that after ordinary washing.

The emulsion was always stirred continuously during mixing and ripening. This was not always practicable during digestion, but stirring was in every case frequent enough to prevent appreciable sedimentation. All emulsions were filtered through very open (Whatman 41) paper before coating, and a little alcohol was added to break froth and aid spreading. Chrome alum was not used on many of the earlier emulsions, but was found essential whenever the Weigert and Lühr method of analysis for silver + silver sulphide was to be applied. It has apparently no effect on sensitivity except by changing pH (9); this was generally neutralized by addition of an equivalent amount of sodium carbonate after the chrome alum solution. pH of the emulsions was determined colorimetrically after removing the silver halide from the sample by centrifuging.

The emulsions cover a considerable range of conditions, but they may all be considered as variations of three basic formulas in which, as far as possible, only single variables were changed. For example, in varying the amount of iodide, the bromide was correspondingly changed to retain the same percentage excess over the silver; if the size of the batch was changed the rate of flow of silver solution was correspondingly altered to maintain constant time of mixing. In the description of each general formula, we have given those factors which were varied in the course of the experiments. The descriptions of individual batches specify the variables which were changed from the values given in the general formula.

A. "Full ammonia" formula

Water	ml	125	Water	ml	225
$AgNO_3$ (0.176 mol)	g	30.0	NH_4Br (0.220 mol)	g	21.5
NH_4OH, concd. (0.353 mol) to redissolve			KI (0.00175 mol)	g	0.29
			Gelatin	g	12.5

The excess of soluble bromide was maintained at 25 per cent as given. The iodide as given corresponds to the formation of 1.0 mol per cent of AgI, assuming complete precipitation of the iodide, but iodide also was varied from 0 to 5 per cent. The solution of ammoniacal silver oxide, at about 35°, was run into the halide-gelatin solution, held at $45.0° \pm 0.5°$ in 2½ to 4 minutes; ripening was continued at 45° C.

In case centrifugal washing was used, nothing further was added to the emulsion before centrifuging. The quantity given was centrifuged in four batches; it was suspended again in 400 ml of 1.5 per cent gelatin, and might be stored over night at 5°, at this point. After centrifuging again, the emulsion was usually suspended in a total of 700 ml of water and 50 g gelatin; it was digested in this suspension. Where the effect of ripening time was under study, the four batches were taken out at intervals during ripening and kept separate thereafter. The necessary time for centrifuging four batches was 20 to 25 minutes, so that there was always at least this much difference in the ripening time of the first and fourth.

For ordinary washing, 37.5 g of "secondary" gelatin, previously swelled for 20 minutes in cold distilled water, was added at the conclusion of ripening, and the emulsion rapidly chilled as soon as it was dissolved. It will be noted that the total amount of gelatin in the final suspension is the same in all cases, except in the emulsions where the gelatin-silver halide ratio was the variable under study.

B. "Full ammonia" formula

Water	ml	250	Water	ml	500
$AgNO_3$ (0.353 mol)	g	60.0	NH_4Br (0.409 mol)	g	40.0
NH_4OH, concd. (0.71 mol) to redissolve.			KI (0.0035 mol)	g	0.58
			Gelatin	g	30.0

This fomula was used only in one size batch, 60 g $AgNO_3$. Iodide was sufficient to give 1.0 to 5.0 mol per cent AgI, the excess bromide being kept constant at 17 per cent. The halide-gelatin solution was kept at 45.0° ± 0.5° during mixing, which took 4½ to 7 minutes, and ripening. After ripening to 25 minutes from the start of the mix, 70 g of swelled secondary gelatin was introduced, taking 7 to 10 minutes, and the emulsion chilled. Washing was always by the conventional method.

C. Neutral formula

Water	ml	450	Water	ml	350
$AgNO_3$ (0.353 mol)	g	60.0	NH_4Br (0.429 mol) or equivalent KBr	g	42.0
			KI (0.0139 mol)	g	2.30
			Gelatin	g	20.0

The excess bromide is here given as 25 per cent, but 12.5 per cent was also used. Iodide was varied from 1 to 4.0 mol per cent. Time of mixing was also varied from 9 to 30 minutes. The usual temperature was 65°, but 55° and 52° were also used. Eighty grams of swelled secondary gelatin was added to a batch of the above size; unless otherwise specified, it was added directly after mixing was completed.

Centrifugal washing was used in a few cases; except in the specified cases, no secondary gelatin was added before centrifuging. The process was the same as in formula A.

3. ANALYTICAL METHODS

Bromide ion concentration in the emulsions was determined by the silver-silver bromide electrode at 30.0° C.: the apparatus is to be described in a future paper on some of the photographic effects of bromide ion concentration in the emulsion. It was not available for some of the earlier experiments.

The silver-silver bromide electrode is described in the literature as quite imperfectly reproducible, which is correct as compared to standard reference electrodes, but by using well-annealed silver wires, carefully cleaned whenever they showed signs of sluggishness, results were reproducible to ± 1 millivolt or better. This is fortunately negligible in determining any of the photographic effects of bromide ion concentration. Determinations in the emulsions are obviously favored by the enormous surface of the silver halide present, which maintains equilibrium.

III. EFFECT OF CERTAIN VARIABLES ON AFTER-RIPENING BY DIGESTION

1. RIPENING

Because of the limited capacity of our centrifuge, the data in Table 2 were necessarily obtained by making a series of emulsions, each subdivided into batches of different ripening time; digestion time was increased from the practicable minimum for all four batches of 8–101, to a maximum of 145 minutes for 8–99. The average grain size increased normally with time of ripening: average projective areas for 8–100 were (1) 0.26 μ^2, (2) 0.39 μ^2, (3) 0.52 μ^2, (4) 1.00 μ^2. In view of the similarity of the other conditions, the differences in maximum speeds reached at optimum digestion times may reasonably be ascribed almost entirely to the change in grain size; a quantitative relation would be very difficult to obtain on these emulsions because of the heavy fog correction. In Figure 4, speed, for given ripening time, is plotted against digestion time; the data are seen to fall into a family of curves, with marked maxima. The optimum time of

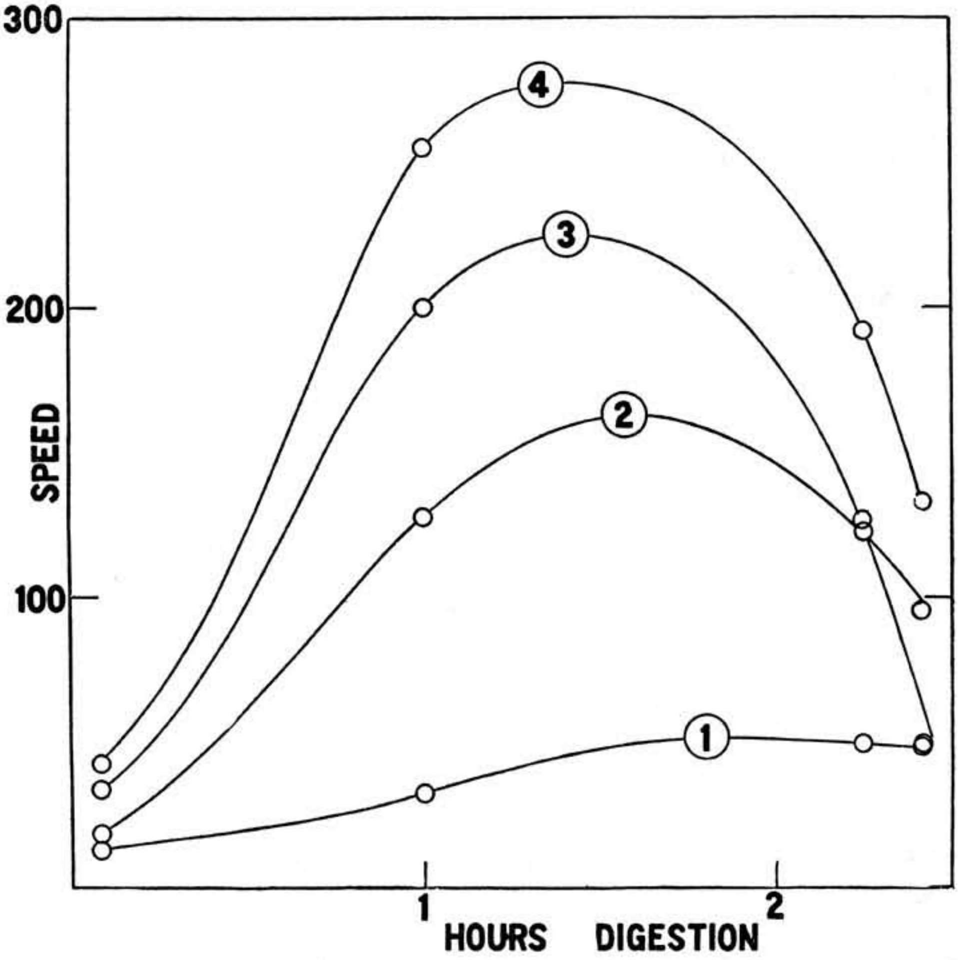

FIGURE 4.—*Speed of centrifuged ammonia-process emulsions at four times each of ripening and digestion*

Ripening time for emulsions in curve 1, approximately 5 minutes; curve 2, 0.5 hour; curve 3, 1.0 hour; curve 4, 2.0 hours digestion decreases as the time of ripening increases; as these emulsions were ripened in 0.9 N NH_3, there must have been relatively rapid formation of sensitivity nuclei during ripening, in spite of the presence of 0.11 N NH_4Br. The time of digestion to attain the optimum formation of nuclei is therefore reduced. It will be noted that the optimum digestion time is the same for one hour and two hours ripening and that the fog in the latter case is actually less; this has been previously observed. (See Table 1, reference 7.)

TABLE 2.—*Effect of previous ripening on after-ripening during digestion*

[Formula A, 1 per cent AgI centrifugal washing; Winterthur (8565) gelatin in mix digestion in untreated Winterthur (8565) gelatin]

Emulsion No.	Ripening time	Time of digestion	Speed	γ			Fog		
				3	6	12	3	6	12
	Minutes	*Minutes at 45°*							
8-101-1	6	<10	13	1.05	1.46	1.60	0.05	0.08	0.11
2	35	<10	19	.50	1.15	1.40	.19	.26	.31
3	63	<10	34	.40	.67	.77	.21	.32	.36
4	121	<10	43	.34	.50	.60	.27	52	.69
8-102-1	7	60	33	1.45	2.15	3.00	.10	.11	.15
2	33	60	128	.70	1.30	1.75	.22	.29	.39
3	63	60	200	.55	1.00	-------	.27	.37	-------
4	119	60	255	.45	.80	1.15	.27	.45	.57
8-100-1	7	135	50	.95	1.45	2.03	.90	.13	.37
2	30	135	127	.70	1.05	1.55	.17	.26	.60
3	62	135	123	.70	1.03	1.37	.24	.46	.85
4	135	135	192	.57	.87	1.33	.28	.41	.82
8-99- 1	12	145	49	1.30	2.14	2.77	.06	.10	.25
2	35	145	96	1.04	1.53	1.95	.14	.27	.56
2	62	145	50	.70	1.20	1.47	.27	.56	1.01
4	120	145	133	.55	.87	1.23	.21	.49	.82

TABLE 3.—*Effect of previous ripening on after-ripening during digestion*

[Neutral (C) emulsions; 1 per cent AgI; normal washing; Winterthur and Nelson No. 1 gelatin; digested at 45°]

Temperature of mix	Time of mix	Excess NH_4Br	Bromide ion concentration during digestion	Time of digestion	Speed	γ			Fog			Emulsion No.	Average grain size (projective area in μ^2)
						3	6	12	3	6	12		
	Minutes	*Per cent*		*Minutes at 45°*									
65°	36	25	$1.6\times10^{-5}N$	10	160	0.23	0.33	0.42	0.01	0.03	0.11	4-63-1	1.05
				60	245	.40	.63	1.01	.02	.05	.19	2	
				120	440	.46	.75	1.30	.06	.09	.25	3	
				180	505	.65	.80	1.45	.06	.11	.29	4	
55°	31½	25	$1.4\times10^{-5}N$	10	80	.25	.36	.48	.00	.02	.05	4-62-1	.53
				80	175	.63	1.09	1.56	.04	.06	.11	2	
				160	265	.81	1.25	1.83	.05	.07	.15	3	
				240	290	.80	1.35	1.89	.08	.11	.20	4	
52°	25½	12.5	$1.8\times10^{-5}N$	[1] 10	34	.36	.55	.66	.02	.04	.08	4-64-1	.34
				60	120	.84	1.22	1.75	.07	.10	.18	3	
				130	205	.92	1.14	1.88	.06	.17	.30	5	
				240	215	1.00	1.55	2.23	.16	.22	.39	7	

[1] Bromide ion concentration $7.6\times10^{-4}N$.

The data on neutral emulsions with the same percentage silver iodide, show the expected differences in maximum speed corresponding to changes in grain size.

The time required for digestion to maximum speed was about 220 minutes for emulsion 4–62, 195 minutes for 4–64, and 180 minutes for 4–63. It was thus reduced by increase in temperature of ripening, and by decrease in excess of soluble bromide; both of these changes obviously favor the formation of nuclei during ripening. In all three cases, it is considerably greater than is required for ammonia emulsions ripened to the same average grain size.

2. TEMPERATURE

The chemical reactions involved in after-ripening may be expected to have a temperature coefficient of two or more for every 10°. The correlation between these reactions and the photographic properties is unknown, but a similar temperature coefficient for after-ripening is a reasonable prediction. Tables 4, 5, 6, 10, and 11 show that it is verified under a variety of conditions. The rate of photographic change with time can not be satisfactorily expressed by any formula which we have tried, so we can obtain only a rough estimate. The time required to reach maximum sensitivity at 45° is about three times as great as at 55°; taking the initial slope of the speed, time of digestion curve, the coefficient is about 4.

TABLE 4.—*Effect of digestion temperature on after-ripening*

[Neutral (C) emulsion 4–58; 4 per cent AgI; Winterthur and Nelson No. 1 gelatin; normal washing; [Br⁻] $2.5 \times 10^{-5} N$ at start of digestion; coating pH 7.2]

Digestion temperature	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes							
45.0°	10	82	0.21	0.32	0.52	0.02	0.03	0.09
	60	137	.39	.67	.86	.02	.05	.14
	128	290	.47	.64	1.20	.05	.05	.11
	240	355	.62	.87	1.37	.06	.10	.17
	360	310	.58	.82	1.24	.21	.33	.51
54.2°	40	330	.60	.92	1.36	.03	.06	.17
	80	475	.56	.90	1.39	.09	.12	.18
	120	495	.55	.84	1.39	.10	.14	.22

TABLE 5.—*Effect of digestion temperature on after-ripening*

[Neutral (C) emulsion 4–65; 1 per cent AgI; Winterthur and Nelson No. 1 gelatin; normal washing; [Br⁻] $9 \times 10^{-4} N$, coating pH 7.0]

Digestion temperature	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes							
45°	10	32	0.32	0.42	0.63	0.00	0.02	0.05
	75	55	.47	.70	1.16	.01	.02	.05
	135	81	.64	.81	1.43	.03	.05	.10
	240	140	.78	1.21	1.90	.05	.08	.14
	360	140	1.02	1.42	2.40	.22	.26	.45
55°	30	102	.52	.80	1.47	.02	.04	.13
	60	180	.73	1.20	2.03	.05	.07	.21
	90	195	1.02	1.44	2.10	.06	.08	.23

TABLE 6.—*Effect of digestion temperature on after-ripening*

‘Full ammonia (B)” emulsion, No. 1-160; 5 per cent AgI; Nelson No. 1 gelatin; initial [Br⁻] during digestion $9\times10^{-6}N$, coating pH 6.9]

Digestion temperature	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes							
45°	10	81	0.30	0.33	0.37	0.00	0.03	0.09
	60	127	.84	1.16	1.60	.02	.06	.15
	120	230	.91	1.43	2.25	.04	.09	.19
	240	240	1.04	1.56	2.43	.06	.09	.21
	360	205	1.10	1.75	2.46	.08	.15	.27
54.5°	45	210	1.07	1.79	2.52	.05	.09	.19
	90	220	.91	1.42	2.37	.18	.27	.36
	135	143	1.10	1.75	2.45	.31	.48	.69

Neutral emulsions with 1 per cent AgI were digested at 45° and 55° in two narrow ranges of bromide ion concentration: Curves of speed against time are given in Figure 5 from data in Tables 5, 10, and 11. It will be noted that in the presence of added soluble bromide ([Br⁻] around 1×10^{-3} N), the temperature coefficient is greater than in the emulsion as washed ([Br⁻] around 1.8×10^{-5} N).

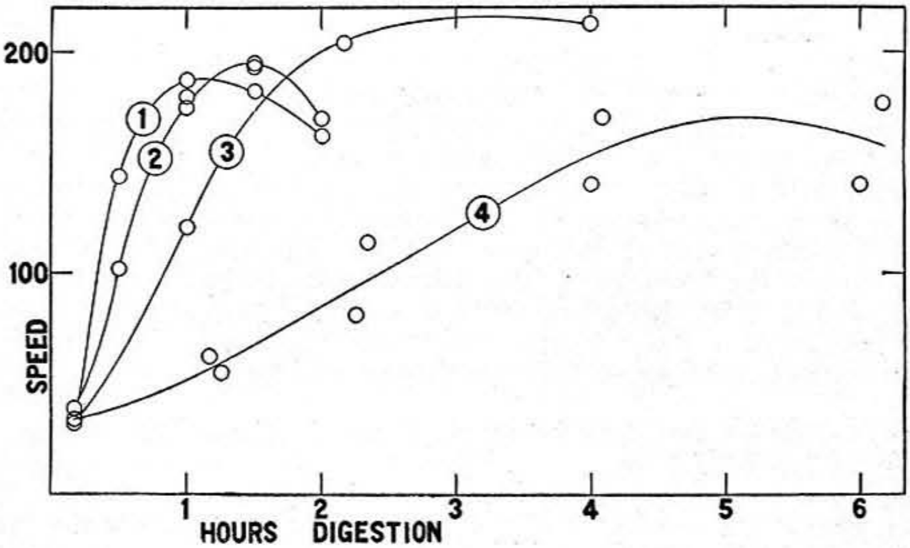

FIGURE 5.—*After-ripening of neutral emulsions, 1 per cent AgI, under varying conditions of digestion*

Curve 1, 55°, as washed; curve 2, 55°, with 5 KBr per 1,000 AgBr; curve 3, 45°, as washed; curve 4, 45°, with 5 KBr per 1,000 AgBr

The maximum sensitivity reached at 45° and at 55° C. is not widely different in any case. In spite of statements in the literature (3), (2), that low temperature and long time are generally desirable, 55° is very definitely better than 45° for the neutral emulsions with 4 per cent AgI. (Table 4.) In the neutral emulsions with 1 per cent AgI, the order depends on the bromide ion concentration during digestion. The ammonia process emulsion with 5 per cent AgI is slightly better at 45°. One feature of the long digestion at 45° is noteworthy—the sudden increase in fog after four hours (Tables 4, 5, and 10); this is not associated with sedimentation, since the emulsions were stirred continuously during this period.

3. BROMIDE ION CONCENTRATION

Any reaction forming silver or silver sulphide from silver bromide is practically sure to liberate bromide ions, the only other alternative being the formation of an un-ionized addition product. It is therefore obvious that after-ripening will be retarded by increasing bromide ion concentration,[7] if it is actually a matter of the formation of silver or silver sulphide nuclei. The extent of the retardation may be expected to throw some light on the mechanism of the reaction, although interpretation of the photographic data is again handicapped because we do not know the relation between the extent of the reaction and the resulting changes in photographic sensitivity. Sheppard and his associates have shown that the formation of silver sulphide during after-ripening takes place by rearrangement of the adsorbed complex of silver bromide and sensitizer, and we believe that the evidence indicates that, if reduction to metallic silver plays a part in after-ripening, it takes place by a similar mechanism. It is at least quite improbable that sensitivity nuclei are produced by the reduction or other reaction of the silver halide in solution in the emulsion. It may safely be assumed that in the emulsion, with the enormous available surface of the silver bromide grains, the product of silver and bromide ion concentrations is practically constant [8] at all times, so that if one is varied, the other changes nearly in inverse ratio. Assuming the simple mass law expression for the reaction of silver ion with the sensitizing material, if the bromide ion concentration of an emulsion is increased by fifty times, the velocity of a reaction involving silver ion should be divided by the same factor. However, bromide ion concentrations determined at 30° must be applied with caution to calculations of conditions at higher temperatures, since, interpolating the available data, the solubility of AgBr at 45° is twice that at 30°, and at 55° is three times the 30° value. The ratio of the bromide ion concentrations in the batches of emulsion with and without added bromide was, therefore, materially less at 45° or 55° than at 30°. Corrections to the mass law for ionic reactions such as that of Bronsted (17), would not change the order of magnitude.

Inspection of the data in Tables 7 to 14 shows that increase in bromide ion concentration decreases the rate of after-ripening, but that there is nothing of the order of an inverse proportion. The analytical evidence (Sec. V of this paper) which is theoretically much better than the photographic, is as decidedly against the hypothesis of an ionic reaction.

The curve of speed against time of digestion has a distinct S shape. This might be interpreted as an autocatalytic reaction; there is some justification for this, in that the formation of the new phase (Ag or Ag_2S) might catalyze the further breakdown of the silver bromide-sensitizer addition product. It is more likely that it represents the varying rate of change in photographic sensitivity with a relatively constant rate of reaction; if we assume that fog is caused by the formation of oversize sensitivity nuclei (18), the enormous increase

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[7] The concentrations used during ripening and digestion were of different orders of magnitude; the maximum amount present during digestion probably tends to decrease the solubility of silver bromide by mass action, rather than to raise it by complex ion formation as do the high concentrations used in ripening.

[8] The solubility product of silver bromide is not affected by the gelatin (Winther, Trans. Faraday Soc., **19**, p. 280; 1923); it must be slightly affected by the proportion of silver iodide, but our statement is correct for the results of adding soluble bromide to a given emulsion.

in fog, which can occur if after-ripening is continued too long, indicates that only a small proportion of the sensitizer has been used when the sensitivity reaches its maximum. On this basis, the relatively flat maximum found in most cases is readily explained by a balance between the grains still increasing in sensitivity and those lost by increase in fog or reduced in sensitivity by competition between nuclei (20). This reasoning must be used with caution, as the growth of fog has some of the characteristics of a secondary reaction. (See discussion (18).) This in turn may be explained by the very probable assumption that the hydrolysis of the gelatin during ripening or digestion continually liberates active sensitizing or fogging materials from less labile compounds. The curves of speed against time of digestion could not be fitted by any simple equation with sufficient accuracy so that the constants would be useful as a measure of change in sensitivity. One of the most obvious extensions of this investigation will be a more accurate and complete determination of the progress of after-ripening under known conditions, such as inert gelatin plus a sensitizer.

Tables 7 to 14 are designed to show the effect of bromide concentration during digestion, with a wide variety of emulsions. The most complete set of data on a single type are given in Table 9 and Figure 6. These represent the digestion of a high-speed type of emulsion as washed, and with three different additions of soluble bromide. On examination of Figure 6, the rate of after-ripening is seen to have decreased steadily as the bromide ion concentration was increased, but the speed for optimum digestion time rose to a maximum at $[Br^-] = 9.6 \times 10^{-4}$; the corresponding amount of bromide added, 5 KBr/1,000 AgBr, was of the same order as is found in most fast commercial emulsions (3 to 10 KBr/1,000 AgBr).[9] The maximum speed fell off again when the bromide was increased to 20 KBr/1,000 AgBr ($[Br^-] = 4.7 \times 10^{-3}$), probably because the direct effect on sensitivity of a high bromide ion concentration (19) counteracts the favorable influence on after-ripening. Bromide present during digestion retards the increase in fog to a greater extent than the after-ripening. The increase in maximum speed which is permitted by the use of the proper amount of bromide appears to be greater than can be explained by the decrease in fog; the same problem comes up when increasing amounts of a nuclear sensitizer, such as allyl thiocarbamide, are added to emulsions under presumably constant digestion conditions (20). Sheppard has introduced the hypothesis of competition between nuclei on the same grain to explain the existence of an optimum concentration of sensitizer. This may equally well be applied to the existence of an optimum time of digestion, and less plausibly, to the increase in maximum speed obtained by adding bromide before digestion. In this last case the reduced rate of reaction might favor the continued growth of a single nucleus as against the further formation of new ones. Many of our emulsions (Sec. IV of this paper) have reached higher sensitivity by storage ripening than by digestion; here we have a slow process in which the formation of a new phase might be strongly inhibited, so that again the

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[9] Our analyses, which agree with those published by the Eastman laboratories at various times, show that soluble bromide is either added after washing, or else the washing is stopped short of completion. Wall, Photographic Emulsions, p. 154, refers to the addition of bromide as "an heirloom from the early days when a clean-working emulsion was practically an exception," but present quantities are, instead, considerably larger than those recommended by Eder.

growth of a nucleus already started would be favored against the beginning of a new one.

The after-ripening of all the types of emulsion is qualitatively very similar. We may make the rough generalizaton that a given amount of soluble bromide (5 KBr/1,000 AgBr) retards after-ripening most in those cases where it is the most rapid at a given temperature; the ammonia-process emulsions furnish the examples of this, probably because of their higher pH. We have already observed the greater effect on emulsion 4–64 (Table 10) which was digested at 45°, as compared to the otherwise identical 4–66, digested at 55° (Table 11). Much more complete data will be necessary for mathematical analysis of any of the cases.

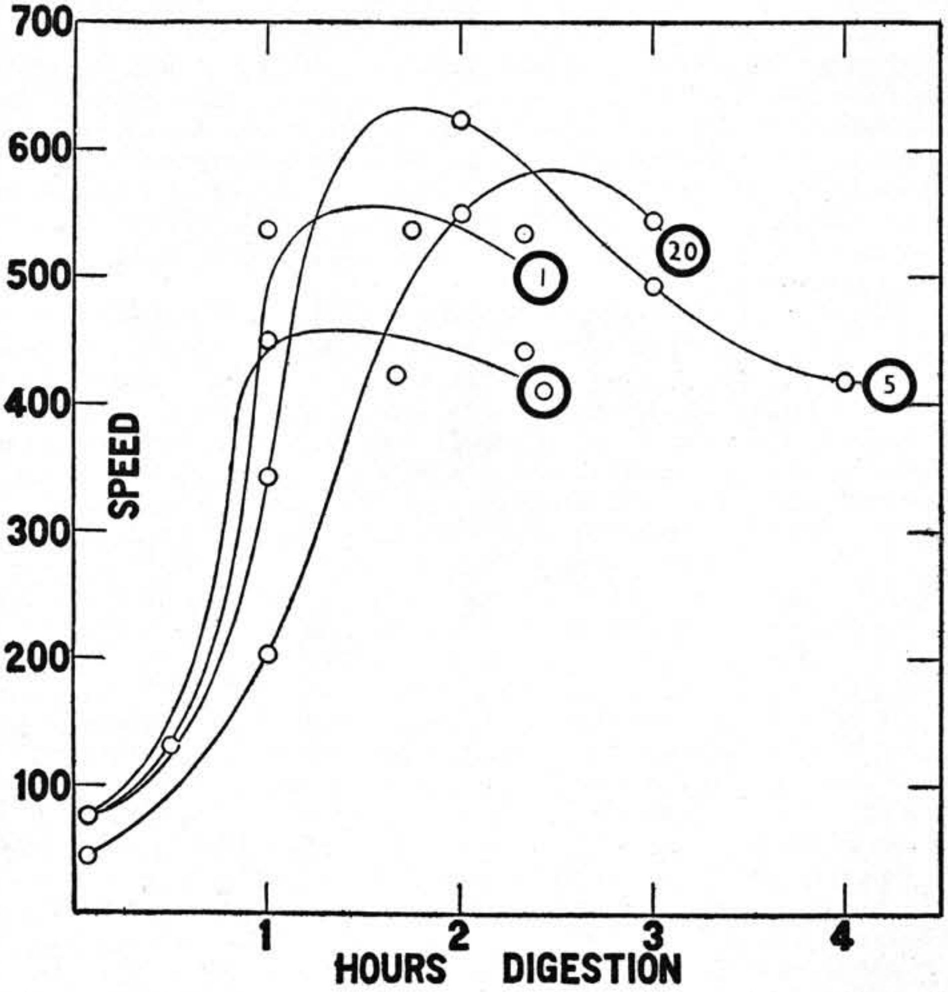

Figure 6.—*After-ripening of neutral emulsions, 4 per cent AgI, at 55°, with varying concentrations of soluble bromide*

Numbers of curves indicate the amount of bromide added, in terms of mols KBr per 1,000 mols AgBr

Increase in fog during after-ripening was less than we had expected. Table 12 gives an unusually favorable case in which there was actually a decrease. In general, the fog increases suddenly after a certain time, but this is usually past that required for the maximum sensitivity: after-ripening is more likely to be limited by decrease in speed than by increase in fog. The addition of soluble bromide considerably increases the margin of safety in time between the points of maximum sensitivity and of rapid increase in fog, and reduces the rate of increase of fog during the useful period of digestion. We have already noted (p. 231) that the cases in which the sudden deterioration began before the maximum sensitivity was reached were on prolonged digestion at 45°.

TABLE 7.—*Effect of bromide ion concentration during digestionon after-ripening*

[Emulsion 4-53; neutral "C" formula; 4 per cent AgI, 25 per cent excess NH_4Br; mixed at 65°; Winterthur gelatin; digested at 55°; coating pH 5.9]

Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes							
6.4×10^{-6} *N* (as washed)	5	42	0.31	0.48	0.63	0.02	0.05	0.09
	30	92	.58	.92	1.21	.02	.04	.13
	60	200	.63	1.01	1.25	.03	.07	.13
	100	350	.64	1.03	1.23	.05	.11	.17
5.1×10^{-4} *N* $\left(\frac{5\ \text{KBr}}{1{,}000\ \text{AgBr}}\right)$	5	17	.27	.35	.40	.02	.04	.09
	30	31	.37	.57	.73	.02	.04	.09
	68	100	.43	.67	.96	.03	.06	.09
	135	270	.54	.86	1.08	.04	.07	.11

TABLE 8.—*Effect of bromide ion concentration during digestion on after-ripening*

[Emulsion 4-59; 4 per cent AgI; 25 per cent excess NH_4Br; Winterthur gelatin; neutral mixed at 65 followed by ammonia ripening at 45°; coating pH 6.8. Digested at 55°]

Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes at 55°							
1.2×10^{-5} *N* (as washed)	5	70	0.34	0.50	0.66	0.03	0.04	0.13
	45	300	.63	1.07	1.49	.04	.10	.21
	90	390	.66	.94	1.24	.09	.11	.16
	135	340	.59	--------	1.45	.20	--------	.31
3.3×10^{-4} *N* $\left(\frac{2.5\ \text{KBr}}{1{,}000\ \text{AgBr}}\right)$	45	182	.49	.85	1.15	.04	.08	.17
	95	400	.60	1.03	1.47	.06	.11	.24
	140	420	.53	.80	1.26	.15	.19	--------
	190	[1] 315	.65	1.01	1.51	.19	.24	.34

[1] No decrease in effective sensitivity.

TABLE 9.—*Effect, on after-ripening, of bromide ion concentration during digestion*

[Emulsions 4-61 and 4-68; neutral (*C*), 4 per cent AgI, 25 per cent excess NH_4Br, Winterthur and Nelson No. 1 gelatin; mixed at 65° in 26-7 minutes]

Soluble bromide added after washing	Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog			Emulsion No.
				3	6	12	3	6	12	
		Minutes at 55°								
None	$1.5\times10^{-5}N$	60	450	0.81	1.04	1.50	0.09	0.14	0.26	4-61-2
		100	425	.65	1.06	1.60	.19	.34	.54	4
		140	440	.64	.96	1.50	.22	.43	.67	6
$\frac{1\ KBr}{1{,}000\ AgBr}$	$1.5\times10^{-4}N$	30	132	.51	.83	1.24	.02	.04	.14	4-68-1
		60	535	.54	1.23	1.45	.06	.10	.20	2
		105	535	.57	.99	1.56	.10	.18	.29	3
		140	535	.66	1.06	1.65	.10	.18	.31	4
$\frac{5\ KBr}{1{,}000\ AgBr}$	$9.6\times10^{-4}N$	5	76	.16	.20	.32	.03	.08	.13	4-61-1
		60	345	.46	.76	1.24	.05	.08	.14	3
		120	625	.64	.90	1.53	.08	.13	.18	5
		180	495	.66	.90	1.43	.16	.29	.37	7
		240	420	.66	1.12	1.68	.13	.24	.40	8
$\frac{20\ KBr}{1{,}000\ AgBr}$	$4.7\times10^{-3}N$	5	45	.21	.25	.47	.00	.02	.05	4-68-5
		60	205	.35	.53	.80	.01	.03	.06	6
		120	550	.42	.73	1.20	.04	.05	.11	7
		180	545	.50	.90	1.54	.06	.09	.16	8

TABLE 10.—*Effect of bromide ion concentration during digestion, on after-ripening*

[Neutral (C) emulsion No. 4-64; 1 per cent AgI, Winterthur and Nelson No. 1 gelatin; digested at 45°]

Bromide ion concentration during digestion	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes at 45°							
$7.6\times10^{-4}N\left(\frac{5\ KBr}{1{,}000\ AgBr}\right)$	10	34	0.36	0.55	0.66	0.02	0.04	0.08
	70	62	.46	.77	1.13	.02	.04	.09
	140	114	.64	.94	1.20	.04	.07	.13
	245	165	.66	1.04	1.76	.07	.09	.16
	370	175	.71	1.13	2.11	.27	.46	.67
$1.8\times10^{-5}N$ (as washed)	60	121	.84	1.22	1.75	.07	.10	.18
	130	205	.92	1.14	1.88	.06	.17	.30
	240	215	1.00	1.55	2.23	.16	.22	.39

TABLE 11.—*Effect of bromide ion concentration during digestion, on after-ripening*

[Emulsion 4-66, neutral (C) formula, 1 per cent AgI; Winterthur and Nelson No. 1 gelatin; digested at 55°]

Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes at 55°							
$1.5\times10^{-5}N$ (as washed)	30	150	1.12	1.83	2.35	0.09	0.13	0.22
	60	190	1.23	1.55	2.38	.15	.24	.37
	90	180	1.01	1.41	2.12	.13	.20	.36
	120	160	.83	1.60	1.91	.11	.21	.48
$1.2\times10^{-3}N\left(\frac{5\ KBr}{1{,}000\ AgBr}\right)$	5	39	.26	.33	.48	.00	.00	.03
	60	175	.65	1.18	1.85	.03	.08	.18
	90	195	.80	1.26	2.29	.08	.11	.26
	120	170	1.02	1.63	1.88	.10	.14	.34

Table 12.—*Effect on after-ripening of bromide ion concentration during digestion*
[Emulsion 1–159; "B" formula, 5 per cent AgI, Nelson No. 1 gelatin. Digested at 45°, pH 8.3; coating pH 6.1]

Bromide ion concentration at beginning of digestion	Time of digestion,	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes at 45°							
$3.3\times10^{-6}N$ (No bromide added after washing)	<10	59	0.41	0.63	0.95	0.01	0.06	0.19
	53	110	.65	1.37	2.27	.01	.07	.28
	110	200	.79	1.37	2.04	.01	.07	.16
	180	200	.85	1.56	2.32	.02	.06	.15
$5.8\times10^{-4}N$ (5 KBr per 1,000 AgBr added after washing)	<10	22	.25	.37	.44	.07	.09	.21
	60	28	.40	.81	1.00	.01	.06	.19
	120	49	.54	.93	1.16	.02	.07	.12
	205	92	.66	1.15	1.60	.01	.06	.09

Table 13.—*Effect on after-ripening of bromide ion concentration during digestion*
[Emulsion 1–161; "B" formula, 5 per cent AgI, Winterthur gelatin. Digested at 45°, pH 8.0]

Bromide ion concentration at beginning of digestion	Time of digestion,	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes at 45°							
$1.8\times10^{-5}N$ (No bromide added after washing)	60	165	0.66	1.28	1.95	0.02	0.08	0.21
	130	320	.73	1.34	1.94	.04	.12	.27
	185	360	.82	1.47	2.14	.07	.12	.29
$8.6\times10^{-4}N$ (5 KBr per 1,000 AgBr added after washing)	<10	66	.22	.51	.61	.00	.03	.14
	90	115	.55	.89	1.12	.01	.04	.15
	180	240	.63	1.03	1.60	.02	.04	.14
	270	340	.71	1.15	1.68	.03	.04	.18
	360	400	.74	1.29	1.77	.11	.13	.24

Table 14.—*Effect on after-ripening of bromide ion concentration during digestion*
[Emulsion 1–162; "B" formula, 1 per cent AgI, Winterthur gelatin. Digested at 45°, pH 8.3]

Bromide ion concentration at beginning of digestion	Time of digestion,	Speed	γ			Fog		
			3	6	12	3	6	12
	Minutes at 45°							
$1.75\times10^{-5}N$ (No bromide added after washing)	60	87	0.95	1.70	2.13	0.01	0.07	0.19
	120	105	1.10	2.04	2.72	.04	.09	.27
	180	108	1.16	1.94	2.72	.06	.13	.33
$8.6\times10^{-4}N$ (5 KBr per 1,000 AgBr added after washing)	<10	46	.88	1.23	1.59	.00	.02	.10
	60	60	1.00	1.36	1.63	.01	.02	.10
	125	75	.95	1.44	1.78	.00	.02	.09
	210	88	1.01	1.51	2.02	.01	.04	.16
	300	107	1.02	1.65	2.23	.00	.06	.19

4. COMPARISON OF BROMIDE AND CHLORIDE IONS

The effect of bromide and chloride ions on after-ripening would be expected to be qualitatively similar; a considerable quantitative difference is introduced because the solubility of silver chloride (in mols per liter) is sixteen times that of the bromide, and the effect of chloride on silver ion concentration is correspondingly smaller. We should hardly have taken up this point if commercial emulsions had not been found (by electrometric titration of extracts) to contain as much as 38 mols of soluble chloride per 1,000 of silver halide. This amount can be introduced into the emulsion by adding gelatin after washing, since some brands, especially those of European manufacture, were found to contain as much as 3.0×10^{-4} mol of soluble halide per gram of gelatin. We have never found it necessary to use this procedure, but it is recommended in many emulsion formulas; the reason, when any is given, is to make the emulsion set more readily.

TABLE 15.—*Comparison of effects of bromide and chloride ions on after-ripening during digestion.*

[Neutral ("C") emulsions, Winterthur gelatin, normal washing]

Mol per cent AgI in emulsion	Soluble halide added after washing, in mols per 1,000 mols AgBr	Time of digestion, hours at 45°	Speed	γ			Fog		
				3	6	12	3	6	12
0.0	0	<0.2	44	0.47	0.78	0.87	0.09	0.18	0.28
	0	2.5	64	.58	.83	1.03	.10	.15	.28
	1 KBr	2.5	69	.70	1.12	1.30	.08	.23	.39
	50 NaCl	2.5	68	.50	.77	.90	.10	.20	.36
0.0	0	<.2	40	.48	.80	1.07	.08	.17	.33
	0	2.5	56	.68	1.00	1.21	.10	.19	.40
	1 KBr	2.5	61	.63	1.10	1.42	.08	.18	.36
	50 NaCl	2.5	39	.64	.93	1.14	.09	.18	.40
1.0	0	<.2	49	.46	.69	.92	.03	.04	.14
	0	2.5	82	.69	1.10	1.58	.05	.12	.25
	1 KBr	2.5	69	.67	.96	1.34	.02	.08	.18
	50 NaCl	2.5	84	.60	.86	1.30	.04	.09	.27
2.25	0	2.5	55	.61	.88	1.25	.03	.11	.20
	1 KBr	2.5	34	.44	.59	.80	.02	.05	.14
	25NaCl	2.5	47	.44	.64	.90	.03	.08	.21
2.25	0	<.2	57	.37	.54	.65	.05	.12	.21
	0	2.5	70	.53	.74	1.12	.08	.14	.27
	1 KBr	2.5	63	.47	.67	1.03	.08	.13	.27
	50 NaCl	2.5	70	.37	.56	.80	.07	.14	.27

TABLE 16.—*Comparison of effects of bromide and chloride ions on after-ripening by digestion*

["A" emulsions, Winterthur gelatin, normal washing]

Ripening temperature	Mol per cent AgI in emulsion	Soluble halide added after washing, mols per 1,000 mols AgBr	Time of digestion, hours at 45°	Speed	γ			Fog		
					3	6	12	3	6	12
40°	0.0	0	2.5	119	1.43	2.02	2.70	0.05	0.08	0.17
		1 KBr	2.5	39	1.35	1.90	2.35	.02	.07	.08
		25 NaCl	2.5	86	1.40	1.90	2.50	.02	.06	.11
	1.0	0	<.2	63	1.45	2.04	2.57	.05	.07	.13
		0	2.5	134	1.80	2.58	3.20	.05	.13	.21
		1 KBr	2.5	87	1.46	2.10	2.70	.02	.07	.10
		25 NaCl	2.5	150	1.55	2.10	2.90	.03	.11	.16
	2.25	0	<.2	27	1.70	2.30	2.60	.02	.08	.19
		0	2.7	58	2.25	3.30	4.60	.05	.10	.29
		1 KBr	2.7	34	2.00	2.60	2.80	.02	.07	.17
		25 NaCl	2.7	63	1.70	2.42	3.04	.03	.09	.25
45°	0.0	0	<.2	63	1.06	1.60	2.38	.06	.10	.24
		0	2.5	125	1.30	1.93	2.40	.06	.12	.30
		1 KBr	2.5	92	1.27	1.83	2.63	.05	.12	.29
		50 NaCl	2.5	141	1.23	1.63	2.32	.04	.11	.27
	1.0	0	<.2	61	.95	1.35	1.85	.03	.09	.25
		0	2.5	146	1.21	1.84	2.70	.06	.09	.34
		1 KBr	2.5	124	1.10	1.65	2.30	.04	.09	.28
		50 NaCl	2.5	167	1.12	1.45	2.15	.03	.11	.30
	2.25	0	<.2	44	1.22	1.90	2.30	.05	.10	.18
		0	2.5	77	1.58	2.24	2.95	.05	.13	.27
		1 KBr	2.5	55	1.55	2.40	3.00	.04	.08	.24
		50 NaCl	2.5	79	--------	1.90	2.64	--------	.10	.27

The experiments recorded in Tables 15 and 16 were made earlier than those in Tables 1, 2, and 3; the silver electrode apparatus was not yet in use, and the emulsions were all digested for 2½ hours at 45°.[9] This was near the optimum time for digestion, without added halide, of all the emulsions on which this point had been determined. It was possibly too much for the pure bromide emulsions, and very probably too little for those with 2.25 per cent AgI, so the results are considerably confused by the varying positions of this single time on the curve; they illustrate more than anything else, the danger of this procedure. The obvious difference between chloride and bromide is the depressing action of the former on the contrast. Higher densities were selectively depressed, with the result that the speed number was frequently highest in the batch digested with chloride.[10] It is impossible from these data to give an accurate estimate of the amount of chloride necessary to produce an effect equivalent to one part of bromide, but the ratio must be of the order of 50 to 1.

5. HYDROGEN ION CONCENTRATION

The reversible effect of hydrogen ion concentration on sensitivity was discovered by Rawling and Glassett (4) in an investigation of after-ripening. Rawling also mentions (9) the existence of an irreversible effect. We have measured changes in sensitivity in connection with the equilibrium between hydrogen ion, silver ion, and gelatin (to be published later), but have done relatively little with the important relation between hydrogen ion concentration and the rate of after-ripening.

The data in Table 17 make it possible to compare the after-ripening, during a single time of digestion, in two portions of the same emulsion at different hydrogen ion concentrations. Since figures are given for unripened and ripened portions at each value of pH, it is possible to eliminate the direct effect of hydrogen ion concentration on sensitivity; the work of Rawling (9) has shown that the ratio of sensitivity at two values of pH is unaffected by sensitization with thiocarbamide, and may, therefore, be expected to be independent of the degree of after-ripening. Comparing the ratios of the digested and undigested portions of both 1–148 and 1–149, it is evident that there was much less after-ripening at the lower pH. In emulsion 1–148, the speed of the undigested portion of pH 6 was 0.89 times that of the undigested portion of pH 8; the corresponding ratio for the portions digested without bromide is 0.56. In emulsion 1–149 the corresponding ratios are 0.85 undigested and 0.65 digested. In both emulsions γ was nearly independent of pH, so that the sensitivity ratio may be measured by the speed alone.

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[9] Data on the undigested emulsions are given for comparison in most cases.

[10] The data on pure bromide emulsions, Table 15, show a higher speed for the batches digested with bromide than those digested as washed; this is almost certainly because the latter were past the optimum.

TABLE 17.—*Variation in both hydrogen and bromide ion concentrations during digestion*

[Emulsions made by "A" formula Winterthur gelatin]

Emulsion No.	Soluble bromide added after washing, mols per 1,000 mols AgBr	pH	Time of digestion	Speed	γ			Fog		
					3	6	12	3	6	12
			Hours at 45°							
1-148, pure AgBr	0	8.1	<0.2	62	0.90	1.57	2.10	0.05	0.09	0.18
	0	8.1	2.3	126	1.12	1.74	2.26	.09	.13	.24
	2	8.1	2.3	70	1.00	1.70	2.10	.05	.09	.14
	0	6.0	<.2	55	.95	1.37	1.98	.06	.09	.21
	0	6.0	2.3	65	1.06	1.67	2.24	.05	.15	.25
	2	6.0	2.3	54	.88	1.50	2.02	.06	.09	.17
1-149 2.25 mol per cent AgI	0	8.2	<.2	33	1.55	1.80	2.40	.06	.12	.33
	0	8.2	2.5	45	2.15	3.05	4.40	.07	.14	.49
	2	8.2	2.5	37	1.86	2.60	3.70	.05	.14	.40
	0	6.5	<.2	28	1.67	2.26	3.00	.05	.12	.37
	0	6.5	2.5	29	1.90	2.78	4.28	.05	.17	.55
	2	6.5	2.5	13	1.90	2.64	3.90	.05	.14	.49

The emulsions listed in Table 18 were not tested without digestion, so that the reversible pH effect can not be eliminated; the object of this series was to compare the effect of a given addition of soluble bromide at two hydrogen ion concentrations. The result of changing pH before digestion is seen to be highly dependent on the gelatin, as already observed by Rawling for the reversible effect. The decrease in sensitivity with decreasing pH was greatest in emulsion 4–41. Emulsions 1–151 and 4–43, made with the same gelatin by different formulas, showed about the same effect, in agreement with the observations of Rawling; the magnitude is less than in 4–41. In emulsion 4–42, the normal effect of pH showed only on addition of bromide; when the emulsion was digested as washed, the very heavy fog at the higher pH indicates excessive after-ripening with consequent loss of speed, which obscures the normal effect. In this connection, it may be pointed out that, while our data agree with those of Rawling that the fog is practically independent of changes in pH just before coating, it is frequently dependent on pH during digestion.

In Tables 17 and 18 there are six cases in which a given amount of soluble bromide was added to two portions of the same emulsion, adjusted to different hydrogen ion concentrations. With the exception of emulsion 1–148, the bromide retarded after-ripening to a greater extent at the lower pH. The comparison was made only at a single time of digestion, and is less satisfactory than the complete curve of after-ripening against time, but it seems sufficient. This result may be stated in another way, that the effect of hydrogen ion concentration on after-ripening is greater at a lower bromide ion concentration. In this form, it may be predicted from the data on bromide ion concentration given in Table 18. On increasing the hydrogen ion concentration of an emulsion, there is a decrease in bromide ion concentration, because silver ions previously in combination with the gelatin are released. This decreasein bromide ion concentration acts in opposition to the increase in hydrogen ion concentration, since it accelerates after-ripening. In thoroughly washed emulsions, with very low bromide ion concentrations, the proportional change in concentration is much larger than in those to which soluble bromide has been added after washing; the observed effect of changing pH is therefore less.

TABLE 18.—*Variation in both hydrogen and bromide ion concentrations during digestion*

[All batches digested two and one-half hours at 45°. Emulsion 1–151 made by formula "A"; emulsions 4–41, 42, 43 made by that given by Rawling, reference 9, with increased time and temperature for the addition of the neutral silver nitrate solution]

Emulsion No.	Mol per cent AgI	Gelatin	Soluble bromide added after washing, mols per 1,000 mols AgBr	pH	Bromide ion concentration *N*	Speed	γ			Fog		
							3	6	12	3	6	12
1–151	1.0	UCOP 3029	0.0	7.0	5.4×10^{-6}	97	1.16	1.77	2.54	0.04	0.08	0.25
			1.0	7.0	4.3×10^{-5}	75	1.08	1.50	2.20	.02	.07	.16
			0.0	5.7	1.0×10^{-6}	83	1.04	1.53	2.70	.01	.11	.22
			1.0	5.7	3.1×10^{-5}	58	.97	1.55	2.08	.00	.08	.21
4–41	4.0	Winterthur	0.0	7.7	7.4×10^{-6}	405	.67	1.04	1.48	.28	.50	.74
			2.4	7.7	2.5×10^{-4}	360	.77	1.35	1.86	.08	.13	.24
			0.0	5.5	$7\ \times10^{-7}$	135	.75	1.25	1.98	.10	.22	.37
			2.4	5.5	2.3×10^{-4}	88	.67	1.25	1.98	.02	.08	.18
4–42	4.0	UCOP R-1333	0.0	7.8	8.5×10^{-6}	330	.71	1.07	1.50	.41	.76	1.37
			2.4	7.8	2.8×10^{-4}	290	.78	1.20	1.77	.24	.50	1.02
			0.0	5.9	1.1×10^{-6}	485	.63	1.15	1.80	.08	.24	.44
			2.4	5.9	2.4×10^{-4}	220	.83	1.40	2.10	.05	.20	.26
4–43	4.0	UCOP 3029	0.0	7	8.5×10^{-6}	160	1.00	1.55	2.25	.07	.11	.21
			1.0	7.5	8.2×10^{-5}	130	1.03	1.52	2.18	.04	.08	.18
			0.0	5.7	1.3×10^{-6}	123	.91	1.51	2.40	.02	.09	.22
			1.0	5.7	5.6×10^{-5}	87	.96	1.52	2.44	.02	.08	.20

6. GELATIN

(a) GELATIN-SILVER HALIDE RATIO

The addition of gelatin to the emulsion after washing frequently results in a decrease in sensitivity. In a few cases only this can be explained by decreased after-ripening as the result of adding chloride with the gelatin. The effect of gelatin-silver halide ratio per se was determined by the use of the centrifuge process, portions of the silver halide from a single batch of emulsion being suspended and digested in varying amounts of gelatin. Table 19 gives the results with two concentrations each of three gelatins of varying activity, the entire experiment being repeated with a change in the gelatin used for emulsification. Table 20 gives data on a single emulsion, with four different concentrations of the same gelatin used for after-ripening. It is evident that the speed is practically unaffected, but there is an appreciable decrease in contrast with increasing gelatin concentration. In Table 20 the values of *c* and *u* for the underexposure region (22) show that the effect is essentially the same here. It may readily be explained by a decrease in the rate of development in the thicker film.

Tables 21 and 22 show the results of adding gelatin to washed emulsions at the start of after-ripening. The depression in contrast was produced in all cases. In the ammonia-process emulsions, the addition of untreated gelatin also produced a distinct decrease in speed, and usually an appreciable increase in fog. If the gelatin had been thoroughly washed, or treated with ammonia and washed, before adding it to the emulsion, neither speed nor fog was affected and only the decrease in contrast was observed. The chloride in the untreated Winterthur gelatin amounted to 13 mols per 1,000 of silver bromide, which would be hardly appreciable. The pH of the ammonia-process emulsions was appreciably decreased, since the untreated Winterthur gelatin has a pH of 5.2, the Nelson No. 1, 7.0. This again is not sufficient to account for the results, although the sum of the chloride and pH effects would be appreciable. It is probable that in the ammonia-process emulsions, which were further sensitized (in the sense of formation of nuclei) before digestion, the addition of the untreated gelatin increased the amount of available sensitizers past the optimum.

TABLE 19.—*Effect of gelatin-silver halide ratio on sensitivity*

["Full ammonia" (A) emulsions, 1 per cent AgI, washed by centrifuge and suspended in 3 different gelatins at 2 concentrations. All batches digested at two and one-half hours at 45°]

Gelatin used for mix and ripening	Gelatin used for digestion and coating	Gelatin-silver halide ratio	Speed	γ			Fog		
				3	6	12	3	6	12
Winterthur (8763) untreated emulsion 8–156.	Winterthur (8763) untreated	1.51:1	34	1.26	2.00	2.80	0.08	0.17	0.38
		2.31:1	32	1.17	1.97	2.20	.07	.11	.25
	Winterthur (8763) washed	1.51:1	12.6	------	1.41	1.78	.08	.11	.14
		2.31:1	15.4	.84	1.26	1.46	.06	.14	.20
	Drescher (6136) digested with NH_3 and washed	1.51:1	14.9	1.50	1.82	2.30	.08	.12	.18
		2.31:1	13.8	1.05	1.54	1.85	.08	.13	.19
Winterthur (8763) washed emulsion 8–155.	Winterthur (8763) untreated	1.51:1	78	1.01	1.53	2.10	.14	.24	.55
		2.31:1	72	.81	1.31	1.80	.08	.27	.55
	Winterthur (8763) washed	1.51:1	11.6	1.00	1.33	1.45	.08	.11	.18
		2.31:1	11.4	.95	1.23	1.55	.05	.14	.21
	Drescher (6136) digested with NH_3 and washed	1.51:1	15.0	1.20	1.63	2.00	.07	.11	.21
		2.31:1	13.9	1.02	1.42	1.75	.06	.14	.22

TABLE 20.—*Effect of gelatin-silver halide ratio on sensitivity*

[Centrifuge-washed (A) emulsion, 1 per cent AgI, suspended in washed Winterthur gelatin at varying gelatin-silver halide ratios, and digested two and one-half hours at 45°]

Ratio gelatin: Silver halide	Speed	γ			Fog			*c*	*u*
		3	6	12	3	6	12		
1.07:1	9.5	1.27	1.65	2.10	0.11	0.14	0.20	0.02	0.38
1.51:1 (normal)	9.	1.10	1.36	1.68	.06	.10	.18	.01	.30
2.14:1	9.	1.04	1.40	1.60	.06	.12	.19	.03	.30
3.01:1	9.	.85	1.06	1.58	.06	.11	.18	.01	.28

TABLE 21.—*Effect on after-ripening of gelatin added after washing*

[Gelatin was added to portions of the emulsion on remelting after washing, raising the gelatin-silver halide ratio from the usual 1.51:1 to 2.31:1]

Emulsion	Time of digestion	Gelatin added after washing	Speed	γ			Fog			pH
				3	6	12	3	6	12	
	Hours at 45°									
1–139, "A" formula 1 per cent AgI.	0.2	None	30	1.54	2.10	2.42	0.01	0.08	0.18	8.0
	2.5	do	66	1.98	2.80	3.60	.04	.10	.28	8.0
	2.5	Winterthur (8763) untreated.	50	1.36	2.05	2.75	.07	.16	.44	7.5
	2.5	Winterthur (8763) digested with NH_3 and washed.	63	------	2.27	3.00	------	.13	.25	8.0
4–28, "C" formula 12 per cent excess KBr 2¼ g AgI.	2.5	None	58	1.07	1.43	2.05	.12	.18	.42	7.0
	2.5	Winterthur (8763) washed in sheets.	61	.74	1.13	1.65	.08	.17	.34	7.0
	2.5	Winterthur (8763) washed in shreds.	69	.75	1.14	1.62	.08	.15	.34	7.0
	2.5	Winterthur (8763) digested with NH_3 and washed.	67	.78	1.17	1.67	.08	.18	.40	7.0
1–140, "A" formula 5 per cent AgI.	.2	None	41	.53	.68	.77	.03	.12	.24	8.0
	2.5	do	140	1.27	1.76	2.05	.05	.12	.28	8.0
	2.5	Winterthur (8763) untreated.	102	1.06	1.60	2.34	.04	.14	.33	7.5
	2.5	Winterthur (8763) digested with NH_3 and washed.	145	.87	1.27	1.60	.03	.14	.30	8.0

TABLE 22.—*Effect on after-ripening of gelatin added after washing*

Emulsion	Gelatin added after washing	Time of digestion	Speed	γ			Fog		
				3	6	12	3	6	12
		Minutes at 45°							
4–11, 5 per cent AgI 12 per cent excess NH_4Br Winterthur gelatin "C" formula.	None	10	20	1.00	1.30	1.70	0.05	0.08	0.13
		75	92	1.15	1.85	2.07	.05	.14	.22
		130	150	1.08	1.70	2.60	.04	.15	.37
		195	155	1.07	1.65	2.50	.07	.17	.38
	60 per cent more	60	94	.86	1.37	1.57	.05	.12	.17
		120	165	1.00	1.60	1.70	.04	.14	.26
		180	205	.90	1.40	1.97	.05	.15	.39
1–118, 1 per cent AgI Nelson No. 1 gelatin "B" formula.	None	10	62	.85	1.30	1.72	.06	.12	.27
		75	195	.92	1.38	1.90	.06	.19	.42
		135	255	.87	1.55	2.08	.09	.20	.56
		210	240	.96	1.44	1.87	.10	.32	.70
	60 per cent more	60	75	.80	1.30	1.75	.09	.22	.50
		125	108	.71	1.10	1.61	.13	.35	.77
		200	105	.63	1.10	1.50	.18	.41	.91

(b) MAKE OR BATCH OF GELATIN

The results of the entire process of emulsion making are notoriously dependent on the gelatin which is used, and after-ripening is affected as much as any other step. We shall not attempt in this paper anything more than recognition of this fact, with a few illustrations of the results of substituting different gelatins in a given formula.

Table 23 compares results for the "C" formula, with 4.0 mol per cent AgI and 25–7 minutes mixing time. With suitable gelatin, such as the Winterthur-Nelson combination, this will give an emulsion which would be rated commercially as very fast. We have included results with a sample of deashed gelatin. The deashing process can cause considerable deactivation, as first reported by C. R. Smith (21), but the connection between removal of ash and of sensitizing materials is apparently accidental; thorough washing with water alone will reduce the activity of most gelatins to a considerable extent. It will be noted that the maximum sensitivity in this case is reached in an hour, followed by relatively slow deterioration. The treatment of the gelatin used in emulsion 46–69, consisting of one-half hour digestion with normal ammonia at 45°, followed by washing for a day, is by no means a complete deactivation, but it approaches it about as nearly as any other which we have tried; it is particularly successful in reducing fog. It will be noted that the contrast of the emulsion is always low. The indications are that the more labile sensitizing materials have been removed, but that there is a reserve of less reactive substances which come into play only on long-continued ripening. Analysis by the method of Sheppard and Hudson (26) indicated that one-third to one-half of the labile sulphur had been removed. As this method uses digestion with concentrated ammoniacal AgCl as a test of lability, it includes sulphur compounds not labile under the conditions of emulsion making.

When two samples of gelatin are compared as to their value for photographic emulsions, the relative rating may be altered or even reversed by a change in the emulsion formula. This condition is to be expected on the very probable assumption that all gelatins contain a mixture of sensitizing materials of varying reactivity. The results of using a gelatin in a neutral formula with the pH never greater than 7 can not be expected to be the same as those from a "full ammonia" formula in which ripening is carried on at a pH of 11, with free ammonia present in a concentration of nearly half normal. Again, it is probable that the optimum ratio of silver or silver sulphide (as nuclei) to silver halide varies with the proportion of silver iodide, and with the conditions under which it is formed. With this in mind, it is not surprising that, for example, the relative behavior of Winterthur and Nelson No. 1 gelatins differs for all three classes of emulsions represented in Tables 23, 24, and 25.

The use of centrifugal washing, which we have found quite useful in some classes of experimental work, creates conditions during after-ripening which can not be made exactly the same as those after conventional washing. This may be illustrated by considering the case of a known sensitizer, allyl thiocarbamide. It is water soluble, and hence can be removed from gelatin by thorough washing. If present in a neutral emulsion during ripening, it forms the water-insoluble complex with silver bromide, which will go through either type of washing process practically unchanged, breaking down to silver sulphide during the after-ripening. If, therefore, untreated gelatin is used both for the original emulsification and for the final suspension of the silver halide, there will be present during after-ripening all the allyl thiocarbamide from both portions of gelatin. The use of washed gelatin for either mixing or digestion approaches, but hardly duplicates, the conditions of conventional washing. Table 26 shows the progress of after-ripening in emulsions of the "C" type, 4 per cent AgI with centrifugal washing; the mixing time was somewhat less than that of the emulsions in Table 23, giving less speed and more contrast. An active gelatin was used for the original mix (emulsification). In one case it was centrifuged without addition of the secondary gelatin and suspended in untreated active gelatins; in the other the full quota of secondary gelatin was added, but the final suspension was in ammonia-treated gelatin. The maximum sensitivity was practically the same in both cases. After-ripening was more rapid in the first case. This is somewhat unexpected, as in the second case the silver halide might have carried with it sufficient sensitizer-silver halide complex without further contribution from the coating gelatin. Tables 27 and 28 illustrate the results of various combinations of active and deactivated gelatins used for mix and ripening, and for after-ripening and coating. In these ammonia emulsions, ripening in an active gelatin may produce the optimum effect, so that further use of active gelatin is a liability (emulsion 8–153); or else there may still be the normal difference between coating gelatins (emulsions 8–103 and 106). The ammonia treatment did not produce a uniform product, but the three treated gelatins are more nearly the same than in their untreated states.

TABLE 23.—*Comparison of after-ripening in emulsions made with different gelatins*

[Neutral emulsions, 4.0 mol per cent AgI; digested at 55° without addition of soluble bromide]

Gelatin	Time of digestion	Speed	γ			Fog			Emulsion No.
			3	6	12	3	6	12	
	Minutes at 55°								
Winterthur (9262) [1]	[2] 5	17.3	0.27	0.35	0.40	0.02	0.04	0.09	4–53–1
	30	92	.58	.92	1.21	.02	.04	.13	4
	60	200	.63	1.01	1.25	.03	.07	.13	6
	100	350	.64	1.03	1.23	.05	.11	.17	7
Winterthur (9262) (60 per cent) and Nelson No. 1 (40 per cent) [3] [4]	5	83	.21	.32	.52	.02	.03	.09	4–58–1
	40	330	.60	.92	1.36	.03	.06	.17	2
	80	475	.56	.90	1.39	.09	.12	.18	4
	120	495	.55	.84	1.39	.10	.14	.22	5
Deashed gelatin from limed calfskin stock, treated by Northrop and Kunitz method	[2] 5	8.9	.43	.54	.65	.00	.08	.12	4–67–1
	60	205	.76	1.43	2.22	.03	.10	.28	3
	120	160	.70	1.31	1.97	.16	.31	.46	5
	180	125	.81	1.27	1.83	.26	.51	.69	7
UCOP (3029) digested with NH_3 and washed	15	95	.15	.26	.29	.02	.03	.11	4–69–1
	50	182	.16	.29	.34	.01	.01	.08	3
	90	150	.26	.44	.58	.01	.04	.08	5
	185	310	.50	.71	1.06	.07	.10	.20	7

[1] Coating pH 5.9.

[2] Figures for undigested portions are for those melted with addition of KBr.

[3] Digested at 54°.

[4] Coating pH 7.2.

TABLE 24.—*Comparison of after-ripening in emulsions made with different gelatins*

["Full ammonia" (B), 5.0 mol per cent AgI; digested at 45° without addition of soluble bromide]

Gelatin	Time of digestion	Speed	γ			Fog			Emulsion No.
			3	6	12	3	6	12	
	Minutes at 45°								
Winterthur (9262)	5	66	0.22	0.51	0.61	0.00	0.08	0.14	1–161–1
	60	165	.66	1.28	1.95	.02	.08	.21	2
	130	320	.73	1.34	1.94	.04	.12	.27	4
	185	360	.82	1.47	2.14	.07	.12	.29	6
Nelson No. 1	10	82	.30	.33	.37	.00	.03	.09	1–160–1
	60	127	.84	1.16	1.60	.02	.06	.15	3
	120	230	.91	1.43	2.25	.04	.09	.19	5
	240	240	1.04	1.56	2.43	.06	.09	.21	7
	360	205	1.10	1.75	2.46	.08	.15	.27	8

TABLE 25.—*Comparison of after-ripening in emulsions made with different gelatins*

["Full ammonia" (B), 1 per cent AgI; digested at 45° without addition of soluble bromide]

Gelatin	Time of digestion	Speed	γ			Fog			Emulsion No.
			3	6	12	3	6	12	
	Minutes at 45°								
Winterthur (9262)	5	46	0.88	1.23	1.59	0.00	0.02	0.10	[1] 1–162–1
	60	87	.95	1.70	2.13	.01	.07	.19	3
	120	106	1.10	2.04	2.72	.04	.09	.27	5
	180	108	1.16	1.94	2.72	.06	.13	.33	6
Nelson No. 1	10	62	.85	1.30	1.72	.06	.12	.27	1–118–1
	70	195	.92	1.38	1.90	.06	.19	.42	3
	130	255	.87	1.55	2.08	.09	.20	.56	5
	205	240	.96	1.44	1.87	.10	.32	.70	7

[1] [Br] $9.8\times10^{-4}N$; digestion of 3, 5, and 6 at [Br⁻] $1.8\times10^{-5}N$.

TABLE 26.—*After-ripening of neutral emulsions with centrifugal washing*

[4 per cent AgI; mixing time, 18½ minutes. Coating pH 6.6. Winterthur (9262) gelatin in original mix]

Secondary gelatin	Coating gelatin	pH during digestion	[Br⁻] during digestion	Time of digestion	Speed	γ			Fog		
						3	6	12	3	6	12
				Hours at 55°							
None	⅗ Winterthur (9262) ⅖ Nelson No. 1.	6.2	$1.7\times10^{-4}N$	0.5	115	0.56	0.83	1.38	0.03	0.26	0.39
				1.0	175	.67	1.19	1.63	.20	.27	.45
				1.5	122	.80	1.15	1.99	.23	.34	.57
				2.0	110	.78	1.23	1.87	.26	.37	.59
Equal parts Winterthur (9262) and Nelson No. 1.	NH_3– treated UCOP (3029)	7.3	$1.0\times10^{-4}N$	0.5	80	.30	.53	.77	.19	.28	.40
				1.0	150	.45	.74	1.13	.20	.28	.40
				1.5	180	.58	1.00	1.48	.19	.31	.40
				2.0	165	.59	1.03	1.53	.30	.51	.70

TABLE 27.—*Comparison of after-ripening in emulsions washed in centrifuge and suspended in different gelatins*

[Formula "A," 1.0 mol per cent AgI, digested at 45°]

Gelatin used for digestion and coating	Time of digestion,	Speed	γ			Fog			Emulsion No.
			3	6	12	3	6	12	
	Minutes at 45°								
Winterthur (8565) untreated	<10	24	1.17	1.78	2.06	0.11	0.14	0.23	8–103–1
	60	94	.97	1.77	2.37	.13	.19	.27	2
	120	126	1.05	1.65	2.25	.14	.24	.41	3
	180	109	1.04	1.62	2.30	.15	.27	.58	4
Winterthur (8565), previously digested with ammonia and washed	<10	18	1.23	1.80	2.15	.15	.18	.22	8–106–1
	60	17	1.43	2.10	2.58	.13	.17	.22	2
	120	22	1.50	2.25	2.70	.16	.18	.24	3
	180	35	1.55	2.10	2.50	.15	.20	.28	4

TABLE 28.—*Comparison of after-ripening in untreated and ammonia-deactivated gelatins*

[Emulsions made by "A" formula, 1.0 mol per cent AgI; washed by centrifuge and suspended for digestion and coating in different gelatins. All batches digested 2.5 hours at 45°]

Gelatin used for mix and ripening	Gelatin used for digestion and coating	Speed	γ			Fog		
			3	6	12	3	6	12
Winterthur (8763) untreated. Emulsion 8-153.	Winterthur (8763) untreated	50	1.10	1.89	2.57	0.06	0.15	0.35
	Winterthur (8763) digested with NH_3 and washed.	55	1.08	2.70	3.30	.05	.10	.18
	Drescher (6136) digested with NH_3 and washed.	55	1.55	2.50	3.30	.05	.10	.18
	American Glue Co. "A" digested with NH_3 and washed.	34	1.90	2.75	3.10	.05	.09	.18
American Glue Co. "A" digested with NH_3 and washed. Emulsion 8-154.	Winterthur (8763) untreated	31	1.71	2.90	3.41	.08	.14	.27
	Winterthur (8763) digested with NH_3 and washed.	15	1.63	2.35	2.53	.05	.10	.18
	Drescher (6136) digested with NH_3 and washed.	12.5	1.95	2.48	2.95	.07	.13	.18
	American Glue Co. "A" digested with NH_3 and washed.	12.6	1.87	2.32	2.63	.07	.11	.21

7. KNOWN NUCLEAR SENSITIZERS

It seemed instructive to make the comparison between after-ripening in emulsions made with active gelatin, and those made with deactivated gelatin plus definite amounts of sensitizing materials known to function by formation of silver sulphide nuclei. As already mentioned, it has so far been impossible to secure a completely deactivated gelatin, but there were available materials of activity very low compared to that of proper amounts of sensitizers. It should, perhaps, be pointed out that our experiments are not considered to represent the optimum results which can be obtained with allyl thiocarbamide or sodium thiosulphate; no attempt was made to do more than approximate the results obtained with active gelatin.

Neutral emulsions with 4 per cent AgI, on which the most after-ripening data were already available, were chosen for the comparison. In order to secure as nearly as possible the same conditions as with the natural sensitizers in gelatin, allyl thiocarbamide was introduced into the emulsions by swelling the secondary gelatin with a solution of it. Sodium thiosulphate had to be introduced after washing; a dilute solution was poured over the "noodles" before remelting. The allyl thiocarbamide can be introduced before washing, since it forms an insoluble addition compound with silver bromide (12), even in the presence of soluble bromide. Sodium thiosulphate must undergo a metathesis with silver bromide, liberating soluble bromide, before there is formed the silver thiosulphate which breaks down to silver sulphide. If introduced into the unwashed emulsion at a high bromide ion concentration, thiosulphate will, therefore, be lost on washing; this was verified by experiment. The metathesis equilibrium is probably far over toward silver bromide, and therefore quite sensitive to bromide ion concentration. The decomposition of silver thiosulphate liberates no bromide, and should be relatively independent of this variable as compared to the decomposition of the silver bromide-thiocarbamide complex. Both decompositions liberate acid, and should be retarded by increasing hydrogen ion concentration. Sheppard has stated that the formation of silver sulphide from thiocarbamides occurs at a "sufficiently alkaline reaction." Silver thiosulphate might decompose more rapidly in alkaline solution, but all thiosulphates are unstable in acid solution, so that there is probably no pH at which it is stable.

The emulsions listed in Table 29 were made with a commercial sample of gelatin which, as shown by the control, was gratifyingly inert if the emulsion was made without addition of ammonia or other alkali. The data on addition of allyl thiocarbamide to an emulsion made with this gelatin are given to illustrate the marked effect of pH on the sensitization; on digestion at pH 6.3 the after-ripening was practically the same as in the control. The thiocarbamide was still there, since bathing in ammonia hypersensitized the finished plates, but not those coated with the control emulsion. It is obvious that conditions of this nature may cause erroneous conclusions as to the value of sensitizing materials if the investigator has not given the attention to details which is necessary in photographic research. The emulsions listed in Tables 30 and 31 were made with different batches of ammonia-deactivated gelatin. At the higher values of pH in these emulsions, the gelatin was more active, especially on very long digestion.

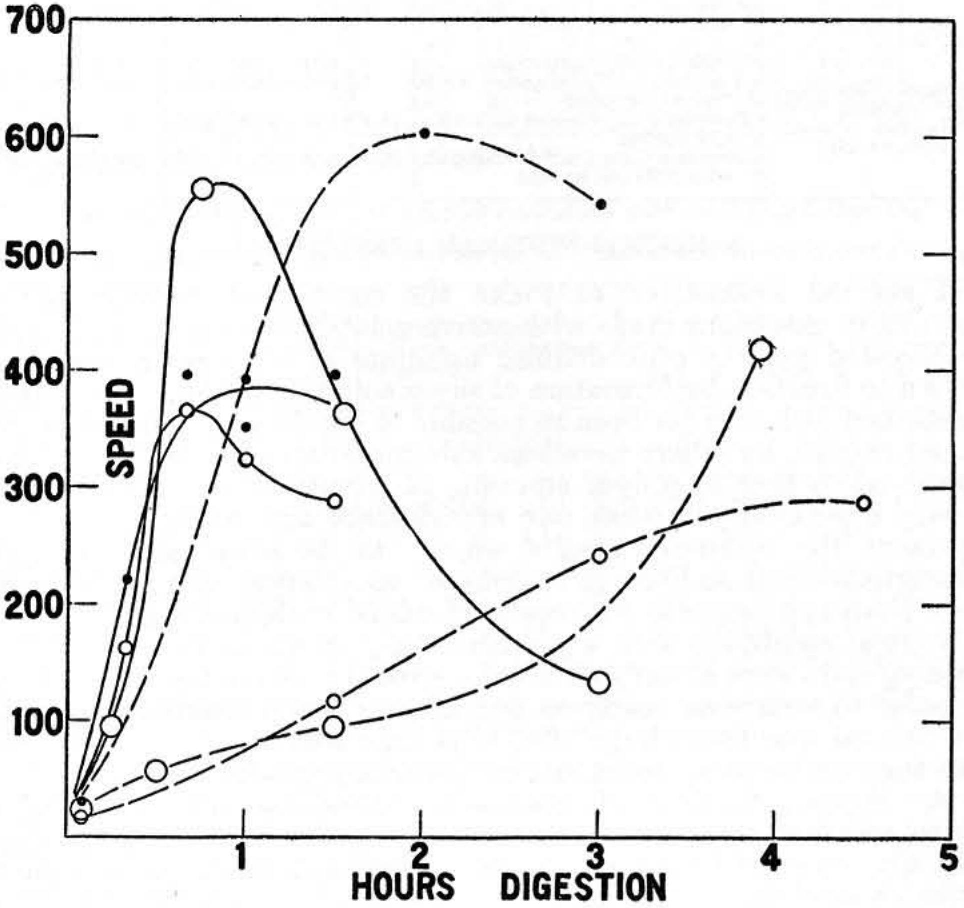

Figure 7.—*After-ripening of neutral emulsions 4 per cent AgI, mixed with inert gelatin*

Solid curves indicate digestion, at 55°, as washed; dashed lines, digestion at 55° with 5 KBr per 1,000 AgBr ●, sensitized with active secondary gelatin; o, O sensitized with allyl thiocarbamide sufficient to convert 1.6×10^{-5} and 2.4×10^{-5}, respectively, of silver bromide to silver sulphide.

After-ripening after addition of allyl thiocarbamide closely resembles that in active gelatin, as would be predicted from the natural occurrence of this sensitizer in gelatin. The qualitative similarity of the curves in Figure 7 is striking, and in view of the way in which photographic sensitivity varies with small changes in conditions, the quantitative agreement is also good. It is strong proof that the processes occurring are of the same character in both cases. There is, however, an important difference which is evident on inspection of Tables 29, 30, and 31, and the curves. The presence of soluble bromide (5 KBr/1,000 AgBr) during digestion retards after-ripening with allyl thiocarbamide much more than with active gelatin. The difference is so marked that it seems a strong indication of the presence of other sensitizers in gelatin, although it can hardly be used as evidence of their character. The difference in the effect of bromide appears in another way. With active gelatin, the maximum speed was higher at increased bromide ion concentration (figs. 3 and 5), but with either of the sensitizers the maximum was higher when the emulsion was digested without addition of bromide.

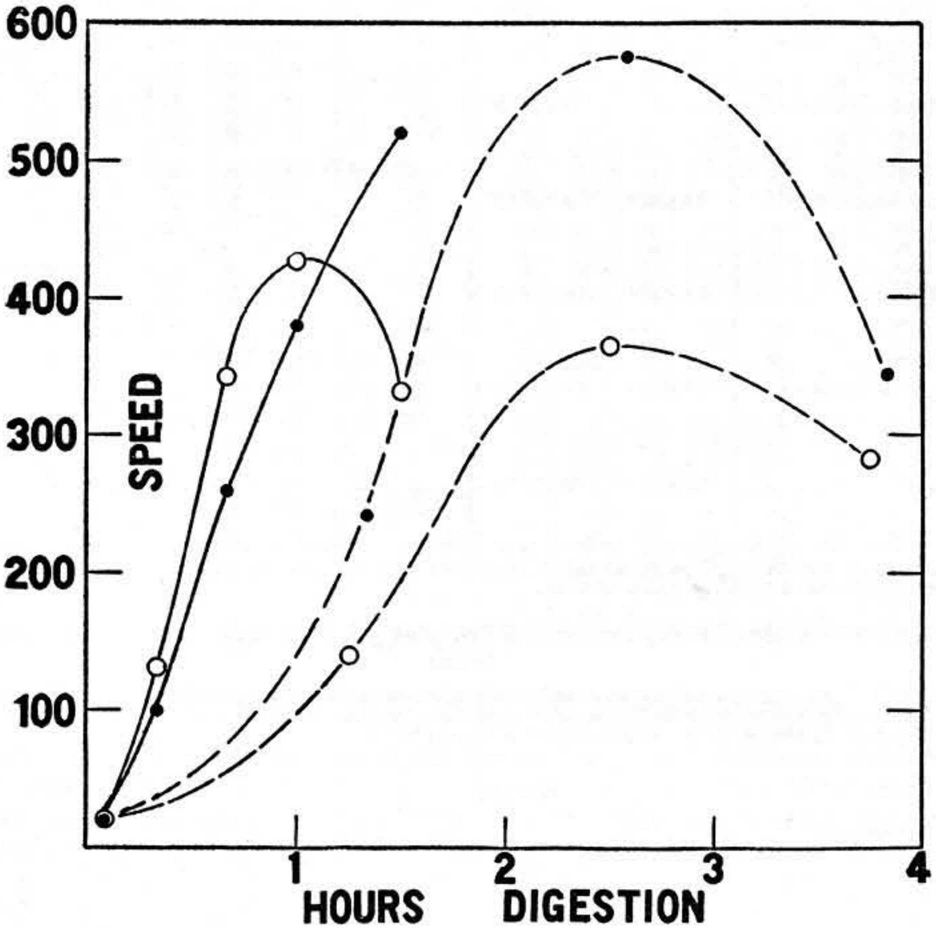

Figure 8.—*After-ripening of neutral emulsions, 4 per cent AgI, made with inert gelatin and sensitized with sodium thiosulphate*

Solid lines indicate digestion as washed; dashed lines, digestion with 5 KBr per 1,000 AgBr. Digested at 55°; ●, pH 6.3; O, pH 7.9.

The data for sodium thiosulphate are presented in Tables 29 and 31 and Figure 8. They are very similar to those for active gelatin and allyl thiocarbamide. The decrease in rate of after-ripening produced by adding bromide is intermediate between the other two; it is greater at pH 7.9 than at pH 6.3. At pH 6.3, the after-ripening with thiosulphate has the peculiarity that the growth of fog is almost unaffected by the bromide.

TABLE 29.—*After-ripening in inert gelatin plus known amounts of sensitizers*

[Neutral (C) emulsions, 4.0 mol per cent AgI, made with commercial inert gelatin (UCOP 2939-1). The allyl thiocarbamide was added with the secondary gelatin; sodium thiosulphate was added after washing. pH during digestion, 6.3]

Sensitizer	$\frac{\text{Ag as Ag}_2\text{S}}{\text{Ag as AgBr}}$[1]	Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog		
					3	6	12	3	6	12
			Minutes at 55°							
None (control)	....	$1.1\times10^{-4}N$	20	30	0.15	0.23	0.36	0.00	0.02	0.08
			40	31	.15	.25	.45	.02	.03	.09
			60	30	.19	.31	.50	.01	.03	.10
			90	39	.17	.31	.52	.00	.02	.09
Do	....	$7.9\times10^{-4}N$	<5	15	.13	.16	.23	.00	.01	.04
			90	29	.17	.30	.40	.02	.02	.09
			180	46	.19	.36	.53	.00	.02	.11
			270	78	.23	.46	.70	.00	.05	.21
Allyl thiocarbamide	2.4×10^{-5}	$4.8\times10^{-5}N$	20	46	.14	.24	.37	.02	.02	.08
			40	47	.15	.27	.38	.01	.02	.08
			60	57	.17	.29	.41	.00	.02	.09
			90	55	.18	.33	.46	.00	.02	.09
Do	2.4×10^{-5}	$1.03\times10^{-3}N$	<5	25	.11	.14	.20	.00	.02	.04
			90	61	.13	.20	.30	.00	.02	.05
			180	83	.17	.30	.39	.01	.03	.08
			270	99	.21	.37	.48	.00	.03	.12
Sodium thiosulphate	2.3×10^{-5}	$2.9\times10^{-5}N$	20	100	.20	.42	.60	.02	.05	.11
			40	260	.38	.57	1.14	.02	.06	.24
			60	365	.38	.75	1.22	.02	.06	.25
			90	520	.46	.82	1.35	.02	.09	.34
Do	2.3×10^{-5}	$1.02\times10^{-3}N$	<5	19	.12	.13	.18	.01	.02	.08
			80	240	.22	.43	.72	.03	.08	.29
			155	575	.39	.61	.07	.04	.24	.73
			230	345	.41	.72	1.20	.06	.39	.96

[1] Assuming that the added sensitizer reacts completely with the silver halide, and not considering the unknown amount of Ag_2S from other sources.

TABLE 30.—*After-ripening in inert gelatin plus a known amount of allyl thiocarbamide*

[Neutral (C) emulsions 4.0 mol per cent AgI, made with ammonia-treated gelatin (UCOP 3029). Allyl thiocarbamide was added with the secondary gelatin of one emulsion; each emulsion was divided in halves, and digested with and without added KBr, at pH 7.5]

Sensitizer	$\frac{\text{Ag as Ag}_2\text{S}}{\text{Ag as AgBr}}$[1]	Bromide ion concentration at beginning of digestion	Time of digestion	Speed	γ			Fog		
					3	6	12	3	6	12
			Minutes at 55°							
None (control)	0	$2.2\times10^{-5}N$	15	95	0.15	0.26	0.29	0.02	0.03	0.11
			50	152	.16	.29	.34	.01	.01	.08
			90	150	.26	.44	.58	.01	.04	.08
			185	310	.50	.71	1.06	.07	.10	.26
Do	0	$1.4\times10^{-3}N$	<5	40	.12	.16	.20	.00	.02	.07
			30	58	.13	.18	.19	.00	.02	.07
			90	81	.17	.27	.34	.00	.03	.07
			225	240	.44	.73	1.03	.04	.06	.13
Allyl thiocarbamide	2.4×10^{-5}	$1.8\times10^{-5}N$	15	95	.33	.41	.61	.02	.03	.16
			45	555	.76	1.17	1.64	.03	.05	.23
			93	360	.69	1.35	1.95	.19	.34	.62
			180	134	.80	1.19	1.60	.55	.94	1.54
Do	2.4×10^{-5}	$1.15\times10^{-3}N$	<5	21.7	.20	.22	.26	.00	.02	.11
			30	57	.22	.22	.23	.00	.04	.12
			90	95	.25	.33	.37	.00	.03	.08
			225	420	.54	.86	1.34	.04	.07	.14

[1] Assuming that the added sensitizer reacts completely with the silver halide, and not considering the unknown amount of Ag_2S from other sources.

TABLE 31.—*After-ripening with allyl thiocarbamide, sodium thiosulphate, and naturally occurring sensitizers of gelatin*

[Neutral (C) emulsions, 4.0 mol per cent AgI, made with ammonia-treated gelatin (American Glue Co. "A"); secondary gelatin, the same where known sensitizers were used]

Sensitizer	$\frac{\text{Ag as } Ag_2S}{\text{Ag as AgBr}}$[1]	Bromide ion concentration at beginning of digestion	pH	Time of digestion	Speed	γ			Fog		
						3	6	12	3	6	12
				Minutes at 55°							
Active secondary gelatin (Winterthur and Nelson)	----------	1.7×10^{-5}	6.8	20	220	0.54	1.07	1.16	0.11	0.15	0.21
				40	400	.67	1.13	1.57	.11	.17	.27
				60	350	.77	1.10	1.80	.19	.28	.36
				90	400	.70	1.33	1.93	.18	.27	.37
Do	----------	8.6×10^{-4}	6.8	<5	36	.26	.34	.41	.00	.03	.08
				60	395	.61	.97	1.34	.06	.10	.14
				120	605	.64	1.06	1.63	.12	.18	.27
				180	540	.66	1.01	1.63	.17	.19	.31
Allyl thiocarbamide	1.6×10^{-5}	1.1×10^{-5}	7.9	20	162	.60	.93	1.95	.14	.20	.34
				40	365	.90	1.36	2.35	.13	.23	.41
				60	320	.87	1.36	2.30	.18	.31	.44
				90	290	1.08	1.53	2.10	.30	.50	.81
Do	1.6×10^{-5}	8.1×10^{-4}	7.9	<5	17	.41	.63	.79	.02	.06	.15
				90	117	.55	.70	.94	.02	.10	.16
				180	240	.57	.90	1.31	.05	.07	.21
				270	285	.74	1.13	1.62	.08	.13	.27
Sodium thiosulphate	2.3×10^{-5}	1.0×10^{-5}	7.9	20	132	.72	1.06	1.69	.05	.10	.23
				40	345	.88	1.30	2.05	.09	.13	.29
				60	430	.87	1.26	1.98	.11	.18	.34
				90	330	.89	1.38	2.17	.19	.30	.44
Do	2.3×10^{-5}	9.2×10^{-4}	7.9	<5	24	.34	.36	.42	.03	.09	.17
				75	140	.74	.95	1.48	.04	.09	.20
				150	365	.87	1.28	1.98	.10	.16	.29
				225	285	.96	1.38	2.35	.15	.23	.41

[1] Assuming that the added sensitizer reacts completely with the silver halide, and not considering the unknown amount of Ag_2S from other sources.

8. PERCENTAGE OF IODIDE IN THE SILVER HALIDE

The use of a few per cent iodide in the silver halide is generally acknowledged to be necessary to a fast emulsion, but the literature gives little specific information as to the effects of variation in iodide content. It is impossible to decide from the available evidence whether there is a fundamental difference in the sensitivity of pure silver bromide and of mixed crystals of bromide and iodide. Huse and Meulendyke (23) have shown that as the percentage of iodide is increased the spectral absorption extends to longer wave lengths; it is very probable that the total energy absorbed from incident white light is also increased, but their data do not shown whether the increase in absorption would cause an appreciable increase in sensitivity. Trivelli (24) suggested that the introduction of silver iodide into the silver bromide crystal lattice should cause a distortion of the latter; Wilsey (25), by X-ray crystal analysis, found that the spacing of the lattice was definitely increased, which might set up strains resulting in greater photochemical sensitivity. Our experiments are entirely too limited for generalization on this subject, but in the neutral emulsions compared in Table 32, we have an example of the type of data which we hope at some time to secure in sufficient quantity to be conclusive. By reducing the temperature of mixing and the excess of ammonium bromide, the emulsions with 1 per cent silver iodide were made to have the same average grain size as those with 4 per cent; the distribution of grain size was similar, although not identical. Both were digested to optimum sensitivity under similar conditions, the time being shorter for the emulsion with less iodide. The difference in maximum speeds under these conditions appears to indicate an inherent difference in the sensitivity of the two mixtures of halides. The ammonia-process emulsions can not be compared at equal grain sizes, since the ripening was the same for both proportions of iodide,[11] but the evidence appears to be qualitatively the same.

Table 32 has been arranged to shown the most definite connection between iodide content and after-ripening, which is that the practicable increase in sensitivity by after-ripening increases with increasing iodide. As would be expected, there is a considerable dependence on the gelatin and the emulsion formula. The emulsions with higher iodide content are notable for very low contrast before after-ripening; if the speeds before and after digestion were expressed by threshold value or by the system of Jones and Russell (13) instead of the H. & D. system, the ratio would be greatly increased.

Inspection of Tables 9, 11, 13, and 14 shows that the rate of after-ripening under comparable conditions decreases with increasing percentage iodide, but the difference is not large.

TABLE 32.—*Comparison of after-ripening in emulsions with 1.0 and 4.0 or 5.0 mol per cent silver iodide*

Formula and No.	Mol per cent AgI	Average grain size	Gelatin	Digestion	Speed	γ			Fog		
						3	6	12	3	6	12
C, 4-68	4.0	μ^2 0.36	Winterthur-Nelson	Minimum	76	0.16	0.20	0.32	0.03	0.08	0.13
				Optimum	625	.64	.90	1.53	.08	.13	.18
C, 4-65	1.0	.34	do	Minimum	39	.26	.33	.48	.00	.00	.03
				Optimum	195	.80	1.26	2.29	.08	.11	.26
B, 1-161	5.0	.34	Winterthur	Minimum	66	.22	.51	.61	.00	.03	.14
				Optimum	360	.82	1.47	2.14	.07	.12	.29
B, 1-162	1.0	.37	do	Minimum	46	.88	1.23	1.59	.00	.02	.10
				Optimum	108	1.16	1.94	2.72	.06	.13	.33
B, 1-160	5.0	.33	Nelson	Minimum	81	.30	.33	.37	.00	.03	.09
				Optimum	240	1.04	1.56	2.43	.06	.09	.21
B, 1-118	1.0	.44	do	Minimum	62	.85	1.30	1.72	.06	.12	.27
				Optimum	255	.87	1.55	2.08	.09	.20	.56

IV. STORAGE RIPENING

As already stated, after-ripening goes on slowly during storage of dried plates coated with undigested emulsions. Tables 33 to 38 give the data on storage ripening of several types of emulsions coated after varying amounts of ripening and digestion. To keep the tables from being too unwieldy, γ and fog are given only for 6-minute devel-

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[11] It must be known to anyone with experience in emulsion making that, with the same ripening conditions, the grain size decreases with increasing proportion of iodide, but we have found only one explicit statement to this effect in the literature. Lüppo-Cramer (1) points out that pure bromide neutral emulsions have a grain very much larger than those with 1 per cent iodide, made under the same conditions. In addition to the data in Table 32, the grain size of emulsion 4-63, 1 per cent AgI, Table 3 may be compared with that of emulsion 4-68, 4 per cent AgI, Table 32 mixed at the same temperature with the same excess bromide.

opment; the speed number is also taken from that curve only instead of from the mean of the three. Random errors of coating and development are, therefore, more conspicuous than in the other tables. Considerably more data have been obtained than are given here.

Inspection of the tables shows that in every case the after-ripening on storage was at least equal to that on digestion; in general, it was somewhat greater. As would be expected, when the emulsion was digested to a maximum sensitivity, there was no after-ripening on storage; there was also the unexpected consequence that deterioration by fog in 1-year storage was generally less than in the undigested portions. Storage ripening in the neutral and ammonia-process emulsions was of the same order of magnitude, proving that it can not be ascribed to traces of free ammonia. (See p. 221 and reference 11.)

TABLE 33.—*Storage ripening of emulsion 4–11*

["C" formula, 5.0 per cent AgI, 15 per cent excess KBr, Winterthur gelatin. All data for six minutes development]

	Time of digestion	Directly after coating			After 1 month storage			After 3 months, storage			After 12 months, storage		
		Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
	Minutes at 45°												
Digested as washed	<10	20	1.30	0.08	105	1.45	0.09	220	1.60	0.11	125	2.05	0.47
	75	83	1.85	.14	110	1.65	.06	180	1.63	.12	160	1.93	.33
	130	160	1.70	.15	125	1.85	.09	140	1.85	.12	175	1.75	.32
	195	165	1.65	.17	165	1.80	.09	180	1.90	.13	180	1.90	.24
Dry gelatin added after washing, 60 per cent of original amount	60	87	1.37	.12	175	1.23	.09	230	1.35	.10	115	1.55	.31
	120	140	1.60	.14	190	1.42	.09	145	1.53	.12	130	1.58	.25
	180	195	1.40	.15	175	1.50	.11	110	1.68	.15	125	1.50	.24

TABLE 34.—*Storage ripening of emulsion 4–14*

["C" formula, 1.0 per cent AgI, 16 per cent excess KBr, Winterthur gelatin. Digested as washed. All data are for six minutes development]

Time of digestion (minutes at 45°)	Directly after coating			After 1 month storage			After 3½ months, storage			After 13 months, storage		
	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
<10	45	1.00	0.05	180	1.45	0.07	315	1.77	0.17	210	1.78	0.55
65	63	1.50	.06	138	1.43	.09	230	1.58	.12	210	1.60	.34
125	100	1.78	.11	150	1.65	.08	210	1.77	.13	220	1.55	.30
180	125	1.80	.14	165	1.65	.09	220	1.87	.16	230	1.50	.29

TABLE 35.—*Storage ripening of emulsion 6–46*

["C" formula, 5 per cent AgI, 16 per cent excess KBr, 14 minutes' mixing time. Washed by centrifuge and suspended in untreated Winterthur gelatin. All data are for six minutes' development]

Time of digestion (minutes at 45°)	Directly after coating			After 1 month storage			After 4 months' storage			After 13 months' storage		
	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
10±5	7.3	1.01	0.19	48	1.34	0.19	91	1.58	0.34	50	1.72	0.49
60±5	38	1.41	.23	69	1.42	.24	------	------	------	60	1.83	.49
120±5	71	1.70	.27	87	1.60	.23	100	1.57	.35	72	1.75	.40
180±5	78	1.80	.30	87	1.75	.28	66	1.90	.35	66	1.77	.48

TABLE 36.—*Storage ripening of emulsion 6–48*

["O" formula, 1 per cent AgI, 16 per cent excess KBr, 14 minutes' mixing time. Washed by centrifuge and suspended in untreated Winterthur gelatin. All data are for six minutes' development]

Time of digestion (minutes at 45°)	Directly after coating			After 1 month storage			After 3 months' storage			After 12½ months' storage		
	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
10±5	33	0.98	0.28	120	1.30	0.30	138	1.78	0.38	138	1.65	0.71
60	43	1.35	.28	105	1.32	.28	150	1.56	.37	160	1.72	.60
120	120	1.54	.29	115	1.60	.33	145	1.65	.40	145	1.58	.56
180	115	1.75	.36	132	1.74	.39	138	1.70	.49	132	1.65	.55

TABLE 37.—*Storage ripening of emulsion 1–118*

["B" formula, 1 per cent AgI, Nelson No. 1 gelatin. All data are for 6 minutes development]

	Time of digestion	Directly after coating			After 25 days' storage			After 3 months' storage			After 13 months' storage		
		Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
	Minutes at 45°												
Digested as washed	<10	62	1.30	0.12	160	1.18	0.10	260	1.80	0.13	330	1.65	0.44
	75	200	1.38	.19	250	1.65	.14	240	1.92	.20	300	1.65	.31
	135	245	1.55	.20	330	1.60	.17	280	1.81	.28	180	1.70	.52
	210	240	1.44	.32	275	1.70	.24	215	1.93	.26	220	1.55	.46
Dry gelatin added after washing, 60 per cent of original amount	60	76	1.30	.22	126	1.37	.18	230	1.48	.22	210	1.13	.65
	135	100	1.10	.35	140	1.30	.29	175	1.44	.41	220	.97	.63
	200	102	1.10	.41	140	1.26	.35	105	1.53	.48	120	1.16	.68

TABLE 38.—*Storage ripening of emulsions made by formula "A"*

[1 per cent AgI, and washed by centrifuge. All data are for 6 minutes development]

Emulsion No. and gelatin	Time of digestion	Time of ripening	Directly after coating			After 1 month storage			After 3 months' storage [1]			After 13 months' storage [2]		
			Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog	Speed	γ	Fog
	Minutes at 45°	*Minutes at 45°*												
8–101, Winterthur, untreated	[3] 10	6	12	1.46	0.08	36	2.30	0.05	66	2.30	0.14	72	2.14	0.34
		35	16	1.15	.26	47	1.50	.21	145	1.60	.29	132	1.60	.35
		63	34	.67	.32	138	.90	.28	350	1.08	.28	265	1.12	.48
		120	43	.50	.52	182	.67	.48	480	1.76	.52	350	1.15	.58
8–100, Winterthur, untreated	135	5	51	1.45	.13	43	1.70	.15	48	1.55	.12	30	1.70	.28
		30	135	1.05	.26	100	1.32	.24	110	1.31	.31	72	1.15	.42
		62	118	1.03	.46	175	1.10	.39	125	1.10	.49	200	.90	.64
		135	200	.87	.41	200	1.00	.46	210	.95	.45	240	.95	.55
8–108, Winterthur, digested with NH_3 and washed	145	7	20	1.63	.11	25	1.85	.13	43	1.60	.15	95	1.55	.14
		29	31	.97	.22	45	1.00	.24	79	1.10	.25	190	1.05	.23
		59	39	.53	.30	39	.68	.31	180	.65	.28	315	.77	.30
		120	50	.34	.33	91	.38	.41	290	.58	.41	550	.68	.38

[1] 4 months' storage of 8–108.
[2] 12 months' storage of 8–108.
[3] Approximately.

After-ripening by storage and by digestion are equally dependent on the gelatin. The ammonia-treated gelatins have a peculiarity which was indicated in Table 27 and is more evident in Table 38, emulsion 8–108; there may be little after-ripening over a considerable time of digestion or storage, followed ultimately by a great rise of sensitivity. In emulsion 4–69, the after-ripening in the last 90 minutes of digestion was greater than in the first 90; in emulsion 8–108, storage for a year produced clean plates of unusually high speed numbers, although the contrast was still below normal. The obvious interpretation of this is that the more labile sensitizing materials were removed by the ammonia treatment but that a considerable amount of slowly reacting sensitizers was left.

The very important question of the effect of soluble bromide on storage ripening and deterioration by fog will be taken up in a later communication, as plates now in storage are expected to furnish data which should be included.

The processes occurring in storage ripening would be expected to be essentially the same as in after-ripening by digestion. The amounts of silver plus silver sulphide, as found by the Weigert and Lühr method (Pt. V of this paper), support this expectation. The only explanation which we can offer for the greater effectiveness of storage ripening has already been given on page 233, that in the slow process of storage ripening there is relatively little tendency toward the formation of new nuclei. It is therefore a process of growth of small numbers of nuclei per grain, leading to the most efficient utilization of the silver and silver sulphide formed, and also leading to rapid increase in fog when the nuclei increase past the optimum size. If the emulsion has previously been digested to maximum speed, this may have resulted in greater numbers of nuclei than if it had been subject only to storage ripening, with the further possibility that a higher proportion of the silver sulphide (or silver) particles have been formed by reaction with dissolved silver halide. These last may be independent of silver halide grains and, therefore, inert both as to sensitivity and fog. The supply of sensitizers has been partly exhausted, so that storage ripening in this case proceeds with a lowered rate of formation of silver and silver sulphide, distributed among a larger number of nuclei, some of which are ineffective; increase of any of the nuclei to the size causing fog is therefore retarded.

V. ANALYTICAL EVIDENCE ON THE MECHANISM OF AFTER-RIPENING

Digestion of silver bromide with gelatin may be expected to result in some reduction to metal. The analysis of the emulsion gelatins used in this investigation, by the method of Sheppard and Hudson (26), gives results of the order of 2×10^{-5} g. labile sulphur per gram of gelatin, at least part of which may react under the conditions of after-ripening. The total fraction of silver bromide converted to other (nonhalide) forms will, however, be very small. The available evidence on the photolysis of silver bromide indicated that the silver of the latent image corresponding to ordinary exposures was less than could be detected by any analytical method. As it was assumed that the ripening nuclei must be a much smaller quantity, it was not until Weigert and Lühr (27) extended their investigations of photolysis from "print-out" to "developing-out" emulsions that there was any attempt to determine the "ripening silver" by chemical analysis. In a forthcoming paper we will describe experiments with the Weigert and Lühr method in full detail; in the discussion of the connection between after-ripening and nonhalide ("ripening") silver, the analytical results may be taken roughly at their face value.

Reduction or other reaction of the silver bromide during digestion could also be detected by an increase in the bromide ion concentration, when it was sufficiently low.

A number of typical results are given in Table 39. It will be noted that the rate of increase at a given temperature is greater for the emulsions with the lower proportions of iodide. It is less in the emulsion made with the deashed gelatin than the corresponding one with normal gelatin. Both these differences would be predicted, since increase in proportion of iodide makes reduction more difficult, and the deashing process probably removes reducing materials. The amount of silver bromide reacting can not be calculated from the change in bromide ion concentration, since there is not only the change in free silver and bromide ions, but a larger one in silver ion combined with the gelatin, and probably another of similar magnitude in bromide ion absorbed to the silver bromide. The errors in determination of these are too large to make the computation of any value.

Table 40 gives the results, both of digestion and of storage ripening, on the nonhalide silver, and photographic properties, of two emulsions. The increase produced by either digestion or storage ripening is much larger than the variations in the silver determinations; the values for each of the latter are given separately to indicate the reproducibility. It is evident that the increase in silver is more rapid at lower bromide ion concentrations, which is according to prediction, although, at 45°, increase in the bromide ion concentration by a factor of 40 divides the rate by 4 only, and at 55° by less than this. The rate of increase at 55°, without added bromide, is between two and three times as great as under the corresponding conditions at 45°, which is the normal value for a chemical reaction. The increase in nonhalide silver on storage was of the same order as that on digestion to a corresponding speed, and the effect of soluble bromide was very similar. On storage of 4–64–1 and 6, the increase in nonhalide silver, expressed in parts per 100,000, was 3.5 and 2.7; in 4–64–7, with no added bromide, the increase was 7.4. In emulsion 4–66, the corresponding values are 9.1 and 9.5 with added bromide, 18.2 without it. The difference between the two emulsions is unexplained. The data for digestion of emulsion 4–59, Table 41, are quite similar to those for 4–64 and 4–66.

TABLE 39.—*Change in bromide ion concentration of emulsions during digestion*

[Photographic data on these emulsions will be found in Tables 9, 10, 11, 12, 14, and 23]

Emulsion No.	Gelatin	Mol per cent AgI	pH	Time of digestion	Temperature of digestion	Bromide ion concentration at beginning of digestion, normality	Bromide ion concentration at end of digestion, normality
				Hours	°*C.*		
4–47	Winterthur	0.0	6.6	1.0	54	1.43×10^{-5}	1.92×10^{-5}
4–64	Winterthur-Nelson No. 1	1.0	6.9	4.0	45	1.8×10^{-5}	2.5×10^{-5}
4–66	do	1.0	7.0	2.0	55	1.5×10^{-5}	3.8×10^{-5}
1–162	Winterthur	1.0	8.3	3.0	45	1.75×10^{-5}	2.25×10^{-5}
4–61	Winterthur-Nelson No. 1	4.0	6.9	2.3	55	1.5×10^{-5}	2.7×10^{-5}
4–67	Deashed, from limed stock	4.0	7.1	3.0	55	1.42×10^{-5}	2.20×10^{-5}
1–159	Nelson No. 1	5.0	8.3	3.0	45	3.3×10^{-6}	5.8×10^{-6}

TABLE 40.—*Effect of digestion and storage on photographic properties and nonhalide silver (determined by the modified Weigert and Lühr method)*

[Emulsions made by "C" formula, 1 per cent AgI, 12.5 per cent excess NH_4Br, Winterthur and Nelson gelatin; mixed in 26 minutes at 52°]

Emulsion No.	Bromide ion concentration during digestion *N*	Time of digestion (minutes) and temperature	Directly after coating				Three months after coating			
			Ratio $\frac{Ag \times 10^5}{AgBr}$	Speed	$\frac{\gamma}{6}$	Fog 6	Ratio $\frac{Ag \times 10^5}{AgBr}$	Speed	$\frac{\gamma}{6}$	Fog 6
4-64-1	7.6×10^{-4}	<10	6.0, 5.6	34	0.55	0.04	9.3	125	1.03	0.04
4-64-6	7.6×10^{-4}	245, 45°	8.6, 7.3	170	1.04	.09	10.7	190	1.37	.12
4-64-7	1.8×10^{-5}	240, 45°	15.9, 15.3	215	1.55	.22	22.0	210	1.52	.34
4-66-5	1.2×10^{-3}	<10	4.4, 10.0 4.5, 4.2	39	.33	.00	13.5	134	.84	.03
4-66-8	1.2×10^{-3}	120, 55°	12.5, 12.4	170	1.63	.14	22.0	130	1.53	.37
4-66-4	3.8×10^{-5}	120, 55°	14.8, 15.1	162	1.60	.21	33.2	150	1.57	.32

TABLE 41.—*Change in nonhalide silver on digestion*

[See Tables 8 and 12 for photographic data on these emulsions]

Emulsion No.	Digestion time	Bromide ion concentration, normality	Nonhalide silver by Weigert and Lühr method $Ag/AgBr \times 10^5$	Digestion temperature	pH
	Minutes				
1-159-2	<10	3.3×10^{-6}	36.8, 28	45°	8.3
4	53		17.6, 11.9		
6	110		16.9, 12.7		
7	180		13.2, 10.1		
4-59-1	<5	1.2×10^{-5}	8.1, 9.8	55°	7.5
7	135		14.3, 12.2		
8	190	3.3×10^{-4}	11.7, 11.6		

In the case of emulsion 1–159 we have an anomalous behavior which was also observed on a smaller scale in the early stages of digestion of other emulsions. More nonhalide silver was found in the undigested portion than in the others; except for the undigested portion, the differences are within the limits of error of analysis. We have no reason to suspect random errors of analysis in these cases. It is possible that conditions favor a considerable systematic error. However, it is significant that the portion of this same emulsion which was digested with added bromide decreased in fog during digestion, so that an actual decrease in the nonhalide silver appears to be a possibility.

Granting that the nonhalide silver is real and that its changes are in most cases to be predicted from the chemistry of the system, the correlation with photographic properties is hardly close enough to be useful. The quantity of nonhalide silver found by the Weigert and Lühr method is invariably too large to be ascribed only to sensitivity nuclei. Reference to Tables 29 to 31 shows the large photographic effects of 2 parts of nonhalide silver per 100,000, when introduced by use of efficient sensitizers. The minimum value by analysis in the insensitive and very clean 4–66–5 was 4 parts per 100,000, and it generally rose to 10 to 15 parts on digestion to maximum sensitivity. In the opinion of the writers, only a small part of this nonhalide silver functions as sensitivity nuclei; the rest is dispersed through the gelatin, but not adsorbed to silver halide grains. The initial amounts in undigested emulsions may have been formed during ripening, but an equally plausible explanation is given by the presence of traces of colloidal silver in silver nitrate, unless exceptional precautions have been taken to prevent it. The increase in nonhalide silver during digestion must, to a large extent, represent reaction of "silver gelatinate" and free silver ions with reducing materials or labile sulphur, leading to a free particle of silver or silver sulphide, in contrast to the adsorbed sensitivity nuclei formed by rearrangement of a compound already adsorbed to the surface of a grain.

VI. SUMMARY

1. This paper is a survey of the changes taking place in a photographic emulsion after it has been washed, and of the effects of eight independent variables or groups of variables.

2. In studying the independent variables of the process, experiments have been repeated using emulsions of varying iodide content, with and without ammonia, and with different samples of gelatin.

3. The dependence of after-ripening by digestion on temperature, bromide ion concentration and hydrogen ion concentration indicates that it is the result of a chemical reaction or reactions of the silver halide. Chemical analysis shows an increase in nonhalide silver roughly parallel to the photographic changes but in quantity too large to be explained as sensitivity nuclei only.

4. Experiments on after-ripening in inert gelatin plus known sensitizing materials (allyl thiocarbamide, sodium thiosulphate) gave results qualitatively very similar to those in active gelatin, although the characteristics of active gelatin can not be explained by allyl thiocarbamide alone.

5. If digestion after washing is omitted, there is a slow after-ripening on storage, with effects generally similar to those of digestion.

VII. ACKNOWLEDGMENT

C. F. Kretchman has assisted in the coating and testing of most of the experimental emulsions recorded in this paper.

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THE PHOTOGRAPHIC EMULSION; THE SILVER ION-GELATIN EQUILIBRIUM

By Burt H. Carroll and Donald Hubbard

ABSTRACT

Electrometric determination of silver ion activity in silver nitrate-gelatin solutions showed strong selective combination of silver ion with gelatin. This decreases with increasing hydrogen ion concentration, but does not vanish on the acid side of the isoelectric point. Similar measurements in silver bromide-ammonia-gelatin solutions detected no combination of gelatin with the silver-ammonia ion. The hydrolysis of silver bromide and chloride in thoroughly washed emulsions was calculated from the electrometric data and verified by direct experiment.

CONTENTS

I. INTRODUCTION

The buffer action of gelatin—its capacity to combine with either acids or bases and reduce the change in hydrogen ion concentration resulting from the addition of the acid or base to the solution—is well known and important in several types of photographic phenomena. The object of this paper is to call attention to a similar capacity of gelatin for combination with silver ions, and some of its photographic consequences.

It should first be pointed out that in the combination of gelatin with acids or bases, the hydrogen or hydroxyl ions are combined in a manner which may under most conditions be considered unique. When, for example, gelatin is added to a solution of hydrochloric acid, the activity of the hydrogen ion as determined by any of the well-known methods is greatly reduced, while that of the chlorine ion is unaffected in dilute solutions. If such a mixed solution is separated by a suitable membrane from water or an electrolyte solution, the behavior of the chlorine ion may be predicted on the assumption that it is held to the gelatin only by electrostatic forces, while the gelatin-hydrogen ion complex must be treated as a single new unit. This applies whether we believe with Loeb, that gelatin acts as an amphoteric electrolyte and the complex is a new ion, differing from other ions mainly by nondiffusibility, or whether we adopt the view supported by Bancroft that the gelatin units are a separate phase, to which the hydrogen ion is selectively adsorbed. The combination with the hydroxyl ion of bases is of the same type as with the hydrogen ion and apparently of about the same strength. On the alkaline side of the isoelectric point, the gelatin-hydroxyl ion complex will therefore hold any available cation at least electrostatically. Loeb [1] has given striking qualitative demonstrations of these phenomena. Using the photochemical reduction of silver ion by gelatin as a test for its presence, it is readily shown that this ion can be washed completely out of gelatin on the acid side of the isoelectric point, but is retained at pH greater than 4.7.

Recent investigations have disclosed numerous cases in which this simple treatment is invalidated by appreciable combination of other ions with the gelatin in such a manner as to reduce their activity. The combination with cations extended well to the acid side of the isoelectric point, and that of the anions to the alkaline side. Northrop and Kunitz [2] have furnished the most data on this subject, using concentration cells, and an ingenious method based on the measurement of membrane potential for those ions for which no electrode was available.

Most of their measurements were made at the isoelectric point, where no combination of the gelatin with any ion is to be expected on the simple theory, but they also studied the effect of varying hydrogen ion concentration. No combination of Na^+ or K^+ was detected, but a single determination with silver nitrate showed appreciable combination of the silver ion. All the bivalent cations tested (Cu^{++}, Ca^{++}, and Mg^{++}) were found to combine with the gelatin in amounts varying with their concentration and the pH, up to 9×10^{-4} gram equivalents per gram of gelatin. This maximum not only agrees with that obtained by Hitchcock [3] for hydrogen, but in mixtures of copper salts and acids the total of combined hydrogen and copper ions was approximately constant at this value. The combined copper was appreciable even at pH 2, although for the same activity it was very much less than the combined hydrogen. The maximum combination with both copper and hydrogen was reduced to 5×10^{-4} gram equivalent per gram of gelatin by deaminizing. Al^{+++} and La^{+++} reached a maximum of about 5×10^{-4} gram equivalent per gram gelatin, although the measurements were carried up to molar solutions; this, like the equivalence of hydrogen and copper, is strong evidence for true chemical combination, since the adsorption of trivalent ions would be expected to be greater than that of bivalent ions.

The measurements with copper were not carried to the alkaline side of the isoelectric point, but those with calcium covered a range of pH 2.5 to 10. Northrop and Kunitz state that "the value (of combined calcium) rises rapidly as the solution becomes less acid and remains approximately constant on the alkaline side of pH 4.7," but to the writers their data are more consistent with a continuous increase with pH.

No combination of nitrate or sulphate ion was detected, but combination with chloride ion up to 3×10^{-4} gram equivalent per gram

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[1] Loeb, Proteins and the Theory of Colloid Behavior.
[2] Northrop and Kunitz, J. General Physiology, vol. 7, p. 25, 1924; vol. 9, p. 351, 1926; vol. 11, p. 481; 1928.
[3] Hitchcock, J. General Physiology, vol. 12, p. 495; 1929.

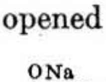
of gelatin was reported in the more concentrated solutions (0.1 *M* or more).

The combination of silver ion and gelatin has been investigated in other cases. Pauli and Matula,[4] using concentration cells, found depression of silver ion concentration on adding gelatin, but their gelatin was not deashed and they give no data on pH.

There have been two investigations in photographic laboratories. Rawling and Mitchell,[5] working on methods of determination of soluble bromide in emulsions, found that they extracted more than should have been present. The effect was greater in silver chloride emulsions and absent in those of silver iodide. They infer from this the existence of a silver gelatin complex in amounts varying with the silver ion concentration.

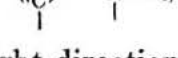
Schmidt and Pretschner,[6] after numerous analyses of photographic emulsions for nonhalide silver, have concluded that the excess silver found in thoroughly washed emulsions was formed during the washing process. They found that the excess was proportional to the solubility of the silver halide, and postulate an equilibrium between the silver halide and silver-gelatin complex depending on the relative solubilities.

One explanation for selective combination of silver ion with gelatin lies in the stability of silver ion-amino complexes. Northrop and Kunitz[7] predicted the combination of copper ion with gelatin on this basis, and apparently had the same idea in mind in their reference to the "expected" combination with silver ion. If this theory is correct, there should be no selective combination of the $Ag(NH_3)_2^+$ ion with gelatin, since the affinity of the silver for amino nitrogen is satisfied. This prediction was verified by experiment. If the analogy with the silver ammonia complex is complete, it involves combination of neutral gelatin molecules with silver ions, to form new positively charged complexes. The effect of hydrogen ion concentration would then be ascribed to a change in the free NH_2 groups with which the silver combines. Assuming the existence of peptide linkages



$$-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$$

in the gelatin, which might be opened by alkali to form



the effect would be in the right direction.

Another alternative is the formation of a silver gelatinate entirely analogous to the sodium gelatinate of Loeb's theory, but distinguished from it by insolubility. The coagulation of proteins by silver salts is evidence for this view. Silver gelatinate would be subject to hydrolysis decreasing with increasing alkalinity. Its existence on the acid side of the isoelectric point is inconsistent with the simple theory as developed by Loeb. However, the isoelectric point represents an

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[4] Pauli and Matula, Biochem. Zeit., vol. 80, p. 187; 1917.

[5] Rawling and Mitchell, Proc. 8th Int. Cong. of Phot. Abstract in Phot. Ind. vol. 29, p. 905; 1931.

[6] H. H. Schmidt, Proc. 8th Int. Cong. of Phot. Abstract in Phot. Ind. vol. 29, p. 906; 1931.

[7] See footnote 2.

equality between the two forms of ionized gelatin; it is not necessarily true that both are equal to zero. It is possible that they are in an equilibrium like the ions of water, with a rapid change in proportions at the isoelectric point like that of the ions of water at the neutral point.

II. EQUILIBRIUM IN GELATIN-SILVER NITRATE SOLUTIONS AT VARYING HYDROGEN ION CONCENTRATIONS

1. APPARATUS

The combination of silver ion and gelatin was studied by making electrometric measurements of silver ion concentration in mixed solutions of gelatin and silver nitrate. Further experiments in silver bromide-gelatin emulsions, which were tested photographically as well as chemically, will be described in a separate communication.

All determinations were made at 30.0° C., using a simple air thermostat. This was a cubical box, 2 feet on edge, lined with heat insulating board on all sides but the front. The door in the front was provided with a double glass window, coated with orange lacquer, which excluded practically all radiation of wave length less than 520 mμ. This precaution was probably unnecessary, as the cell was illuminated only by relatively dim artificial light, but for measurements of silver ion concentrations in photographic emulsions the possibility of error from photolysis was not to be disregarded. The air was circulated in the thermostat by a blower of 55 cubic feet per minute capacity. By making the bulb of the thermoregulator a grid of 10 mm tubing placed across the inlet of the blower, and using a heater of fine bare wire in the outlet tube, lag was reduced so that fluctuations as measured by a mercury thermometer were less than 0.02°; all measurements were made at 30.0° ±0.1°.

The electrical measurements were made with a Leeds and Northrup "student" potentiometer, calibrated in the resistance section of this bureau and found to be accurate to 0.1 millivolt. The galvanometer was the Leeds and Northrup type 2500e, designed for electrode work.

A 0.1 N calomel electrode was used for reference. This was connected to the silver electrode by a salt bridge somewhat modified from that of Clark.[8] The arrangement, which is shown in Figure 1, was designed primarily for electrometric titrations, but was found suitable for potential measurements. The calomel electrode vessel was of the Clark [9] type, but the upturned tip of the connecting tube was replaced by a short piece of heavy walled tubing, about 1.5 mm bore. This passed through a rubber stopper, along with the T tube of heavy walled 1.5 mm tubing which completed the bridge. The whole apparatus was supported so that it could be lifted and swung to one side. In making connections, the cup which fitted over the rubber stopper was nearly filled with the ammonium nitrate solution. It was then forced up until it made a tight joint with the stopper; ammonium nitrate solution was forced out through the T tube, filling it. The cell and bridge were then swung over so that the upturned tip of the bridge could be lowered into the solution under test, which was ordinarily contained in a beaker with a mechanical stirrer.

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[8] W. Clark, J. Chem. Soc., p. 749; 1926.

[9] W. Mansfield Clark, The Determination of Hydrogen Ions, 2d edition, p. 194, E.

There was no indication that chloride from the calomel electrode diffused through the bridge even over a period of hours. Potentials were reproducible to less than one millivolt. They were not appreciably improved by the use of a wider (5 mm) tip on the connecting tube.

The electrodes used for the silver ion-gelatin equilibrium were 1 mm wires of pure silver, annealed and frequently cleaned with cyanide solution and hot water whenever they became appreciably sluggish. They checked within 0.5 millivolt or less. The silver wires were sealed into glass tubes with de Khotinsky cement or ceresin so that the metal was completely under the surface of the liquid. For some of the earlier work (emulsions 6–83 to 86) silver plated platinum wires were used; these were also reproducible to 0.5 millivolt, but were somewhat slower to reach equilibrium. For determinations

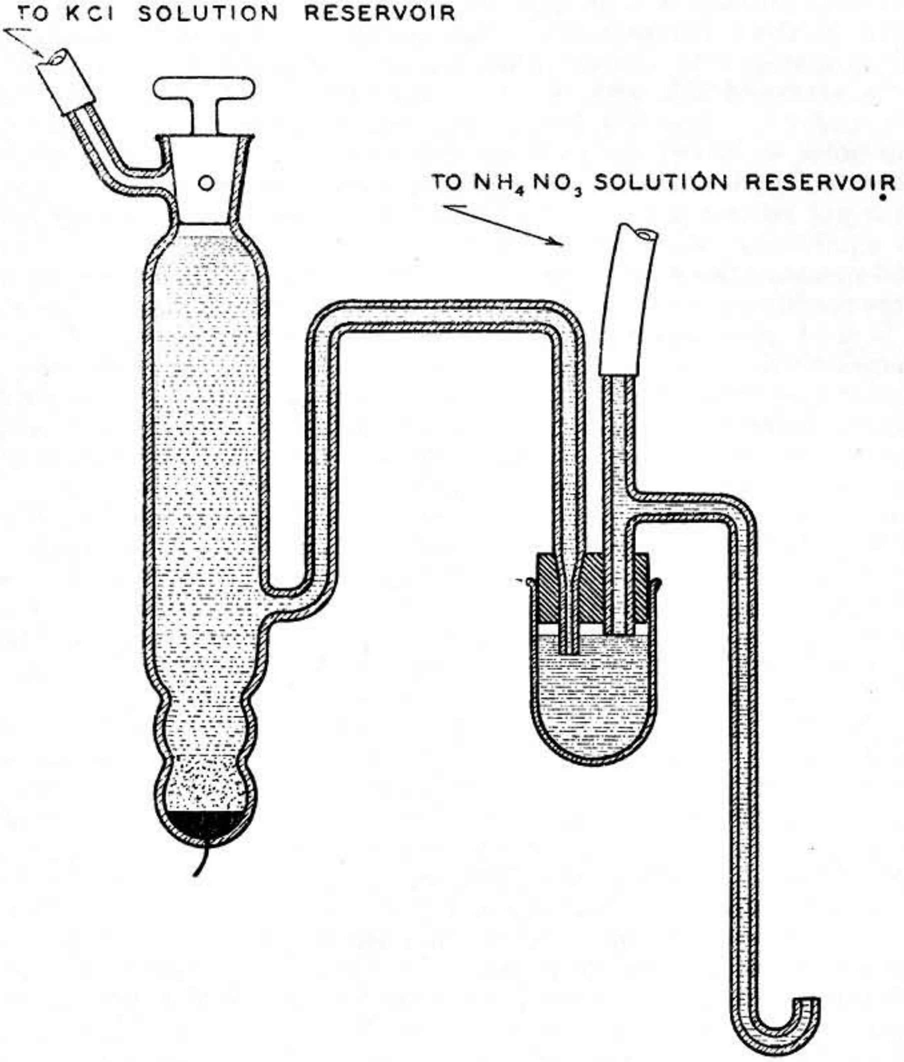

FIGURE 1.—*Calomel electrode and salt bridge for determination of silver ion concentration*

of bromide ion concentration in other solutions and for all measurements in emulsions, the electrodes were momentarily made anode in a dilute bromide solution and washed before use. With this treatment the electrodes reached equilibrium with the solution much more rapidly.

Fifteen per cent ammonium nitrate solution was used in the salt bridge, saturated potassium chloride being obviously out of the question for measurements of silver ion concentration. Liquid junction potentials appeared to be eliminated within the limits of error in the measurements. For example, the e. m. f. of the cell changed only 0.7 millivolt when 0.0100 N KBr pH 6.9, was replaced by mixtures of KBr and H_2SO_4, each 0.0100 N KBr but with pH 5.2, 3.0, and 2.1. The NH_4NO_3 introduced a source of error in alkaline solutions, as, if any diffused out into the solution, free ammonia was liberated and affected the silver ion concentration. In mixtures with pH greater than 8, it was necessary to bring the silver electrode to equilibrium with the solution and then connect the salt bridge and measure the e. m. f. as rapidly as possible. The electrodes also were readily poisoned in alkaline mixtures of silver nitrate and gelatin.

It is obvious that no high order of accuracy can be claimed for the electrometric measurements as such. It will be equally obvious that this accuracy was quite sufficient for the purposes of this investigation, being better than that of any of the photographic measurements. As our measurements were made at 30°, they can not be compared directly with accepted values, but we may note that, using the values of Lewis and Storch,[10] the e. m. f. of the cell Hg, HgCl, KCl $(0.1M)\|NH_4NO_3$ (15 per cent) $\|$ HBr $(0.01\ M)$, AgBr, Ag should be 0.1411 volt at 25°, while we obtained 0.1405 volt at 30°. The temperature correction is probably not over 1 millivolt. Combining the above value with an e. m. f. of -0.2820 volt for Hg, HgCl, KCl $(0.1\ M)$ $\|$ NH_4NO_3 (15 per cent) $\|$ $AgNO_3$ $(0.001\ M)$, Ag, we obtain $9.6 \times 10^{-7}\ M$ for the solubility of AgBr at 30°.

The same apparatus was used for electrometric titrations. The solutions were added from a burette with a long tip passing through the top of the thermostat so that it was unnecessary to open the air thermostat during the titration. While the potential was read after each addition, the end point was always determined from a plot of $\Delta E/\ \Delta v$, as in a differential titration. It was necessary, in work with small quantities near the end point, to be sure that the burette reading always corresponded to an integral number of drops, since the volume of a single drop might lead to a large error in Δv. The necessary potentiometer readings were found to add relatively little to the time required for the electrode to come to equilibrium after each addition of solution, so that this method was little slower than a differential titration, while it had a very real advantage in that the silver ion concentration indicated clearly the approach of the end point. This last was especially useful for titration of a solution for both bromide and chloride. The solutions were stirred continuously by a small mechanical stirrer belted to a motor outside the thermostat. The belt drive was convenient from the standpoint of space, but it was necessary to ground the stirrer carefully to avoid error from static charges.

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[10] Lewis and Storch, J. Am. Chem. Soc., vol. 39, p. 2544; 1917.

Hydrogen ion concentrations were measured at 30° in the same thermostat, using a saturated calomel electrode and a bubbling hydrogen electrode. A quinhydrone electrode was also used on some of the acid mixtures. As neither can be used in the presence of silver ions, the pH of emulsions was determined colorimetrically by comparison with standard buffer solutions after the emulsions had been cleared by centrifuging.

2. SILVER ION CONCENTRATIONS

The gelatin used in these experiments was known to have been made from limed calfskin stock. It was deashed by the method of Northrop and Kunitz,[11] but as the conductivity of the gelatin after the recommended number of washings was somewhat high (7×10^{-5} reciprocal ohms for a solution of 2.3 g in 100 g of water, at 30°) it was washed with four more changes of distilled water (conductivity 1×10^{-6}). This raised the pH of the gelatin to 5.4. The air-dry material was found to contain 13 per cent moisture when dried at 105° to 110°. All solutions were made up with 1.150 g of air-dry gelatin to 100 ml.

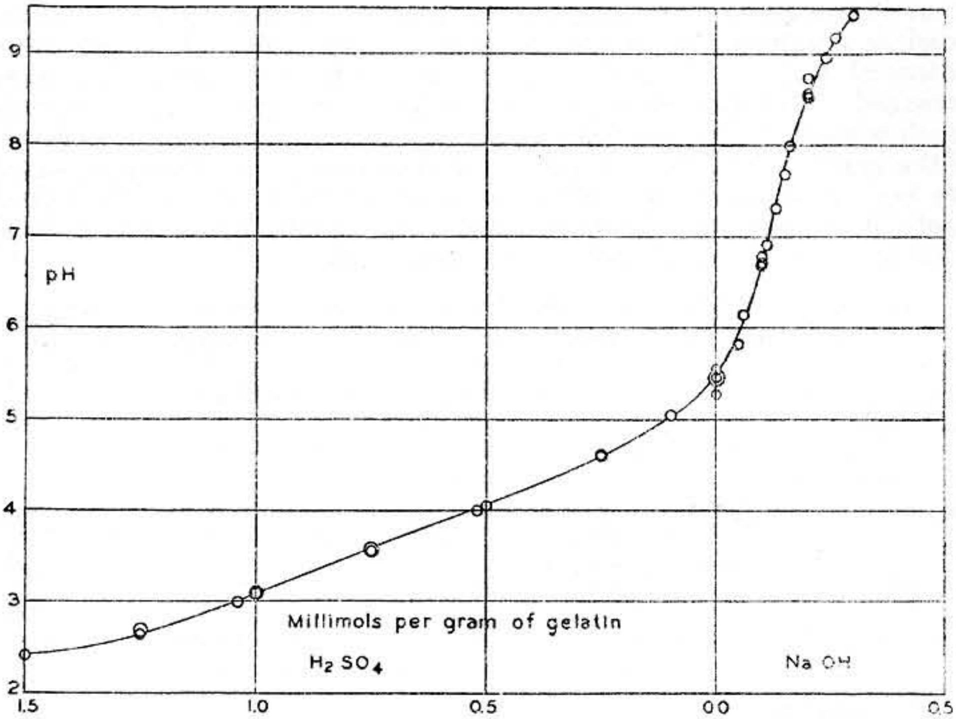

Figure 2.—*Titration curve of isoelectric gelatin used in experiments, at a concentration of 1.00 g per 100 ml*

The hydrogen ion concentration was adjusted by appropriate amounts of sulphuric acid or (carbonate-free) sodium hydroxide. The titration curve is reproduced in Figure 2. Mixtures were found to be readily reproducible to less than 0.1 pH unit except on the steepest part of the curve, around pH 7, where the error may have reached 0.2.

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[11] Northrop and Kunitz, J. General Physiology, vol. 11, p. 477; 1928.

The equilibrium measurements were first made on three series of mixtures, each series containing a constant amount of silver nitrate and gelatin at varying pH. Attempts to carry the measurements to higher silver concentrations (10^{-2} N $AgNO_3$) were unsuccessful. The electrodes were very readily poisoned, apparently by coagulated gelatin, and as the changes in concentration were smaller, the results were much less reliable. The data for silver ion activities in mixtures of 1.00 g gelatin per 100 ml over a range of pH 2.4 to 9.5 and a range of $AgNO_3$ normality 10^{-3} to 10^{-5}, are given in Table 1. Table 2 gives the data for mixtures at pH 7.0, 10^{-3} and 10^{-4} N $AgNO_3$ and varying gelatin concentration.

Some measurements were made on mixtures of gelatin and bromide solutions on the acid side of the isoelectric point where the combination of silver ion and gelatin was relatively small, in an attempt to detect possible combination of bromide ion and gelatin. The changes in potential were small and erratic, the electrodes readily becoming poisoned. Any combination of bromide ion and gelatin is apparently much weaker than that of silver ion and gelatin, even on the acid side of the isoelectric point. In the electrode readings in emulsions, which are kept in equilibrium with silver bromide by the large amount of finely divided solid, the potentials were steady and reproducible, with little tendency to poison the electrodes.

TABLE 1.—*Activity of silver ion in mixtures of silver nitrate and gelatin*

1.00 g gelatin per 100 ml in all mixtures; silver nitrate and hydrogen ion concentrations varied

Concentration of $AgNO_3$ in mixture, N	Activity of silver ion in mixture, at pH							
	2.4	3.0	3.5	4.0	4.5	5.0	5.5	6.0
1.00×10^{-3}	6.7×10^{-4}	6.0×10^{-4}	5.6×10^{-4}	5.4×10^{-4}	4.9×10^{-4}	4.1×10^{-4}	3.3×10^{-4}	3.0×10^{-4}
9.7×10^{-5}	3.42×10^{-5}	3.30×10^{-5}	2.70×10^{-5}	2.32×10^{-5}	1.53×10^{-5}	7.9×10^{-6}	3.9×10^{-6}	1.9×10^{-6}
1.04×10^{-5}	----------	1.60×10^{-6}	----------	1.14×10^{-6}	----------	2.9×10^{-7}	----------	5.1×10^{-8}

Concentration of $AgNO_3$ in mixture, N	Activity of silver ion in mixture, at pH						
	6.5	7.0	7.5	8.0	8.5	9.0	9.5
1.00×10^{-3}	2.65×10^{-4}	2.42×10^{-4}	2.20×10^{-4}	1.55×10^{-4}	1.1×10^{-4}	4.3×10^{-5}	1.17×10^{-5}
9.7×10^{-5}	9.4×10^{-7}	6.0×10^{-7}	3.6×10^{-7}	2.4×10^{-7}	1.5×10^{-7}	8.4×10^{-8}	4×10^{-8}
1.04×10^{-5}	----------	1.45×10^{-8}	9.0×10^{-9}	5.6×10^{-9}	3.3×10^{-9}	2.1×10^{-9}	9×10^{-10}

TABLE 2.—*Silver ion activity in mixtures of silver nitrate and gelatin*

pH constant at 7.0; gelatin and silver nitrate concentrations varied

Concentration of gelatin, g per 100 ml	Silver ion activity	
	Silver nitrate 9.7×10^{-4} N	Silver nitrate 9.7×10^{-5} N
1.00	2.4×10^{-4}	6.0×10^{-7}
.50	5.1×10^{-4}	3.6×10^{-6}
.25	7.0×10^{-4}	1.65×10^{-5}
.125	7.8×10^{-4}	4.3×10^{-5}
.063	8.7×10^{-4}	6.1×10^{-5}

3. DISCUSSION

Results for both series of measurements of silver nitrate-gelatin solutions are presented in Figure 3, calculated as gram equivalents of silver combined with one gram of gelatin. In making the calculations, the silver ion concentrations have been computed from the activities by means of the ionic strength tables given by Lewis and Randall.[12] They were practically identical except in the more acid mixtures, which contained up to 0.015 N H_2SO_4. In making this com-

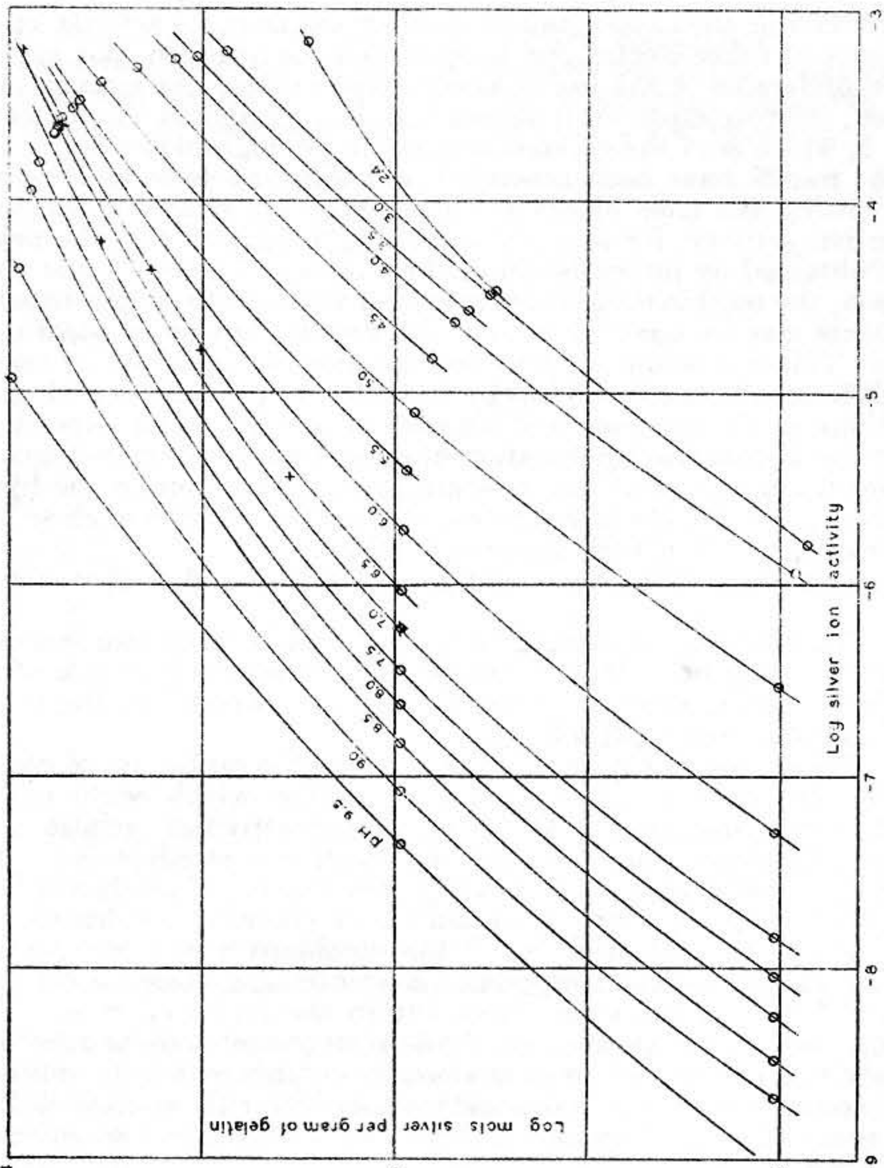

FIGURE 3.—*Combination of silver ion and gelatin at 30°. Circles represent determinations at a concentration of 1.00 g per 100 ml; crosses, determinations at other gelatin concentrations and pH 7*

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[12] Lewis and Randall, Thermodynamics, p. 382.

putation, we are using the same assumption as Northrop and Kunitz,[13] that the gelatin does not affect the ionic strength. To put it differently, the complex gelatin-hydrogen ion affects the ionic strength by the same amount as the hydrogen ion, so that it is the same in the gelatin-acid mixture as in the pure acid. In this case the contribution of the bivalent sulphate ion to the ionic strength is much the larger, so that any error in the assumption is minimized. The whole calculation of the concentration of silver ion from its activity in the presence of other electrolytes is open to some question, but appears to be preferable to the use of uncorrected values. As already mentioned, the correction for ionic strength is negligible in the pH range 5 to 9, which is of the greatest interest in photographic work.

The results have been presented in a different form in Figure 4, by plotting the mols of silver ion per gram of gelatin at constant silver ion activity, for four values of $[Ag^+]$, against pH; the points were obtained by interpolation of the curves of Figure 3. For comparison, the combination of hydroxyl ion with gelatin is presented in the same way by the dashed line with crosses, but on one-tenth the scale. This was computed from the titration curve simply by taking the difference between the free hydroxyl ion in the sodium hydroxide solutions in the presence and absence of gelatin. The implied assumption is that the combination of gelatin with either hydrogen or hydroxyl ion is zero at the isoelectric point, but even on the hypothesis suggested in the introduction, it would be small enough so that the values would not be materially affected.

On inspection of Tables 1 and 2, and Figs. 3 and 4, it is evident that—

1. The silver ion combined with unit weight of gelatin increases with increasing pH. It does not fall to zero on the acid side of the isoelectric point, although there is a definite "break" in the curves of Figure 4 at about pH 4.7.
2. The curves of Figure 3 indicate a possible maximum of combination, but only at silver ion concentrations which could not be reached experimentally. At corresponding activities, gelatin combines with many times as much hydroxyl ion as silver ion. The silver ion-gelatin reaction is nevertheless capable of producing large changes in silver ion concentration under emulsion conditions.
3. At constant pH and $[Ag^+]$, the combined silver per gram of gelatin was independent of gelatin concentration, since all the data for pH 7 fall on the same curve within the limits of error. This permits us to eliminate the hypothesis of an insoluble silver gelatinate of definite proportions formed in amounts varying with the conditions, as it would require that with constant total silver the combined silver per gram of gelatin should increase as the gelatin concentration decreased.

The nearly straight lines of Figure 3 show that the combination closely follows the adsorption isotherm. The value of $1/n$ is somewhat higher than usual, varying from 0.5 at pH 9 to 0.6 at pH 3. In the present state of colloid chemistry, it is hardly worth while to discuss, on the basis of the available evidence, whether this combination is to be designated as selective adsorption or as chemical combination. The silver is probably attached to the amino groups of the gelatin,

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[13] Reference 2.

since the silver-ammonia ion is not adsorbed. (Sec. III of this paper.) It will be noted that the "break" in the curves of Figure 4 at the isoelectric point becomes more pronounced with increasing silver ion concentration, so that the combination more nearly approaches the prediction of the simple chemical theory.

It is probable that the decrease in silver ion activity produced by the gelatin tends to stabilize the emulsion from the photographic standpoint, retarding the reduction or other reactions of the silver ion. Reaction by rearrangement of the silver ion-gelatin complex is, of course, possible but likely to be slower. Photographic evidence will be considered in connection with the equilibrium in emulsions.

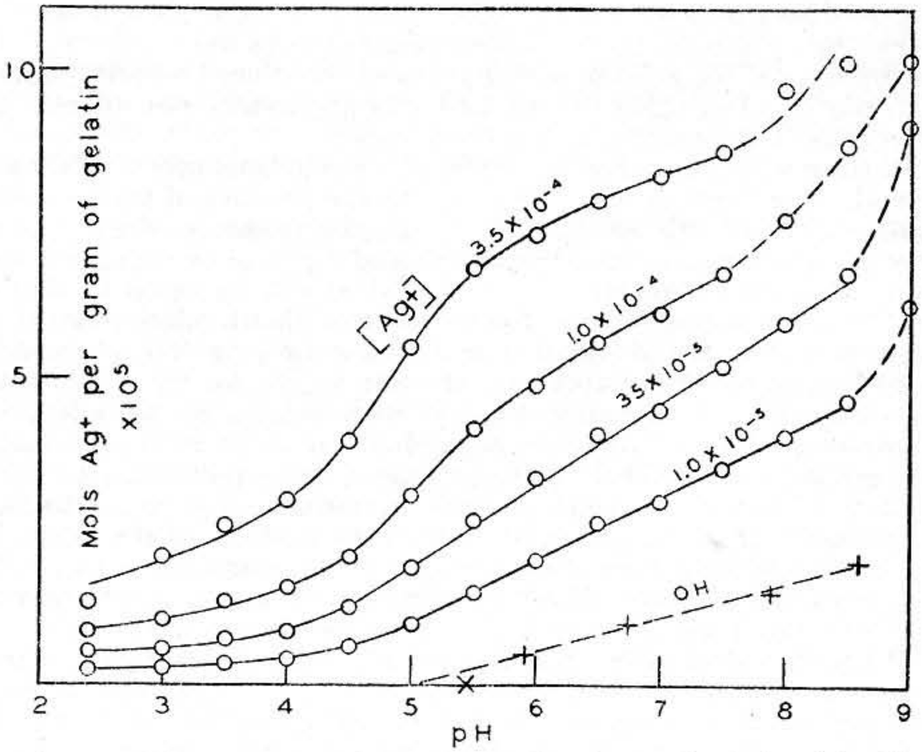

FIGURE 4.—*Change in combination of silver ion and gelatin with pH*

Crosses represent combination of hydroxyl ion and gelatin, on one-tenth the scale

As the combination is quite appreciable even at the silver ion concentration of saturated silver bromide ($10^{-6}N$ at 30°), the solubility of silver bromide is increased in the presence of gelatin by an amount depending on the pH and gelatin concentration. Experiments under emulsion conditions indicate that it can easily reach $4\times10^{-5}N$ as against $1.0\times10^{-6}N$ in pure water.

III. EQUILIBRIUM IN SILVER BROMIDE-AMMONIA-GELATIN SOLUTIONS

Since ammonia is added to many emulsions for the purpose of accelerating the ripening process, the equilibrium between the gelatin and the dissolved silver salts is of considerable interest. This was also investigated by e. m. f. measurements in the same apparatus, as it was found reliable readings for bromide ion concentration could be obtained in the presence of ammonia provided that care was taken to keep the solution saturated with silver bromide. A small closed cell, without stirrer, was found to be satisfactory. The assumption is made that the presence of the ammonia does not change the solubility product of silver bromide, that is, that there is no change of solvent. This appears to have been justified.

The necessary data, which are given in Table 3, consisted simply of determinations of the bromide ion concentration in ammonia solutions of varying concentrations, saturated with silver bromide. The solutions were made up in pairs, with and without the addition of 1.00 gram gelatin per 100 ml. The solutions were kept in the 30° thermostat, in glass-stoppered Pyrex flasks, agitated at intervals and sampled every day until readings on three successive days were constant. In the presence of the gelatin, which peptized the silver bromide, equilibrium was reached more rapidly and was apparently not affected by hydrolysis of the gelatin as had been feared.

Starting with pure silver bromide, equivalent amounts of silver and bromide ions must go into solution, and the product of their concentrations at 30.0° will be 9.2×10^{-13}. In the presence of even small amounts of ammonia, the concentration of Ag^+ will be negligible with respect to that of $Ag(NH_3)_2^+$, so the latter will be equal to that of Br^-. The measurements on the solutions without gelatin constitute a determination of the equilibrium between Ag^+, $Ag(NH_3)_2^+$ and NH_3 at 30°, and give reasonably reproducible values for the equilibrium constant. The combination of Ag^+ with gelatin at the silver ion activities in these solutions, is negligible. If there were appreciable combination of $Ag(NH_3)_2^+$ with the gelatin, the equilibrium would be disturbed, with consequent increase in bromide ion concentration. As is evident from inspection of table 3, the readings of the cells with and without gelatin were the same with the experimental error. The combination of the $Ag(NH_3)_2^+$ ion with gelatin must at least be very small compared with that of Ag^+ at the same activity and pH.

The failure of the silver-ammonia ion to combine with gelatin is of interest in connection with ammonia ripening of emulsions. During ripening before washing, soluble bromide is present in concentrations of the order of 0.02 to $0.1N$; the silver ion concentration is correspondingly small ($10^{-9}N$ or less, depending on temperature). Adding ammonia under these conditions, the amount of silver bromide which can go into solution is negligible with respect to the soluble bromide present; the bromide and silver ion concentrations are therefore practically unchanged. The silver ion bound to gelatin will increase because of the increased alkalinity, but must remain very small. The increased solubility of silver bromide results in increased rate of change of grain size, but the silver-ammonia ion is quite unlikely to undergo direct reaction to silver or silver sulphide. The increased rate of formation of sensitizing nuclei in the presence of ammonia is therefore to be ascribed to the increased alkalinity.

TABLE 3.—*Equilibrium at 30.0° in ammonia solutions saturated with silver bromide, with and without gelatin*

Ammonia concentration N	E. m. f. of cell (silver electrode negative)	Bromide-ion concentration	Equilibrium constant $\frac{[Ag^+]\times[NH_3]^2}{[Ag(NH_2)_2^+]}$	E. m. f. of cell with gelatin
	Volts			*Volts*
0.05	0.0366	1.75×10^{-4}	7.5×10^{-8}	0.0365
.10	.0550	3.5×10^{-4}	7.4×10^{-8}	.0539
.20	.0726	7.0×10^{-4}	7.5×10^{-8}	.0716
.40	.0909	1.41×10^{-3}	7.3×10^{-8}	.0887
.80	.1082	2.73×10^{-3}	7.9×10^{-8}	.1064

These data, it will be noted, apply to the addition of ammonia to liquid emulsions. When dried emulsions on photographic plates are bathed in ammonia solutions, as in hypersensitizing, the resulting equilibrium involves other factors. This will be discussed in a separate communication on hypersentization.

IV. THE COMPOSITION OF EMULSIONS WASHED TO EQUILIBRIUM

Under practical conditions, the washing of a photographic emulsion is carried only far enough to reduce the soluble bromide below a predetermined value. The test commonly recommended is to add silver nitrate to a sample, with potassium chromate as indicator. The minimum amount of soluble bromide which can be detected in this way must be very large compared to the bromide-ion concentration of saturated silver bromide. Most commercial emulsions as coated contain soluble bromide in a molar ratio 3–10 to 1,000 of silver bromide, although this may have been added after washing.

It is common knowledge [14] that emulsions which have been washed too thoroughly are liable to fog. We have already [15] presented data on the effect of bromide-ion concentration during after-ripening which illustrates this.

Recently Schmidt and Pretschner [16] have analyzed thoroughly washed emulsions by digestion with nitric acid and gravimetric determination of the soluble silver in the filtrate. They originally considered that this was metallic silver, formed by reduction of the silver halide during the preparation of the emulsion, but correctly decided that it could not be identified with the ripening nuclei, since there was no correlation between the amount of excess silver and the sensitivity. They have since,[17] on the basis of other evidence, realized that the silver was not present as metal but in combination with the gelatin. They found that the amount of excess silver increased with the solubility of the silver salt. Recalculating their results reported in reference 16 to gram equivalents of silver per gram of gelatin, on the assumption that their emulsions contained about 1.6 grams gelatin per gram of silver bromide, they found that the excess silver varied from zero in silver iodide emulsions to 3 to 4 $\times 10^{-6}$ in silver bromide

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[14] Wall, Photographic Emulsions, p. 145. Eder-Wentzel, Die Fabrikation der photographischen Platten • • •, p. 127.

[15] Carroll and Hubbard, B. S. Jour. Research, vol. 7, p. 219; 1931.

[16] Schmidt and Pretschner, Zs. wiss. Phot., vol. 25, p. 293; 1928.

[17] Reference 6.

emulsions, and 2×10^{-5} in silver chloride emulsions. They used 700 g samples of emulsion "noodles," which had been washed 10 hours in running tap water, then 24 hours in distilled water, the washing being continued 4 to 5 hours after the washings gave no turbidity with silver nitrate. This is much more thorough than any practical emulsion washing, but as the emulsion was in "noodles" several mm. thick, it is almost certain that it did not reach complete equilibrium with the wash water.

In their most recent communication,[18] which is available only in abstract, they report that on sufficiently long washing the excess silver tended to decrease; this was not observed in any of the experiments in this laboratory. This was attributed to the difference in solubility of the silver halide grains of commercial brom-iodide emulsions, produced by differences in size and composition. The effect of size per se seems unlikely to be appreciable, but the smaller and larger grains of a brom-iodide emulsion differ widely in percentage of iodide [19] in such a way that the size effect may be enormously accentuated. However, even the smallest and most soluble grains would be removed only on very extensive washing.

If pure silver bromide dispersed in a gelatin jelly is allowed to come to equilibrium with water, the resulting bromide-ion concentration will be higher than that of saturated silver bromide, since silver ion will combine with gelatin, and the equivalent amount of bromide ion will remain in solution. The silver ion in combination with the gelatin will, therefore, be less than corresponds to the silver-ion concentration of saturated AgBr. If the wash water is repeatedly changed, removing the soluble bromide, the gelatin will ultimately come to equilibrium with the silver-ion concentration of saturated silver bromide, and further washing will remove Ag^+ and Br^- in equivalent amounts. At 30° and pH 7, for example, this corresponds to 1.2×10^{-5} g equivalents of Ag^+ per g of gelatin; the amount will vary with the temperature and pH.

Our first experiments on the effect of continued washing on the excess of silver over bromide were made to check the results of Schmidt and Pretschner, and the emulsions were extracted with 3 per cent HNO_3 according to their method. Working with the emulsion stripped from 5 by 7 inch plates, electrometric titration of the extract with 0.0010 N KBr was substituted for gravimetric analysis, with complete satisfaction.

It was found, in this way, that both with commercial and experimental emulsions, the excess silver became constant only after plates had been washed in running tap water for about 20 hours; washing is obviously much more rapid in the very thin coating of a plate than in emulsion noodles. The constant value obtained this way was 1.4 to 1.5×10^{-5} g equivalent Ag^+ per g gelatin, at a pH of 8 to 8.5. This amounts to 0.4 per cent of the total silver in the plate.

It was later found [20] that the excess silver could be determined by extraction with dilute acid, or by simply acidifying the stripped emulsion to pH 2 to 3, thus reducing the silver ion-gelatin combination and making a direct electrometric titration without extraction.

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[18] Reference 6.

[19] Renwick and Sease, Phot. J., vol. 64, p. 360; 1924.

[20] Preliminary note in Technical News Bulletin of Bureau of Standards, September, 1930. Details will be given in a separate communication on analysis of emulsions for excess silver or bromide.

This method was used in further washing experiments which gave a satisfactory check with the equilibrium values obtained in solution.

Experimental emulsions were made up with pure silver bromide and chloride and coated in known amounts per unit area. The plates were washed for 48 hours in running tap water and for 24 hours in frequent changes of distilled water, both at 20°. The stripped emulsions were then acidified and titrated, using 0.0010 *N* KBr for the bromide emulsion and 0.010 *N* KCl for the chloride emulsion.

At 20° the silver-ion concentration of saturated silver bromide is 5.5×10^{-7} *N*; at this concentration and pH 8 gelatin is in equilibrium with 1.4×10^{-5} g equivalent Ag^+ per g (Figure 3). In the washed plates, the values found by titration were 1.79, 1.76×10^{-5}. Similarly, for saturated silver chloride at 20°, the silver-ion concentration is 1.05×10^{-5} *N*; the Ag^+ per g gelatin at pH 8 is 4.1×10^{-5} g equivalents by Figure 3 and 3.2, 3.1×10^{-5} by titration of the washed plates.

V. SUMMARY

1. The equilibrium between silver ion and gelatin has been studied by the silver electrode over a considerable range of silver and hydrogen-ion concentrations. Gelatin may cause large changes in silver-ion concentrations under conditions similar to those in photographic emulsions.

2. No combination of gelatin with the silver-ammonia ion was detected.

3. Prolonged washing of silver bromide or chloride gelatin emulsions causes appreciable hydrolysis of the silver halide, leaving the emulsion with analytically detectable excess silver in combination with the gelatin.

WASHINGTON, September 22, 1931.

U. S. GOVERNMENT PRINTING OFFICE: 1931

RP430

THE PHOTOGRAPHIC EMULSION: SILVER ION AND HYDROGEN ION CONCENTRATIONS AND SENSITIVITY

By Burt H. Carroll and Donald Hubbard

ABSTRACT

The paper is introduced by discussions of previous experimental and theoretical work on silver and hydrogen ion concentrations in emulsions, and description of experimental technique. These variables are taken up first according to their effects on afterripening, and second according to their direct effects on sensitivity when changes in afterripening are eliminated (in experiments after digestion). The rate of afterripening increases with increasing silver ion concentration and increasing pH; the corresponding effects on sensitivity are much larger than those produced by the direct effect of environment (after digestion). The combination of silver ion with gelatin reduces the effect of excess silver. Illustrations are given for the distribution of excess bromide or silver in the emulsion with changing pH. The desensitizing action of bromide (after digestion) is found to increase with increasing acidity; conversely, the effect of pH is dependent on the silver ion concentration. Spectral sensitivity of the emulsions is found to be independent of hydrogen or silver ion concentrations; these variables must, therefore, influence sensitivity through secondary reactions in latent image formation. Results are discussed in terms of a new concept of the adsorption of gelatin to silver bromide, based on the "zwitterion" theory of ampholytes.

CONTENTS

I. INTRODUCTION

It has long been common knowledge that the photochemical sensitivity of silver halides is increased by the presence of soluble silver salts. The effect of acidity or alkalinity has been less clearly recognized, but early work on both these variables in silver bromide-gelatin emulsions is to be found in Eder's Handbuch.[1] While these variables must always be studied by using acids or alkalies in one case, and soluble silver salts or bromides in the other, it is now recognized that the results of experiments upon the effects of acids and bases may most frequently be generalized by considering the resulting concentration

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[1] J. M. Eder, Ausführliches Handbuch der Photographie, vol. 3, 5th ed., pp. 50, 131, 1903

(or activity) of the hydrogen ion which is the common variable in all such experiments. In silver bromide emulsions, the effects of adding silver salts or bromides may similarly be expressed in terms of the resulting silver ion concentrations. In aqueous solutions the concentrations of hydrogen and hydroxyl ions may always be expressed by the relation $[H^+] \times [OH^-] = 10^{-14}$. Similarly, in silver bromide emulsions, at 30° C., $[Ag^+] \times [Br^-] = 9.2 \times 10^{-13}$. The solubility product of silver bromide here plays a part analogous to the dissociation product of water, since the enormous available surface of the highly disperse silver bromide insures that the emulsion may at all times be considered saturated with respect to this salt. The silver ion concentration may be determined by the potential of the silver-silver bromide electrode exactly as the hydrogen ion concentration is determined by the hydrogen electrode. It is also possible to express the results in terms of the excess of one material or another which is present, but as gelatin combines both with hydrogen ions and silver ions,[2] the relations of the chemical composition to the ion concentrations may be quite complicated. Data on these relations of chemical composition to ion concentrations will be given in this paper, but we will in general discuss the results in terms of the ion concentrations. As just explained, silver ion and bromide ion concentrations are interrelated like hydrogen ion and hydroxyl ion concentrations and either may be used to specify a given condition. The silver ion-gelatin combination being dependent on the hydrogen ion concentration, the silver ion and hydrogen ion concentrations of an emulsion are not entirely independent variables and are, therefore, treated together in this paper.

The relation of any variable to sensitivity of photographic emulsions changes with the stage of emulsion making which is under consideration. We shall deal in this paper only with the effects on the washed emulsion, omitting the ripening process before washing. Even with this limitation of scope it seems necessary to distinguish between two possible mechanisms. In the first place, both silver and hydrogen ion concentrations of an emulsion during digestion will influence sensitivity through the rate of afterripening; we[3] have previously given considerable data on the effect of silver ion concentration on afterripening, and preliminary results on hydrogen ion concentration. In the second place, there may be an effect caused directly by the existence of a given hydrogen or silver ion concentration in the emulsion at the time of exposure. Sheppard and Wightman[4] have referred to this as the effect of environment on sensitivity; they do not specifically define the term, but we infer that it means the thermodynamic environment of the silver halide grains, and we shall use it in that sense. The effect of environment might a priori be expected to be reversible; that is, on reproducing a given set of conditions, the corresponding sensitivity should also be reproduced. The afterripening process is, in contrast, irreversible, but obviously both effects must be superimposed when the hydrogen ion concentration of an emulsion is changed before afterripening.

This paper presents data on afterripening under a wide range of both hydrogen and silver ion concentrations, and on the relation of sensi-

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[2] Carroll and Hubbard, B. S. Jour. Research, vol. 7 (RP376), p. 811, 1931.
[3] Carroll and Hubbard, B. S. Jour. Research, vol. 7 (RP340), p. 219, 1931.
[4] Sheppard and Wightman, Phot. J., vol. 69, p. 22, 1929.

tivity to these variables under conditions such that the afterripening effect has been eliminated. Similar experiments with emulsions containing sensitizing dyes will be reported in a separate communication.

II. REVIEW OF LITERATURE

We are indebted to Rawling and his associates[5] at the British Photographic Research Association for the first quantitative studies of the effect of the hydrogen ion concentration of emulsions on their sensitivity. In many of their experiments the pH of portions of the emulsion was adjusted to the desired value (by addition of acid or alkali) during or after washing, and the total effect measured after the separate portions were digested "to equilibrium." In another series they changed the pH of emulsions two or more times during digestion, coating test plates after each change, and found that the sensitivity changed immediately with the change of the hydrogen ion concentration and returned to its original value (corrected for the slow continuous increase due to afterripening) when the original pH was restored. Rawling refers to this latter as the "reversible effect," as distinguished from the slow "irreversible effect" of afterripening. The ratio of speed at two values of pH was found to be independent of emulsion formula, of grain size within the emulsion, or of the presence of nuclei derived from sulphur sensitizers, but was dependent on the gelatin. Fog and the shape of the characteristic curve were also reported to be independent of the pH during afterripening, and no extension of spectral sensitivity to longer wave lengths was detected.

While the emulsions in the earlier papers are described as "digested to equilibrium," the curves in the 1929 paper indicate that at the higher pH the afterripening was still progressing slowly during the experiments. At pH 5 the afterripening stopped entirely, and there was even a slight decrease in sensitivity in some cases.

Sheppard and Wightman[6] confirmed Rawling's observation of a reversible change in sensitivity when the pH of liquid emulsions was changed before coating. They found that some irreversible process occurs on drying, since the sensitivity of dried plates was not affected by immersing them in buffer solutions ranging from pH 3 to 11. Their data in some cases show a distinct increase in fog with pH.

There has been little quantitative work dealing with the effect of silver ion concentration on sensitivity. Sheppard and Wightman[7] demonstrated that sensitivity is appreciably reduced by the presence of 0.001 *N* soluble bromide, the effect increasing with concentration. Control experiments proved that the results could not be explained by action of the bromide on the latent image or by absorption of light by its solution. In dilute solutions at least, sensitivity was restored by washing out the bromide before exposure. When plates were exposed under 0.01 *N* silver-nitrate solution, acidified to pH 4, and the silver removed before development (by washing with dilute acid), there was no effect on sensitivity.

Fajans and his students[8] have investigated the effect of adsorbed ions on the sensitivity of silver bromide. As their experiments dealt

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[5] Rawling and Glassett, Phot. J., vol. 66, p. 495, 1926. Rawling and Vick, Phot. J., vol. 67, p. 42, 1927. Rawling, Phot. J., vol 69, p. 83, 1929. Rawling, Proc. 7th Internat. Cong. Photography (London), p. 192, 1928.

[7] Sheppard and Wightman, Phot. J., vol. 69, p. 134, 1929.

[8] Summary in Lüppo-Cramer, Grundlagen der Phot. Negativverfahren, p. 633.

with the photolysis of colloid-free material, extension of their results to developable sensitivity in emulsions must be justified by experiment. They found that silver bromide with adsorbed bromide ions had the same spectral sensitivity as pure material, the threshhold being at about 430 mμ. Adsorbed silver or hydroxyl ions extended the spectral sensitivity to at least 615 mμ; careful measurements detected a corresponding change in spectral absorption, although the increase in rate of photolysis was much greater than the increase in absorbed energy under the same conditions. Fajans attributes the effects of the adsorbed ions to deformation of the outer electron shells of the surface bromide ions in the silver bromide by electrostatic attraction, which facilitates the transfer of electrons from bromide to silver ions. Luppo-Cramer[9] tested for the existence of this effect in silver bromide-gelatin emulsions by bathing them in dilute NH_4OH or NaOH solutions, washing, and drying. Plates thus treated were blackened by light without development much more rapidly than before treatment; their sensitivity to red light with development was also increased, but the sensitivity to white light with development was little affected. Factors other than adsorbed hydroxyl ions may have entered into these results.

Various hypotheses have been offered to explain the effect of hydrogen ion concentration on sensitivity, especially the reversible effect.

Slater Price[10] has described experiments by Rawling and Owens which show that the rate of reaction of gelatin with hypochlorite or hypobromite increases with increasing pH. The equilibrium in the solutions shifts with increasing pH toward the OCl^- or OBr^- ions, which are apparently the reactive forms. This indicates that the pH effect on sensitivity may be explained by change in the rate of reaction between the gelatin and the bromine liberated on exposure. A serious difficulty is introduced by the quantitative agreement between the reactivity of three samples of gelatin, although the photographic effect of pH is rarely the same for two different samples of gelatin. However, the conditions chosen for study of the reaction appear to have been unsuitable for the detection of such differences. In the illustrative data the weight of available chlorine in the hypochlorite solution was slightly greater than the weight of gelatin, corresponding to a very large chemical excess; in the curve of Figure 1, the gelatin had absorbed up to 6 per cent of its weight of chlorine. In view of the very small quantity of bromine liberated in the formation of the latent image, it seems as though differences between samples of gelatin might be more obvious in experiments where the gelatin was in great excess and only the earliest stages of the reaction were studied.

Gramse[11] has also used the hypothesis of reaction between the gelatin and bromine liberated by photolysis as a factor in the formation of the latent image. He demonstrated experimentally that the rate of reaction between bromine and gelatin increases with increasing pH, explaining this by the formation of hydrobromic acid, which retards the reaction unless taken up by alkali. He also offers the suggestion that since iodine or sulphur can act as halogen carriers in this reaction, the effect of silver iodide or sulphide on sensitivity may be explained in terms of this function.

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[9] Lüppo-Cramer, Phot. Ind., vol. 22, p. 357, 1924.
[10] Slater Price, Phot. J., vol. 71, p. 59, 1931.
[11] Gramse, Zeit. f. wiss. Phot., vol. 30, p. 40, 1931.

Calzavara[12] has recently suggested that the effect of pH on sensitivity may be explained in terms of its effect on oxidation-reduction potential, but has apparently not given any experimental evidence in support.

In a speculative paper[13] Sheppard has suggested that adsorption of gelatin to silver halides takes place at azine linkages which are in equilibrium with heterocyclic ring structures not capable of similar oriented adsorption. As the equilibrium between the different conditions of the nitrogen would be dependent on the hydrogen ion concentration, this might affect sensitivity through changes in the protective action of the gelatin.

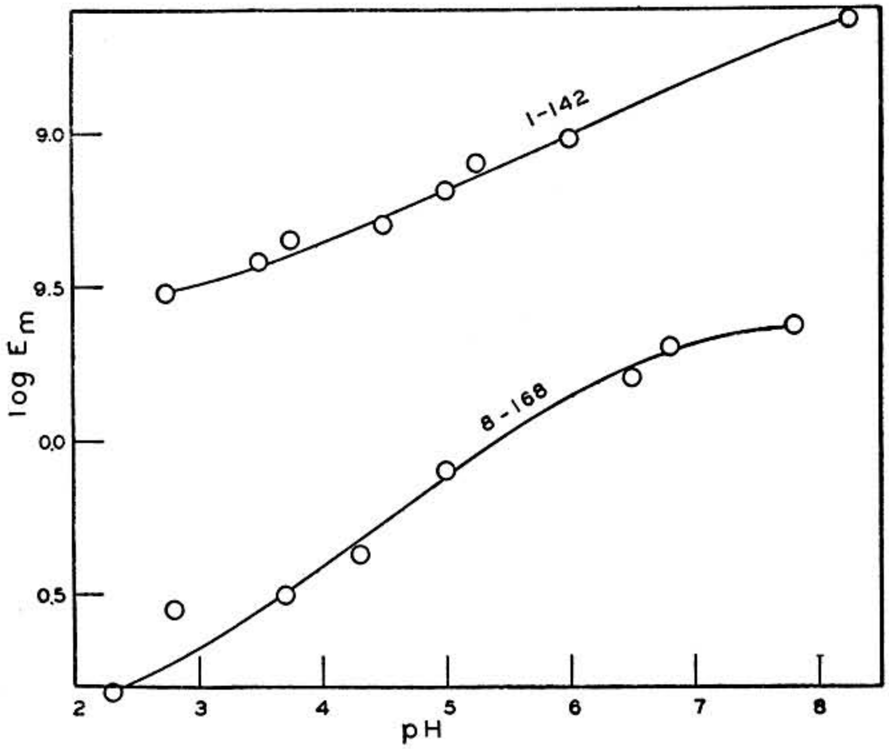

FIGURE 1.—*Variation in sensitivity of emulsions with pH during digestion for constant time*

III. EXPERIMENTAL TECHNIQUE

The methods of emulsion making and sensitometry in use in the photographic emulsion laboratory of the Bureau of Standards have recently[14] been described in detail in connection with our communication on afterripening. We shall here use the same letters to designate the type emulsion formulas given in detail in that paper.

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[12] Calzavara, Sci. et Ind. Phot. (2), vol. 2, p. 472, 1931.

[13] Sheppard, Phot. J., vol. 69, p. 330, 1929.

There has been one change in the methods of emulsion making. During the period of most of the experiments on afterripening, the Potomac River, which is the source of the Washington water supply, was very low and clear as the result of drought, being fed largely by springs in limestone formations. The quality of the water was, therefore, quite constant. Since January, 1931, surface water has made up a much larger proportion of the flow and the quality is less reliable; tests indicate the presence of traces of sensitizing and fogging materials. Emulsions since March, 1931, have been washed with distilled water plus 1¼ g $MgSO_4.7H_2O$ per liter, as recommended by Rawling.[15] (A few exceptions have been made where the emulsions were not to be compared with other batches.)

Silver ion concentrations in the emulsions were measured with the silver-silver bromide electrode at 30°, using the same apparatus described in reference 2. With the exception of some of the earlier results given in Figure 3, the measurements were reproducible to ±2 millivolts (10 per cent in terms of concentration, or 0.03 in terms of the ion exponent). The emulsions may legitimately be considered to have been saturated with silver bromide at all times, so that at 30° the silver and bromide ion concentrations were connected by the equation $[Br^-]\times[Ag^+]=9.2\times10^{-13}$. Concentrations could not be measured in the finished plates; the concentration of the ion in excess would obviously be increased by the drying process.

Hydrogen ion concentrations were determined colorimetrically by comparison with standard buffer solutions, after the emulsions had been cleared by centrifuging.

Hydrogen ion concentrations of emulsions or gelatin solutions were adjusted to the desired value by adding sodium hydroxide or sulphuric acid, in half normal or weaker solutions. Silver sulphate and potassium bromide, tenth normal or less, were used for the adjustment of silver ion concentrations. The other ions thus introduced (sulphate and alkali metals) appear to be photographically inert in any reasonable concentrations according to experiments by Rawling, which were confirmed in this laboratory.

While our methods of determining the characteristic curves of experimental emulsions were unchanged, the expression of the sensitivity in numerical terms has been altered in some cases. We have continued to use the speed number derived from inertia where a series of emulsions had satisfactory straight lines in their characteristic curves, and could be compared at the same γ. In following changes such as those occurring during afterripening, where both speed and contrast increase, it was found more satisfactory to use the speed number derived from minimum useful gradient, which appears to express the change in effective sensitivity better than any other single number. A minimum gradient of 0.2 for 6-minute development was normally used, but on some of the steeper curves a higher value could be read more accurately and appeared better to represent the results judged from the entire curve.

IV. HYDROGEN ION-SILVER ION-GELATIN EQUILIBRIUM AND ITS EFFECTS ON SENSITIVITY

1. ADJUSTMENTS BEFORE DIGESTION

(a) HYDROGEN ION CONCENTRATION, WITH VARYING TIME OF DIGESTION

When the pH of an emulsion is adjusted before digestion, and the sensitivity determined after constant time and temperature of digestion, both the reversible effect on sensitivity and the effect on rate of afterripening are involved in the final result. We have given a few illustrations of this case in Tables 17 and 18 of reference 3. Similar data covering a wider range of pH are given in Figure 1 of this paper; the different portions of the emulsions were adjusted in pH, then all digested for two hours at 45°. Both emulsions were of the ammonia type. Bromide ion concentrations in 8–168 varied with pH from 3 to 12×10^{-5}; in 1–142 they were not determined, but were probably about one-fifth these amounts. In these emulsions there was a distinct minimum of contrast around the isoelectric point. The variation in sensitivity was most conveniently represented by the exposure required for a given minimum gradient. In this case it was necessary to use a gradient of 0.5 on the curve for 12 minutes development, which was least affected by the pH. Plotting the

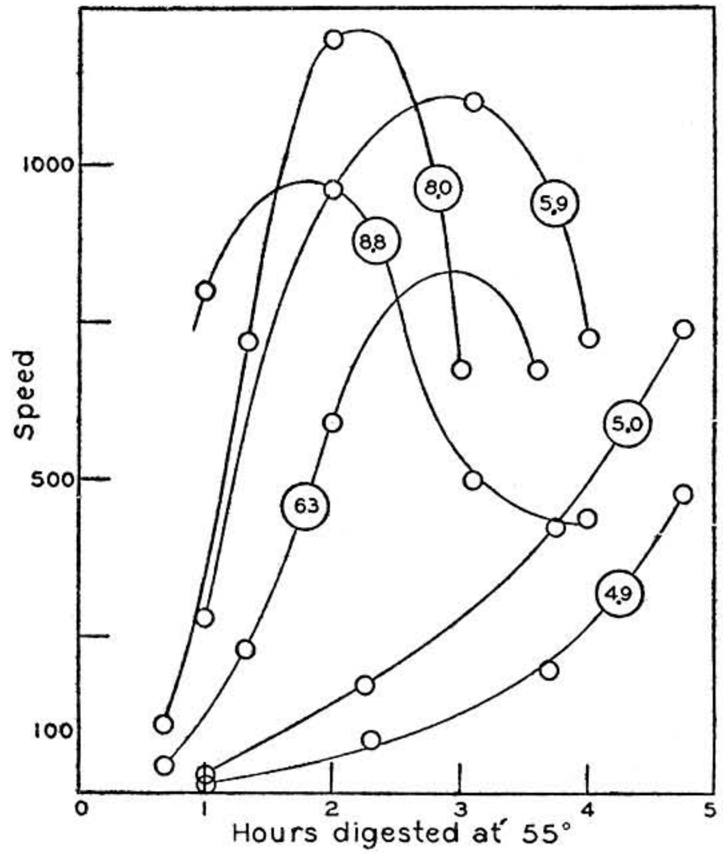

FIGURE 2.—*Changes in sensitivity during digestion for neutral type emulsions at varying pH*

logarithm of this exposure against pH, the curves are approximately linear in both cases; that is, the change in sensitivity was roughly constant for unit change of hydrogen in concentration. The slope of the curve for 8–168 is larger, which may be ascribed to its greater bromide ion concentration; as previously explained in reference 3, page 240, this increased slope is to be expected because higher bromide ion concentrations are less affected by pH so that the true pH effect is less opposed by increasing [Ag^+].

The results of comparison on a constant time of digestion were given because this condition might be encountered in practice. More complete information was obtained from curves of sensitivity against digestion time for a number of hydrogen ion concentrations. These are presented in Figures 2 and 3. The data in Figure 2 were obtained from neutral emulsions ("C" formula in reference 3, p. 227, using 4 per cent AgI, 25 per cent excess NH_4Br and 25-minute mixing time at 65°). These were all made from the same batch of washed gelatin, and washed with distilled water; the pH of the emulsions was 4.9 as washed, and was adjusted before digestion by addition of NaOH. Bromide ion concentrations were all within the range 6.5 to 13×10^{-4} *N*. Sensitivity is represented by the speed calculated as the reciprocal of exposure for minimum useful gradient, in this case the standard value of 0.2 gradient for 6-minute development. The data in Figure 3 were obtained from ammonia process emulsions ("A" formula in reference 3, p. 226, with 5 per cent AgI); these were made from untreated gelatin and washed with distilled water. The pH as washed was 8.3; it was adjusted before digestion by addition of H_2SO_4. Bromide ion concentrations were within the range 6.5 to 9.0×10^{-4} *N*.

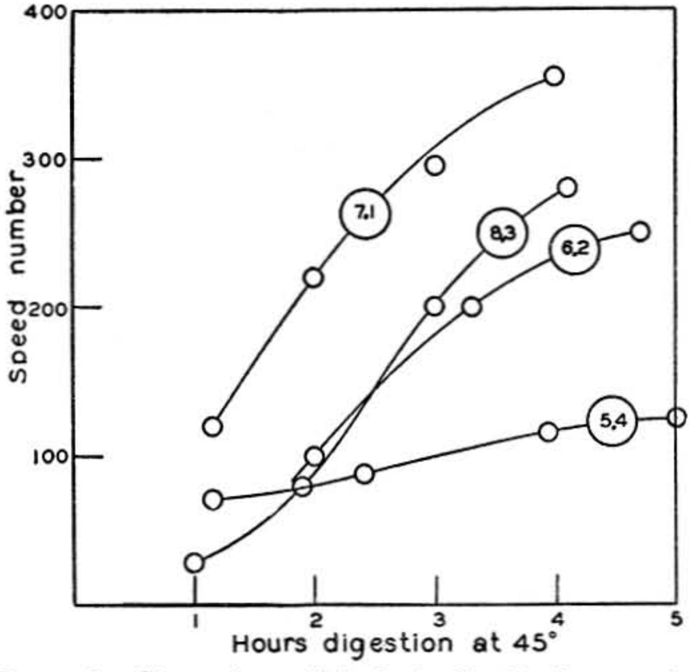

FIGURE 3.—*Changes in sensitivity during digestion for ammonia type emulsions at varying pH*

It was found unusually difficult to reproduce results in these experiments. However, it is evident that the rate of afterripening increased rapidly with increasing pH between 5 and 7. The increase in rate is greater than the increase in maximum sensitivity, so that it is not merely the result of the reversible pH effect which would increase sensitivity at all stages of ripening.

In both series of emulsions there was a decrease in maximum sensitivity for pH > 8, with no indication of a decrease in rate of afterripening. In the neutral emulsions, there was serious fog at pH 8 or higher; one batch digested at 9.7 was completely ruined. The NaOH used for adjustment of pH was tested for the presence of fogging impurities by neutralizing a portion of it larger than used for adjustment and adding this to a portion of emulsion during afterripening at pH 7.3; there was no increase in fog over a control batch.

The fog in the ammonia emulsions was practically independent of pH over the range 5.4 to 8.3, so that the decrease in sensitivity at pH > 8 in this case can not be ascribed to the increase in fog. On the available evidence we may say that the rate of afterripening increases rapidly from pH 5 to 7, and that the time required to reach maximum sensitivity decreases continually with increasing pH. At alkalinities greater than the practical maximum, pH 8.5, deterioration is rapid, and may be greater than would be expected from the increased tendency to fog.

The effect of silver ion concentration on the rate of afterripening has already been described in some detail.[16] In contrast to the effect of hydrogen ion, which alters both the rate of afterripening and the maximum sensitivity, increased bromide ion concentration may only decrease the rate of afterripening, the sensitivity for optimum digestion being little affected up to concentrations higher than those in common use.

(b) HYDROGEN AND SILVER ION CONCENTRATIONS WITH CONSTANT TIME OF DIGESTION

Since the combination of silver ion with gelatin varies with the hydrogen ion concentration,[17] any adjustment of pH involves also a change of free silver ion concentration and in bromide or silver ions adsorbed to silver bromide. It is therefore impossible to give the effects of silver and hydrogen ions on sensitivity distinct and separate treatments. We present first the results of varying both silver and hydrogen ion concentrations in emulsions before afterripening them by digestion.

All four emulsions were made by the following formula:

Bromide solution	Water	ml	175
	KBr (12.5 per cent excess)	g	23.7
	Gelatin	do	10.0
Silver solution	Water	ml	225
	$AgNO_3$	g	30.0

The silver solution was added to the bromide solution in 6 to 7 minutes at 65.0° ± 0.2°. Centrifugal washing,[18] in three batches, was started at 9 to 10 minutes from the start of mixing and finished at 36 to 38 minutes. The silver bromide was resuspended in 400 ml of

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[16] Carroll and Hubbard, J. Phys. Chem. vol. 31, p. 910, 1927

1 per cent gelatin, at a pH of 4.7 − 4.9. Two batches of this size were then combined, and the silver ion concentration adjusted by appropriate additions of silver sulphate solution; the suspension was then divided into eight 100 ml portions, and left in the refrigerator over night. The next day the separate portions were carefully remelted as needed, centrifuged again, and the final emulsion made by suspension of the silver bromide in 12.5 g gelatin and 235 ml water. The pH of the eight batches of emulsion was adjusted by additions of sulphuric acid and each was digested for two hours at 45°. In order to reduce fog in the batches with higher silver ion concentrations, gelatin which had been treated with ammonia and thoroughly washed was used for emulsifying the silver bromide after centrifuging. Pure bromide emulsions made with this partly deactivated material necessarily had relatively low sensitivity. Sensitometric tests were made with a special *p*-aminophenol developer [19] found to give speed numbers equivalent to the usual pyrogallol formula on the normal batches of these emulsions, and less fog on those with increased silver ion concentration.

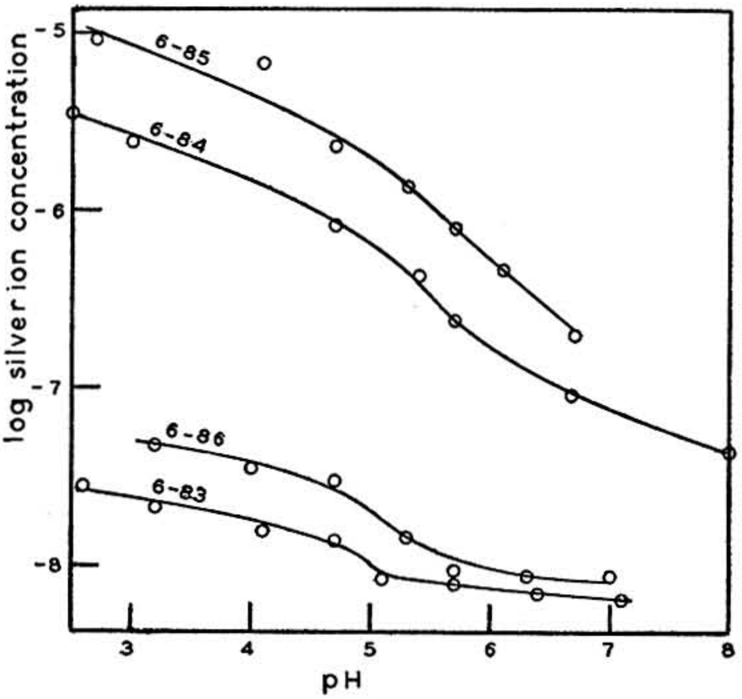

FIGURE 4.—*Variation of silver ion concentration of emulsions with pH*

Figure 4 gives the relation between silver and hydrogen ion concentrations in these emulsions. Silver ion concentrations in the first resuspensions, which determine the range of silver ion concentrations in the final emulsions, were as follows:

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[19] Formula:

p-aminophenol hydrochloride	g	3.6
Na_2SO_3	do	25.0
Na_2CO_3	do	25.0
KBr	do	0.6
Water to make	liter	1.0

2, 4, and 8 minutes brush development at 20° C.

TABLE 1

	N
6–85	6.6×10^{-4}
6–84	8.2×10^{-5}
6–86	6.1×10^{-9}
6–83	8.8×10^{-10}

It is evident that the slope of the curves is greater at higher silver ion concentrations. This is readily predicted from the data in reference 2 on the combination of silver ion and gelatin; silver combined with unit weight of gelatin becomes increasingly dependent on pH at higher silver ion concentrations. The concentration of free silver ions is therefore more affected under these conditions by the change in combined silver with varying pH. It will further be noted that although the curves show an appreciable break at the isoelectric point of gelatin, they are essentially continuous.

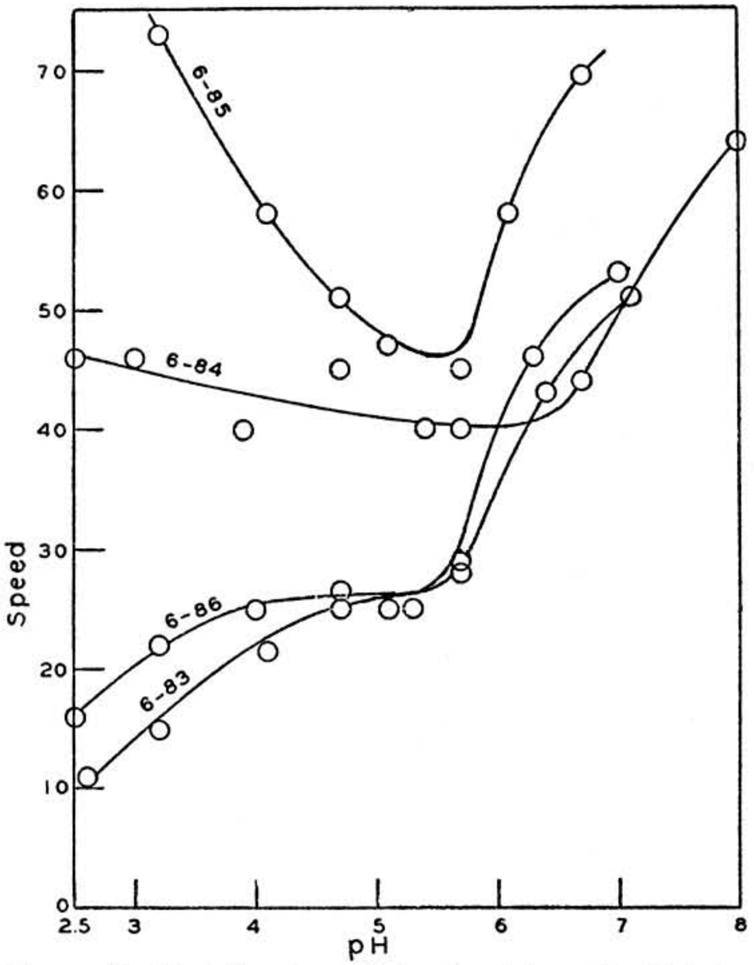

FIGURE 5.—*Variation of sensitivity of emulsions with pH during digestion, for constant time of digestion*

In Figure 5, speeds of these same emulsions are plotted against pH. For these emulsions, speed is expressed as the reciprocal of the exposure necessary for a gradient of 0.3 at the maximum development time; while there were satisfactory straight line portions of the characteristic curves, γ changed with pH, so that the speed from inertia alone was not the best single number expressing sensitivity. Within the normal range of pH (5.5 or higher) the sensitivity for constant digestion time in each curve shows the usual rapid increase with increasing pH. Comparing the four curves, it increases with increasing silver ion concentration, as is to be expected from the effect of silver ion concentration on after ripening.[20] (The last two points of the curve for 6–84 are out of place in both Figures 4 and 5, and possibly unreliable.) All four curves have points of inflex ion or minima at pH 5 to 5.5; the corresponding characteristic curves have minimum values of γ in this region. On the acid side of the isoelectric point the shape of the curves is highly dependent on the silver ion

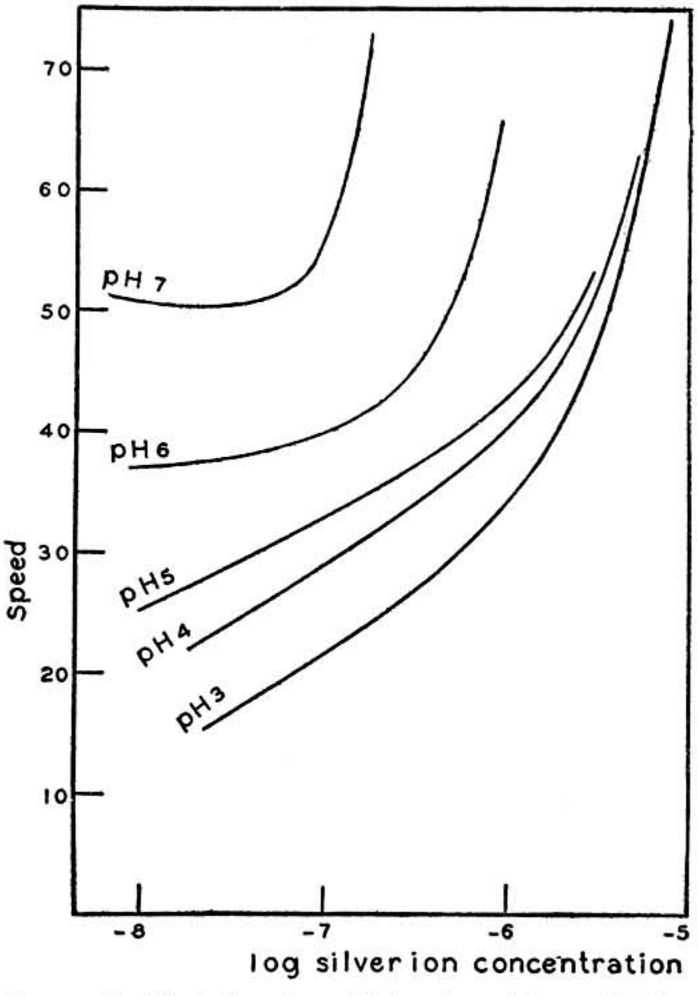

Figure 6.—*Variation of sensitivity of emulsions with silver ion concentration during digestion, for constant time of digestion*

concentration. We have already noted [21] that on changing the hydrogen ion concentration of an emulsion, the resulting change in silver ion concentration is in the direction which tends to counteract the photographic effect of the original change of pH. Under ordinary conditions, as in emulsion 6–83, the change in silver ion concentration is relatively small and the rate of afterripening increases with pH, although the shape of the curve is decidedly different on the two sides of the isoelectric point. In the emulsions with excess silver (6–84 and 6–85) the silver ion concentration increases so rapidly with decreasing pH that its effect on the rate of afterripening more than offsets the effect of the acidity, and at $pH < 4.7$ sensitivity actually increases with increasing acidity, under constant time and temperature of digestion. It should be emphasized that in all batches of a given emulsion, as 6–85, the excess of silver over bromine was constant, but its distribution between free and combined ions varied with the pH with the consequences here indicated.

In Figure 6 the data from the two previous figures have been combined as smoothed curves indicating the change in sensitivity with silver ion concentration at constant values of pH. The original expectation had been that these curves would show a sudden increase in sensitivity when the silver ion concentration exceeded the equivalence point ($[Ag^+] = 10^{-6}$ N). This is roughly the case for emulsions at pH 5 or less, but on the alkaline side of the isoelectric point the point of increase comes at decreasing values of silver ion concentration. It should be remembered that actual equivalence of silver and bromine in the emulsion at normal values of pH corresponds to silver ion concentration much less than 10^{-6} N. At pH 7, and concentrations similar to these emulsions, the bromide in solution is equivalent to the silver in combination with the gelatin at $[Ag^+] = 2 \times 10^{-8}$ ($[Br_-] = 5 \times 10^{-5}$).

In discussion of these emulsions, no attempt has been made to calculate changes in silver ion concentration from changing acidity, since the emulsions were digested after adjusting the pH. It is further doubtful whether the data in reference 2 are accurate for all samples of gelatin; the available emulsion gelatins appear to vary in their capacity for combination both with silver and hydrogen ions although the qualitative behavior and order of magnitude of the effects is always the same. The measurements of reference 2 were made on de-ashed gelatin which fulfills the tentative specifications [22] of the American Chemical Society for a standard gelatin as to source and ash content.

2. ADJUSTMENT AFTER DIGESTION

(a) SILVER ION CONCENTRATION AT CONSTANT pH

Data in this section were obtained from emulsions which had been digested nearly to maximum sensitivity before adjustment of the silver ion concentration; while we do not feel justified in referring to them as at equilibrium, the rate of change of sensitivity with time was nearly at its lowest point. The emulsions were usually digested at least one hour at 55° C., then filtered, being cooled to 35° to 40° C. in the process. They were then divided into smaller batches, the silver ion concentrations adjusted by appropriate additions of silver

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[22] Davis, Sheppard, and Briefer, Ind. Eng. Chem., Analytical Ed., vol. 1, p. 56, 1929.

sulphate or potassium bromide solutions, and the emulsion coated as rapidly as possible. The maximum difference between any of the batches was 15 minutes, which, at a temperature not over 40°, introduced negligible changes in sensitivity; the temperature coefficient of afterripening is such that this interval at 40° corresponds to less than five minutes at 55°. These data may safely be considered to represent the direct effect of silver ion concentration on sensitivity, rather than the larger indirect effect which is the result of varying silver ion concentration during afterripening. The greatest effect was observed at hydrogen ion concentrations which very greatly retard afterripening.

Figure 7 presents results for a number of emulsions, all of the neutral ("C") type, with 4.0 mol per cent silver iodide. Speeds are derived from inertia values, γ being practically constant, except for emulsion 4–81 for which the minimum gradient value was more satisfactory. The normal range of silver ion concentrations in emulsions at coating is between $10^{-7.5}$ and 10^{-9}. The most striking feature of the data is the practically constant value of speed over an enormous range of silver ion concentration when the emulsions were at normal values of pH.

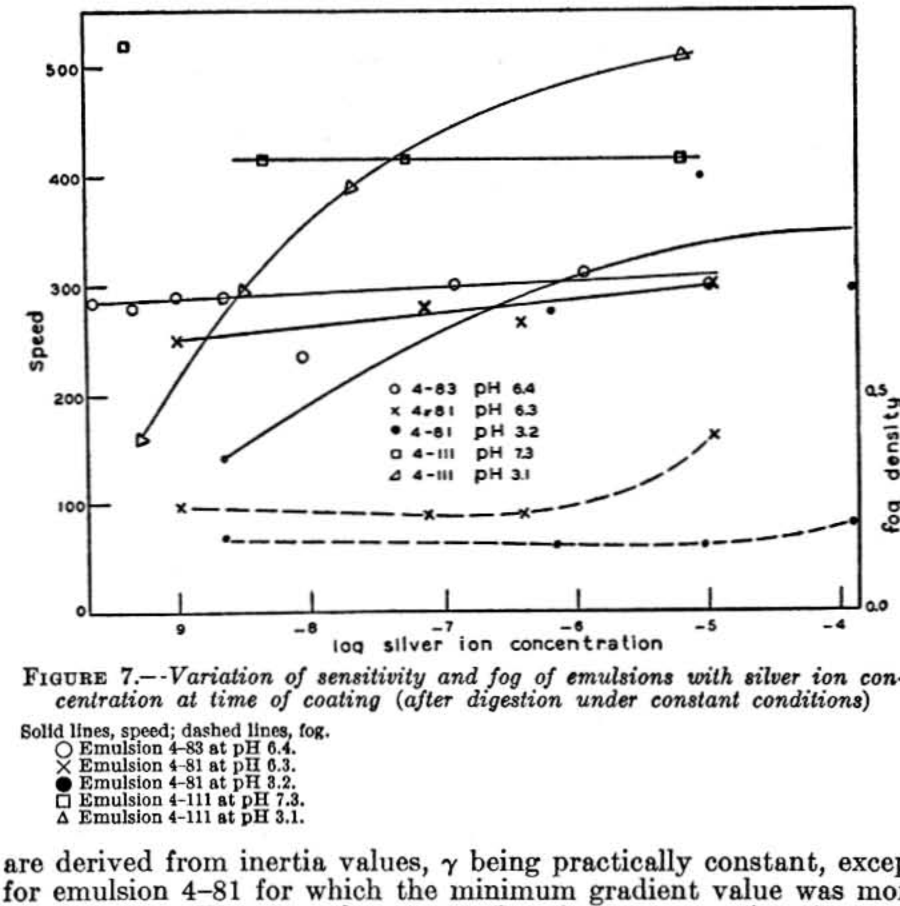

FIGURE 7.—*Variation of sensitivity and fog of emulsions with silver ion concentration at time of coating (after digestion under constant conditions)*

Solid lines, speed; dashed lines, fog.
○ Emulsion 4-83 at pH 6.4.
× Emulsion 4-81 at pH 6.3.
● Emulsion 4-81 at pH 3.2.
□ Emulsion 4-111 at pH 7.3.
Δ Emulsion 4-111 at pH 3.1.

On the acid side of the isoelectric point the effect of silver ion concentration was much greater. As the figure is plotted on the basis of silver ion concentrations, the excess of silver over halogen at corresponding abscissas was less in the case of the batches on the acid side of the isoelectric point, since the silver combined with gelatin was less. The difference between the neutral and acid batches would, therefore, be even greater if the results were presented in terms of excess bromide or silver.

Fog densities for 12-minute development of the different portions of 4–81 are also plotted in Figure 7, using dashed lines and the same symbols for the points as for the plot of speed of the corresponding portions. While there is a sudden increase in fog at the higher silver ion concentrations, not only excess of silver over bromine, but excess of free silver ions failed to produce large values of fog immediately; the batches with excess silver and normal pH deteriorated very rapidly, while those with excess silver at pH 3 were usable for over a month. The maximum fog in 4–111, made with ammonia-treated gelatin, was 0.06.

The marked effect of excess silver on the blackening of silver bromide without development, and the extension of spectral sensitivity toward the red reported by Fajans,[23] have both been studied mainly using silver bromide without protective colloid or protected by collodion, which does not have the capacity of gelatin to combine with silver ions. Tests were accordingly made with three emulsions 4–111, using both the neutral and acid batches, a similar emulsion: (4–110) available both with excess silver and bromide and having only 1 per cent AgI so that the sensitivity did not extend as far to the red as in 4–111, and an ammonia-process emulsion (1–166) with 4 per cent AgI.

The direct blackening was tested simply by exposing strips of corresponding pairs of plates (excess silver and excess bromide) to diffuse daylight, and observing the changes visually. The excess silver produced only a slight increase in the 4–110, and no appreciable difference in the 4–111 in either pair (pH 7.3 and 3.1).

TABLE 2.—*Distribution of silver and bromide ions in emulsion 4–81, on adjustment of pH and [Ag^+]*

[Results calculated to 1 liter of emulsion, containing 0.23 mol AgBr and 58 g gelatin]

pH	Added Ag^+ or Br^-	[Ag^+]	Excess in solution	Ag^+ combined with gelatin	Apparent change in adsorbed Br^- per mol AgBr
	g equivalent	*N*	*g equivalent*	*g equivalent*	*g equivalent*
6.3	0	7.4×10^{-8}	$1.23\times10^{-5}Br^-$	1.04×10^{-4}	0.
	$1.01\times10^{-3}Br^-$	1.05×10^{-9}	$8.8\times10^{-4}Br^-$	6×10^{-6}	$+1.7\times10^{-4}$.
	$2.3\times10^{-4}Ag^+$	3.9×10^{-7}	$1.8\times10^{-6}Br^-$	3.0×10^{-4}	-1.3×10^{-4}.
	$1.16\times10^{-3}Ag^+$	1.09×10^{-5}	$1.08\times10^{-5}Ag^+$	1.45×10^{-3}	-9×10^{-4}.
3.3	0	6.6×10^{-7}	$6\times10^{-7}Br^-$	3.6×10^{-5}	0.
	$1.01\times10^{-3}Br^-$	2.2×10^{-9}	$4.0\times10^{-4}Br^-$	3×10^{-6}	$+25\times10^{-4}$.
	$2.3\times10^{-4}Ag^+$	8.6×10^{-6}	$8.5\times10^{-6}Ag^+$	1.7×10^{-4}	-2.2×10^{-4}.
	$1.16\times10^{-3}Ag^+$	1.22×10^{-4}	$1.22\times10^{-4}Ag^+$	8.1×10^{-4}	-12×10^{-4}.

Spectral sensitivity was tested by exposure to a continuous source in a small grating spectrograph giving high intensity.[24] A Wratten "minus blue" filter was used to reduce the effect of stray light so that the exposure could be followed to regions of low sensitivity. The plates were brush developed to insure uniformity and measured with a microphotometer. No detectable change in spectral sensitivity

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[24] Carroll and Hubbard, B.S. Jour. Research, vol. 4 (RP173), p. 692, 1930.

was produced by the excess silver in any of the sets compared. These same emulsions were also tested for a change in spectral sensitivity with pH, carrying the measurements well to the acid side of the isoelectric point of gelatin. The results were again negative with the possible exception of those batches of 1–166 containing excess silver; in this case the decrease in sensitivity for the longer wave lengths produced by decrease in pH from 7.7 to 3.2, if real, is of a smaller order of magnitude than the effect of changing from 4 to 1 per cent AgI.

In Table 2 the data are given for the adjustment of silver ion concentration in emulsion 4–81, which was made with the same sample of isoelectric gelatin used for the experiments on silver ion-gelatin combination. This emulsion was thoroughly washed with tap water, reaching a pH of 6.3 and $[Ag^+]$ of $7.4 \times 10^{-8}\,N$ as given in the first horizontal row. Half of it was adjusted to pH 3.3 by the addition of sulphuric acid; each half was divided into four batches to which silver sulphate or potassium bromide solutions were added in the indicated quantities. The quantities of free ions in solution and of silver ions combined with the gelatin were calculated from the electrode readings and the data of Figure 3 of reference 2. The calculation may be illustrated by the figures in the second horizontal row. 1.01×10^{-3} g equivalent of bromide was added per liter of emulsion. The silver ion concentration, determined directly from the potential of the silver-silver bromide electrode, became 1.05×10^{-9}; the corresponding bromide ion concentration calculated from the solubility product was 8.8×10^{-4}. The solution, therefore, contains bromide in excess by $(8.8 \times 10^{-4}) - (1.05 \times 10^{-9}) = 8.8 \times 10^{-4}$ g equivalent per liter. At a pH of 6.3 and silver ion concentration 1.05×10^{-9}, we find from Figure 3 of reference 2 that 1×10^{-7} g equivalent of silver ion will combine with 1 g of gelatin, or 6×10^{-6} g equivalent with the 58 g in 1 liter of emulsion. The bromide in solution has, therefore, increased by $(8.8 \times 10^{-4}) - (1.23 \times 10^{-5}) = 8.7 \times 10^{-4}$ g equivalent over the original condition of the emulsion. The silver combined with the gelatin has decreased by $(1.04 \times 10^{-4}) - (6 \times 10^{-6}) = 0.98 \times 10^{-4}$ g equivalent from the original condition of the emulsion. These add up to 9.7×10^{-4} g equivalent. But 1.01×10^{-3} g equivalent of bromide was added. The difference is 0.4×10^{-4} g equivalent of bromide per liter ef emulsion, or 1.7×10^{-4} per mol of AgBr, which has apparently been removed by adsorption on the AgBr.

The sum of the changes in these quantities fails to agree with the addition in every case by an amount which is larger than the experimental error. If ascribed to changes in the bromide (or silver) ions adsorbed to the silver halide of the emulsion, the results are of the right sign and order of magnitude. Numerous calculations of this type indicate that approximate values can be obtained for adsorbed bromide, but it is obviously necessary to have data on the combination of silver ion with the gelatin in question to insure reliable results. Data from emulsion 4–83 in the higher bromide ion concentrations, and from emulsions 4–61 and 4–68 (reference 3) both give values for adsorbed bromide which fit the Freundlich equation within the limits of error, but the constants are quite different.

The increased effect of silver ion concentrations in acid emulsions is responsible for a curious effect which we have already mentioned.[25]

Carroll and Hubbard, B. S. Jour. Research, vol. 1 (R P 20), p. 583, 1928.

This effect is further illustrated in Figure 8; the emulsions are described in Table 3. All were made with neutral silver nitrate solution; after mixing and ripening they were centrifuged and the silver halide suspended in dilute gelatin. The silver ion concentration of this suspension was next adjusted by addition of silver sulphate where desired, and it was then divided into portions, the pH of which was adjusted by sulphuric acid. The resulting range of silver ion concentrations is indicated in Table 3. These portions of the wash suspension, all containing the same excess silver or bromide and varying only in pH and the resulting distribution of silver ions, were then centrifuged again and the silver halide suspended in fresh gelatin at constant pH. They were coated without digestion; other experiments showed that the effect tended to diminish on digestion, the after ripening bringing them to a common higher level of sensitivity. Ammonia-treated gelatin was used for the final suspension in all cases, to reduce fog in the emulsions with excess silver.

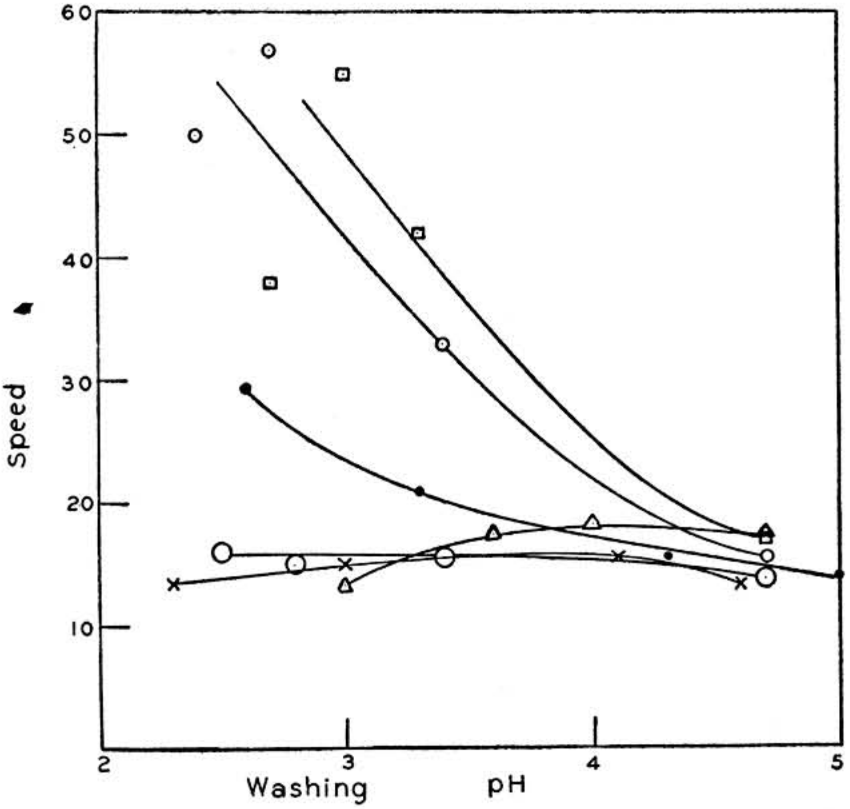

FIGURE 8.—*Variation of speed of centrifugally washed emulsions with pH of first resuspension*

In the emulsions with excess bromide (6–80, 6–82) and in one with a small excess of silver (6–79), there was practically no effect produced by the changing pH of the wash suspension. In those with excess silver (6–76, 6–77, 6–81) there was a marked increase in sensitivity with increasing acidity. As the silver ion concentration of the wash suspensions increased with increasing acidity over the range given in Table 3, there was a corresponding change in the final suspension, but it amounted to a maximum of 60 per cent, which could not account for the change in sensitivity. It is necessary to assume that a given silver ion concentration sensitizes the silver halide grains by an amount increasing with the acidity, most probably because there is increased adsorption of silver ions. A possible explanation will be discussed later in the paper. Entirely analogous results were obtained with ammonia process emulsions; illustrations are given by the "control" batches in Table 9 of reference 25. Colloidal silver and gold (reference 25) were found to sensitize only when introduced into emulsions containing excess silver, and hydrogen ion concentrations at least 10^{-3} *N;* apparently only under these conditions did the grains acquire sufficient positive charge to attract the negatively charged colloidal metals.

TABLE 3.—*Emulsions illustrated in Figure 8*

Emulsion No.	Symbol in Figure 8	Mol per cent AgI	Coating pH	[Ag⁺] in wash suspension
6-76	(.)	0.0	3.4	1.4 to 1.6×10^{-3}.
6-77	(○)	.0	3.4	6×10^{-4}.
6-79	(◯)	.0	3.4	4.7×10^{-6} to 4.4×10^{-4}.
6-80	(×)	2.3	3.4	3.1 to 3.5×10^{-10}.
6-81	(□)	.0	3.4	3.4 to 4.6×10^{-4}.
6-82	(Δ)	.0	8.2	3.5 to 4.2×10^{-9}

TABLE 4.—*Changes in distribution of silver and bromide ions in emulsion 4-80 on adjusting pH*

pH	[Ag⁺]	Excess of Br⁻ over Ag⁺ in solution	Ag⁺ combined with gelatin	Excess of Ag⁺ over Br⁻ in emulsion, excluding adsorbed Br⁻	Apparent change in adsorbed Br⁻, per mol AgBr
		g equivalent	*g equivalent*	*g equivalent*	*g equivalent*
8.7	1.8×10^{-8}	5.0×10^{-5}	1.8×10^{-4}	1.3×10^{-4}	$+4.4 \times 10^{-4}$.
6.4	8.3×10^{-8}	1.10×10^{-5}	1.1×10^{-4}	1.0×10^{-4}	$+3.2 \times 10^{-4}$.
5.4	1.5×10^{-7}	5.8×10^{-6}	5.5×10^{-5}	4.9×10^{-5}	$+1.0 \times 10^{-4}$.
4.9	2.2×10^{-7}	4.0×10^{-6}	4×10^{-5}	3.6×10^{-5}	$+5 \times 10^{-5}$.
4.5	3.3×10^{-7}	2.5×10^{-6}	3.5×10^{-5}	3.2×10^{-5}	$+3 \times 10^{-5}$.
4.1	4.2×10^{-7}	1.8×10^{-6}	3×10^{-5}	2.8×10^{-5}	$+2 \times 10^{-5}$.
3.4	5.0×10^{-7}	1.35×10^{-6}	2.5×10^{-5}	2.4×10^{-5}	0.
2.2	6.4×10^{-7}	7.9×10^{-7}	2.5×10^{-5}	2.4×10^{-5}	0.

All results calculated to 1 liter of emulsion, which contained 0.24 mol AgBr and 60 g dry gelatin.

(b) HYDROGEN ION CONCENTRATION

Silver ion concentrations may readily be adjusted at constant pH, since small amounts of practically neutral salts may be used, but as already pointed out, change in hydrogen ion concentration involves a change in silver combined with gelatin and, therefore, a change in silver ion concentration. The smaller the amount of soluble bromide present in the emulsion the larger will be the change, both in relative and absolute units. Table 4 gives the results of changing the pH in an emulsion made with the standard de-ashed gelatin used for investigation of the silver ion-gelatin combination. This emulsion was thoroughly washed (six hours in running tap water) and contained only a very small excess of total halogen over silver. Changes in distribution of silver and bromide on changing pH have been calculated from the electrode readings and the data of Figure 3 of reference 2; values for adsorbed bromide are again only relative, the absolute amount being unknown. The change in adsorbed bromide is about what would be expected from the change in bromide ion concentration; the evidence is not sufficient to decide whether there is any effect of pH on the adsorption.

We have already [26] called attention to the fact that the change in silver ion concentration tends to oppose the direct effect of changing pH. When there is no subsequent afterripening, as in this case, the change in silver ion concentration becomes relatively unimportant. In a thoroughly washed emulsion, such as 4–80, the silver ion concentration may change tenfold between pH 8.3 and 4.9. If, on the other hand, the emulsion contains about 1 per cent soluble bromide ($[Ag^+]$ approximately 10^{-9} N) the change in silver ion concentration may be as low as 20 per cent between the same limits of pH; as may be judged from inspection of Figure 7, this is quite negligible.

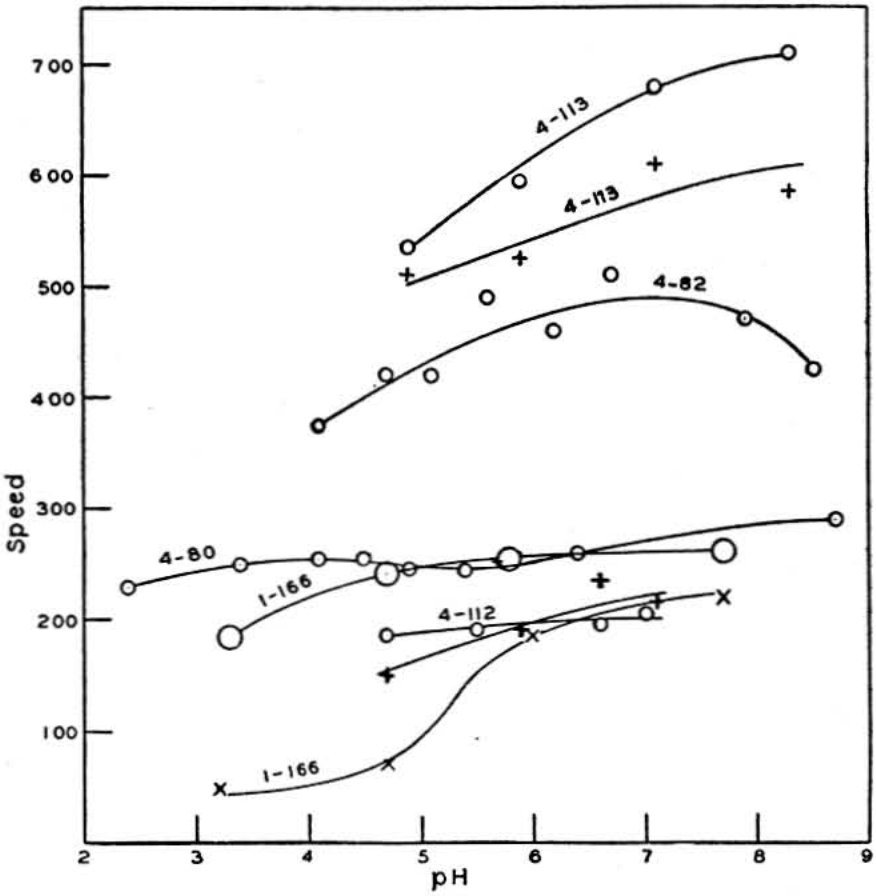

Figure 9.—*Variation of speed of emulsions with pH at time of coating (after digestion)*

Figure 9 presents the results of changing pH of a number of emulsions just before coating. Three of the emulsions were divided in half, and the silver ion concentration of each half adjusted before adjusting the pH. Most of the data are for thoroughly washed emulsions (indicated by circles), but three sets (indicated by crosses) are for emulsions containing about 1 per cent soluble bromide. The emulsions are described more fully in Table 5. The inertia of some of these emulsions tended to vary appreciably with the degree of development. Since the rate of development varied with the emulsion pH, as would be expected, the speeds are those for development to a constant value of γ (1.0 for emulsions 4–112 and 4–113 and 1–166; 1.5 for emulsions 4–80 and 4–82); this was obtained by interpolation where necessary.

TABLE 5.—*Emulsions in Figure 9*

Emulsion 1–166 was made by the ammonia process, the others by the neutral (C) formula.

Emulsion No.	Gelatin	$[Ag^+]$ before adjustment of pH
4–80	De-ashed	8.3×10^{-8}.
4–82	Winterthur	6.7×10^{-8}.
4–112	do	7.7×10^{-9}. [1] 7.0×10^{-10}.
4–113	Ucopco	1.5×10^{-7}. [1] 7.5×10^{-10}.
1–166	do	[1] 8.3×10^{-10}. 3.7×10^{-6}.

[1] Indicated by crosses in Figure 11.

The effect of pH observed in these experiments corresponds to Rawling's reversible effect; we did not test for reversibility. It is much less than the effect on after-ripening and almost vanishes under some conditions. Rawling [27] has demonstrated its dependence on the gelatin. Inspection of Figure 7 shows the extent to which it may be dependent on silver ion concentration, since the data for emulsions 4–81 and 4–111 make possible comparison of the sensitivity at two values of pH and constant silver ion concentration. Here the pH effect passes through zero, actually changing its sign as the silver ion concentration increases. The results with emulsions 4–112 and 1–166 (fig. 9) are of the same type, the effect increasing with decreasing silver ion concentration, but the order is apparently reversed for 4–113, although the difference in slope of the curves is possibly within the experimental error.

V. DISCUSSION

The data in this paper, like those of our previous communication (reference 3), are uniformly consistent with the hypothesis that after-ripening is the result of chemical reactions of the silver halide to form silver sulphide or possibly metallic silver. Such reactions must lead to the formation of acid and of halide ions, and should, therefore, be retarded by increase in bromide or hydrogen ion concentrations. This was found experimentally in every case. There is an apparent contradiction in the decrease of sensitivity in the emulsions with $pH > 8$, but it will be noted that the velocity of the change continued to increase, the maximum of sensitivity being reached in less time than for lower values of pH. The available evidence indicates that the quantity of silver sulphide is not the only variable in the effectiveness of a nucleus, so that photographic sensitivity might begin to fall off even though the process of forming silver sulphide was not retarded. The effects of hydrogen and silver ion concentrations during digestion are thus as accountable as any features of the after-ripening process.

The effect of environment pH is apparently independent of previous afterripening, since Rawling found it to be independent of the presence of nuclei formed by known additions of allyl thiocarbamide. It must be explained by hypotheses which do not involve changes in the nucleation of the grains. We have an analogous case in the mechanism of spectral sensitization, since Sheppard [28] found that the relative spectral sensitivity of a given emulsion-dye combination was not affected by addition or removal of nuclei which produced great changes in the total sensitivity.

It will be useful first to consider the nature of the adsorption of gelatin to silver bromide. Reinders [29] demonstrated that the adsorption of gelatin reduces the adsorption of other materials, but it has been tacitly assumed in many cases that the adsorption of ions and of protective colloids had distinct mechanisms and were relatively independent. According to the "Zwitterion" theory of ampholytes,[30] however, gelatin is considered to be very largely in the ionic state, even though most of the ions (or micelles) are externally neutral because they carry an equal number of positive and negative charges. Such zwitterions should be capable of oriented polar adsorption to a crystal lattice like silver bromide; assuming the existence of amino acid groups the gelatin zwitterion would be adsorbed to silver ions of the surface by electrostatic attraction between Ag^+ and $-COO^-$, and to the bromide ions by their attraction for $-NH^+_3$. Undissociated molecules would not be adsorbed. The externally charged ions of the earlier theory, which exist in increasing proportions as the pH departs from the isoelectric point in either direction, would be adsorbed only to the corresponding ions of the silver bromide surface. In every case, adsorption of the gelatin should be polar, and competitive with the adsorption of other ions, even those of silver bromide itself.

It seems reasonable that this type of adsorption explains the superiority of the proteins over un-ionized colloids as protective colloids for silver bromide, expecially with regard to protection of the unexposed silver bromide against development if we assume that adsorption of the developer ion is the first step in that process.

The zwitterion concept also implies a relatively rapid change in the number of free NH_2 groups with the pH. As pointed out by Slater Price, this may effect the reactivity of the gelatin with bromine. It also appears to explain the marked dependence of the silver ion-gelatin combination on pH, assuming this to take place at the amino group, much better than the opening of peptide linkages which are assumed in our previous discussion of this subject [31] or the structural changes suggested by Sheppard (reference 13).

We believe that our results may best be explained on the assumption that gelatin is adsorbed to silver halides in preference to all other materials present. Only the bromide ion (which is adsorbed more strongly than the silver ion) will also be appreciably adsorbed, especially in acid solutions where the acid dissociation of the gelatin is reduced so that the $-COO^-$ ion groups are less available for

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[28] Sheppard, Colloid Symposium Monograph, vol. 3, p. 3.
[29] Reinders, Zeit. f. phys. Chem., vol. 77, p. 677, 1911.
[30] Bjerrum, Zeit. f. phys. Chem., vol. 104, p. 147, 1923.

adsorption to the Ag^+ ions of the crystal lattice. Our data in agreement with the work of Slater Price and his associates show that the effect of hydrogen ion concentration on sensitivity is greater at higher bromide ion concentrations. As is evident from Figure 7, this may better be expressed that at low values of pH, bromide has an increased desensitizing effect. It has already been mentioned that under these conditions it should be more capable of displacing adsorbed gelatin, with consequent desensitization. Silver ions will, in general, be adsorbed in appreciable quantity only at relatively high concentrations. (It will be remembered that the silver ion concentration in an emulsion at normal values of pH exceeds the bromide ion concentration only when the emulsion contains about 0.4 per cent excess silver.) Our most direct evidence for this is the independence of the spectral sensitivity of the silver and hydrogen ion concentration. There was no indication that even the considerable excess of silver present in some of the emulsions caused an increase in sensitivity to the longer wave lengths. There is, furthermore, evidence that the adsorption of the gelatin causes such a shift, since the sensitivity of pure silver bromide in gelatin has its maximum at about 450 mμ as against 420 mμ for silver bromide collodion[32]; Eder's sensitivity curves show an unmistakable shift of the whole curve to the red in the presence of gelatin. It is therefore probable that in the grains of a silver bromide-gelatin emulsion the deformation of the external bromide ions of the crystal lattice is already accomplished so that it is unaffected by silver or hydroxyl ions at moderate concentrations.

The effect of excess silver on the sensitivity of gelatin emulsions has been found to be unexpectedly small in view of its marked effect under other conditions, such as the photolysis of medium-free silver bromide. The most important factor is the combination of gelatin with silver ions, which retards the increase of silver ion concentration when soluble silver salts are added to an emulsion, and prevents the formation of the "silberkorper" of Fajan's experiments. There is a further influence to be considered. In the photolysis of medium-free silver bromide excess silver increases the rate of reaction under constant illumination by a factor of several times, although the increase in absorption of light can be detected only by careful measurement. This result can not be explained wholly by the change in the primary photochemical process; the silver must also influence secondary reactions, probably by acting as a bromine absorbent. Some bromine absorbent is essential to prevent regression in the photolysis of pure silver bromide. In the emulsion, the case is quite different, and an absorbent as inefficient as a silver salt does not add to sensitivity. The evidence indicates that some more effective material is normally present, and that the effects of such variables as hydrogen ion concentration are to be explained in terms of some secondary reaction, probably connected with the bromine liberated during exposure.

This is the basic hypothesis used by Slater Price [33] to explain the effect of pH on sensitivity. We fully agree with him that the photochemical reaction leading to the latent image, like practically every other photochemical reaction which has been studied, involves a primary process which is the direct consequence of the absorption of

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[32] Vogel, Eder's Ausführliches Handbuch der Photographie, vol. 3, p. 143, 5th ed., 1903. Eder, Handbuch, vol. 2, Figure 162, p. 377; 1st ed., 1897.

light, and subsequent secondary reaction or reactions which are purely chemical in nature. The secondary reactions are subject to the same influences as other chemical reactions, and consequently the total chemical reaction associated with a given primary absorption may be widely modified by changing conditions such as the pH. There have been statements that in the photographic emulsion the primary and secondary reactions are the formation of the latent image and development, respectively. While this statement may be a useful analogy in the discussion of photochemistry, it is pure assumption that the formation of the latent image involves only the primary process; there is no evidence that such is the case. A priori it is highly improbable that in a system as complicated as the photographic emulsion there are no secondary reactions, and the existence of the intermittency and reciprocity effects are strong evidence that the secondary reactions do occur. The quantum theory of photochemical reactions implies that the primary process is the necessary consequence of the absorption of a quantum of the proper frequency; a change in the quantum yield with constant absorption, as in exposures at different intensities, must, therefore, be ascribed to secondary reaction.

The shift in spectral sensitivity observed by Fajans involves the primary process, since a smaller quantum has become effective. In contrast to this, the increase in atoms of silver liberated, over and above the increased quantum absorption, must mean a change in the secondary reactions—decreased regression, for example.

While the existence of secondary reactions in latent image formation is practically necessary in the light of general photochemistry, there is no direct evidence of their chemical nature. Slater Price adopts the most obvious chemical theory—that the secondary reactions are connected with the disposal of the bromine liberated by photolysis of silver bromide. In some form or other this theory has been used since the earliest days of gelatin emulsions to explain their superior sensitivity. The gravest objection to it is the general failure of halogen absorbents to act as photographic sensitizers in gelatin emulsions. Materials such as thioanilides [34] and sulphites,[35] even though they are halogen absorbents and may be adsorbed to silver bromide so as to be in the most favorable position for reaction with the bromine, are found to be desensitizers. However, they greatly accelerate the visible photolysis of silver bromide, and delay or prevent solarization. It is, therefore, necessary to assume that silver bromide-gelatin emulsions normally contain something which as an absorbent for the very small quantities of bromine which are liberated in the formation of latent image corresponding to a working density is more efficient than any of the materials which may be added. It must be present only in minute amounts or have only a small capacity, because it can be supplemented by other halogen absorbents for the longer exposures corresponding to solarization and direct blackening. Slater Price believed this to be the gelatin, and demonstrated the parallel between the effect of varying hydrogen ion concentration on the reactivity of bromine and gelatin on the one hand and the sensitivity on the other. The capacity factor just mentioned was not discussed, but it might have been explained by assuming that only

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[34] Sheppard and Hudson, Phot. J., vol. 67, p. 359, 1927.
[35] Sheppard and Wightman, Phot. J., vol. 69, p. 83, 1929.

the gelatin in immediate contact with the grain can react rapidly enough to be effective.

Admitting the existence of an efficient bromine absorbent in silver bromide-gelatine emulsions, we believe that consideration of all the evidence favors Hickman's[36] hypothesis that it is silver sulphide. It does not seem necessary to accept Hickman's further hypothesis that the reaction leads to increased liberation of metallic silver; it is sufficient if we assume that it merely prevents regression, since the quantum yield for the photolysis of silver bromide in photographic emulsions is more probably less than one, rather than greater than one. The silver sulphide is present in quantities of the right order of magnitude to correspond to the capacity observed. On the hypothesis that the silver sulphide nuclei orient[37] the photolysis of the silver bromide, they may become preferred bromine absorbents merely by virtue of position, and the orientation hypothesis may be retained even though the latent image is explained in terms of structure of photolytic silver rather than quantity.

The behavior of highly disperse (Lippman type) emulsions offers an apparently crucial distinction between gelatin and silver sulphide as bromine absorbents. The silver bromide of these emulsions has a maximum specific surface for adsorption of gelatin. They have had a minimum of ripening and, therefore, contain a minimum of silver sulphide. Lüppo-Cramer[38] has furnished quantitative data showing that in these emulsions, unlike ordinary types, the developable sensitivity may be increased by halogen absorbents, such as nitrite and bisulphite. This indicates that the normal bromine absorbent is absent, so that the silver sulphide rather than the gelatin must normally have this function.

It is probable that atomic bromine reacts directly with silver sulphide, if at all; the calculations of Lambert and Wightman[39] indicate that this gives a larger decrease of free energy than if water is involved, as well as being more rapid. However, if we assume that the reaction involves water, the effect of hydrogen ion concentration may still be explained by its effect on the hypobromous acid equilibrium, as calculated by Slater Price. Otherwise, as the reaction between atomic bromine and silver sulphide would not be directly affected by hydrogen ion concentration, there could only be an indirect effect through reaction of gelatin with the by-products of the first reaction.

This discussion has been based on the commonly accepted theory that the latent image is the result of the photolysis of silver bromide. Weigert[40] has recently advanced a "micellar" theory of the latent image which is receiving serious consideration because it is based on his important contributions to the photographic effects of polarized light. He postulates that the latent image is the primary product of the absorption of several quanta by a micelle of silver or silver sulphide, the micelle being raised to a higher energy level which is stable until the energy is used to activate the developer. Regression and such phenomena as the intermittency and reciprocity effects are explained by a secondary reaction, the "inner development" of the

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[36] Hickman, Phot. J., vol. 67, p. 34, 1927.
[37] Sheppard, Trivelli and Loveland, J. Franklin Inst., vol. 200, p. 51, 1925.
[38] Lüppo-Cramer, Zeit. f. wiss. Phot., vol. 30, p. 201, 1931; and earlier articles.
[39] Lambert and Wightman, J. Phys. Chem., vol. 31, p. 1249, 1927.
[40] Weigart, Zeit. f. Wiss. Phot., vol. 29, p. 191, 1930.

micelle by the medium, whereby the energy is lost and no longer available to start development. The secondary reaction being exclusively a regression effect, increase in pH, which would tend to increase the reduction potential of the gelatin and the tendency to inner development should decrease rather than increase sensitivity. The effect of silver ion concentration would be difficult to predict.

We conclude that under normal conditions in the photographic emulsion the adsorption of gelatin to the silver bromide grains is such as to reduce the adsorption of other materials and their consequent effects on sensitivity. Replacement of adsorbed gelatin by bromide ions, which causes desensitization, is favored not only by increased bromide ion concentration, but also by increased hydrogen ion concentration. All effects of environment on photographic sensitivity which do not involve changes in absorption of light must be explained in terms of secondary reactions in latent image formation. The most obvious of these secondary reactions, the elimination of bromine, is better explained by reaction with silver sulphide rather than with gelatin.

VI. Acknowledgment

In the making and testing of the emulsions described in this paper C. M. Kretchman rendered valuable assistance.

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THE PHOTOGRAPHIC EMULSION: ANALYSIS FOR NONHALIDE SILVER AND SOLUBLE BROMIDE

By Burt H. Carroll and Donald Hubbard

ABSTRACT

This paper is a critical study of methods proposed for the determination in emulsions of silver in forms other than silver halide, and a description of a new method of extracting soluble bromide from emulsions. The method of Weigert and Lühr, based on double fixation with thiosulphate, is found to be reliable; the principal danger is decomposition of silver thiosulphate to sulphide. The method of Schmidt and Pretschner, direct extraction with nitric acid, is too insensitive. Soluble bromide may be quantitatively extracted from plates by three changes of dilute acid; error from formation of silver-gelatin complex is thus eliminated. Electrometric titration at pH2 or less may be used for liquid emulsions, and is preferable for analysis of plate extracts, but it is also possible in the latter case to determine the bromide by oxidation to cyanogen bromide, with subsequent iodometric titration, according to Lang.

CONTENTS

I. DETERMINATION OF NONHALIDE SILVER

1. INTRODUCTION

The existence in ripened silver bromide-gelatin emulsions of sensitivity nuclei attached to the silver bromide grains is now established so thoroughly that it need not be discussed. The mechanism of their action is outside the scope of this paper. We are here concerned with the methods proposed for the determination of nonhalide silver in emulsions, their reliability and accuracy; and with the evidence on the nature and distribution of the nonhalide silver which is furnished by these analytical methods.

The methods used for the determination of silver liberated on exposure, in attempts (1)[1], (2) to verify the Einstein equivalence equation for photolysis of silver salts in photographic materials, are not sufficiently sensitive to detect nonhalide silver in unexposed emul-

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[1] Figures in parentheses here and throughout the text refer to bibliography at the end of the paper.

sions. By extrapolation of the data for silver formed on longer exposures, it has been estimated that photo-silver corresponding to normal image densities is of the order of 10^{-8} part of the total silver (3). The assumption that the sensitivity nuclei represent a fraction smaller, if anything, and quite beyond the reach of analysis, has been commonly made. The data of Sheppard (4) on sensitization by allyl thiocarbamide demonstrated that much higher proportions could be converted to silver sulphide at optimum conditions for sensitization, but there was no proof that all of this was necessarily effective. The analytical determination of nonhalide silver in unexposed developing-out emulsions was first announced by Weigert and Lühr (5). Their results showed a steady increase in the "Ursilber" of silver chloride and bromide emulsions during ripening, as is to be predicted if it is the product of this process. The amount of nonhalide silver was greatest in silver chloride emulsions, and least in those made with silver iodide; in the iodide emulsions it remained practically constant during ripening, in contrast to those made with the other halides. The absolute amounts of nonhalide silver were in all cases far above those for photo-silver corresponding to normal exposures.

In subsequent contributions (6), (7), (8) Weigert and Lühr have given full details of their methods and results. Their results have unfortunately been reported entirely in terms of weight of silver per unit plate area; as the results of other investigators have also been given in somewhat arbitrary terms, we have reduced everything to the common basis of the atomic ratio of nonhalide silver to the total silver in the emulsion. Weigert and Lühr's experimental emulsions were coated at 4.1×10^{-4} g equivalent AgBr per 100 cm² of plate; for commercial emulsions we have taken Eder's (9) average value of 9×10^{-4} for German plates. The Ag/AgBr ratio for commercial plates was approximately 2×10^{-4}; in experimental pure bromide emulsions it was 1.5 to 4×10^{-4} depending on the time of ripening.

Weigert and Lühr's procedure is based on the elimination of silver halide by fixing with sodium thiosulphate and washing, and analysis of the silver remaining in the emulsion film. The great increase in sensitivity over previous methods based on the same principle was obtained by differential electrometric titration of the silver with very dilute iodide solution. After fixing and washing, the emulsion film was scraped off the plate (9 by 12 cm) and boiled for five minutes with 0.8 ml of nitric acid, specific gravity 1.2, to break down the gelatin. The solution was then made up to 25 ml with the addition first of 1 ml of concentrated ammonia, next 0.5 ml glacial acetic acid, leaving it faintly acid. The prepared solution was divided between two crucibles, each provided with a silver electrode and a mechanical stirrer; the cell was completed by a salt bridge filled with agar jelly containing potassium nitrate. Potential differences between the electrodes were determined by connecting the cell directly to a highly sensitive galvanometer and reading the throw of the instrument after 30 seconds. The cell was short circuited between readings. In making the titration, iodide solution was added from separate burettes to each of the vessels, one being kept in excess by a small amount, usually 0.1 ml. Using 0.0001 N KI, the method was sensitive to 1×10^{-6} gram silver. Careful control determinations established that if the gelatin was broken down by the above procedure it caused no interference, and that the attack of the solution on the electrodes was negligible. Lühr noted that the first titration with the electrodes after they had been out of use for some time was generally low.

In the earlier part of their work, Weigert and Lühr simply fixed the plates in an alkaline thiosulphate bath[2] and washed thoroughly before stripping and analyzing. Experiments on plates coated with plain gelatin and bathed in fixing baths containing silver indicated that there was a blank of approximately 1×10^{-6} g equivalent of silver per g of gelatin, which could not be removed by washing after such treatment. They accordingly altered their procedure by the addition of a second fixing and washing after the first treatment; in view of the common practical use of double fixation to eliminate the last traces of silver salts from photographic materials, it is somewhat surprising that this had not been used in previous analytical methods depending on thiosulphate fixing. With this modification the blanks approached the limit of error of the titration. They lay considerable stress on thorough washing of the plates between the two fixing baths, reasoning that the removal of the silver held by the gelatin will be more complete as the ratio of sodium thiosulphate to silver thiosulphate is increased and that the optimum condition for use of the second bath is accordingly after the silver salts have been removed as far as possible by water. Their data show a decrease in the silver with increasing time of washing between the fixing baths. In some cases it reached an apparently constant value after washing for four hours, but more frequently there was an appreciable further decrease when the washing time was extended to five hours. In the case of ripened emulsions there is little room for doubt that there was a real quantity of silver much larger than the uncertainty of extrapolation to theoretically complete washing. A standard time of four hours was finally adopted.

Weigert and Lühr recognized that there is loss of silver during the fixing and washing processes since the solutions contain dissolved air, and any oxidation of the very finely divided metal will be followed by solution of the oxide in the thiosulphate. They tested the effect of from 2 to 10 successive fixing baths, 10 minutes each, on a ripened emulsion, the decrease in silver being very considerable with the larger numbers. The loss was less in 5 than in 20 per cent solution; after experiments with more dilute solutions, 5 per cent thiosulphate was adopted for the second fixing bath. We are unable, however, to find that Lühr determined the loss when plates containing known amounts of colloidal silver were given the standard treatment—10 minutes in alkaline 20 per cent thiosulphate, 4 hours washing in running tap water, 10 minutes in alkaline (?) 5 per cent thiosulphate and further washing. This was done with plates containing colloidal silver sulphide in quantities similar to the "Ursilber" of ripened emulsions; the loss, while probably real, was within the limits of error of the procedure.

It is obvious from the nature of the analytical procedure that the "Ursilber" would include both the silver sulphide and the metallic silver present in the emulsion. Weigert and Lühr came to the conclusion that it was almost entirely silver, because the "Ursilber" was greatly diminished by treatment with persulphate. In control

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[2] A reference to the work of Chapman Jones on the attack of fixing baths on the developed image indicates that the bath contained 200 g $Na_2S_2O_3.5H_2O$, 5 g Na_2SO_3, and 1 g Na_2CO_3 per liter, but we have been unable to find an explicit statement as to the amount of alkali.

experiments with colloidal silver sulphide in gelatin, persulphate failed to dissolve silver sulphide. These results are directly contradicted by Sheppard (10) in a recent communication in which he reports that known silver sulphide nuclei in emulsions were completely destroyed by persulphate. These emulsions were found also to contain silver in amounts somewhat smaller than the silver sulphide.

Weigert and Lühr's results have been attacked (11), (12), (13), principally because of the use of thiosulphate fixation, which other investigators had found to leave appreciable blanks depending on conditions such as the thickness of the emulsion film. These criticisms are answered by the use of the second fixing bath, in so far as they are based on the adsorption of silver thiosulphates by the gelatin. The very erratic results obtained by Arens and Eggert (12), using Weigert and Lühr's method, appear to reflect more on their experimental technique than on the method. Kieser (13) has pointed out that silver in the quantities reported ($Ag/AgBr = 1$ to 10×10^{-4}) might be detectable by its color; this also applies, however, to silver sulphide produced by sensitizers like allyl thiocarbamide, and it is not excluded that it actually would be visible by refined methods of comparison.

Shortly after Weigert and Lühr's first communication, Schmidt and Pretschner (14), working independently and by an entirely different method, reported the presence of excess silver in unexposed emulsions. Their values, reduced to the same basis, were about two or three times those obtained by Weigert and Lühr; for fast bromiodide emulsions, $Ag/AgBr = 8$ to 9×10^{-4} by one method, 2 to 3×10^{-4} by the other. Like Weigert and Lühr, they found that the amount of nonhalide silver increased with the solubility of the silver halide present in the emulsion and could not be correlated with the photographic properties of the emulsion. This apparent confirmation of Weigert and Lühr's results turned out to be accidental. Schmidt and Pretschner worked with large quantities of emulsion (about 0.7 kg) in the "noodles." The emulsion was thoroughly washed in tap water, followed by about 24 hours in changes of distilled water. It was then digested with nitric acid, 3 per cent of the total volume, which broke down the gelatin and coagulated the silver halide, and the silver in solution determined by very carefully corrected precipitation as silver chloride. Schmidt and Pretschner at first apparently considered that the silver determined in this way was present as metal. They later found (15) that on centrifuging emulsions the larger part of it remained in the gelatin, in contrast to photo-silver which was carried out with the silver halide of exposed emulsions. Further experiments (16), (17), (18) on sedimentation and on fixing silver chloride emulsions with sodium sulphite led them to the conclusion that most of the excess silver was not metal, but in some way combined with gelatin. Their final conclusion (19), (20), which we believe to be essentially correct, was that the excess silver was formed during washing by hydrolysis of the silver halide. They ascribed this, however, to the difference in rate of migration of the silver halide ions, which can not account for the results. The present authors in a preliminary note (21) have pointed out that the combination of silver ion with gelatin is responsible for this reaction; quantitative verification of this is given in our communication on the silver ion-gelatin equilibrium (22).

Sheppard (3) has recently reported the application of colorimetric determination of traces of sulphur compounds (23) to the determination of silver sulphide in the silver halide grains centrifuged from ripened emulsions. These results show the predicted increase in $Ag_2S/AgBr$ ratio with increasing specific surface of the grains (although it is noteworthy that the "medium" size grains have a distinct minimum, indicating that the "large" grains, first formed in the precipitation, reduced the concentration of labile sulphur compounds before the others were formed). They constitute an entirely independent confirmation of the existence of nonhalide silver in unexposed emulsions in the quantities first reported by Weigert and Lühr.

Our interest in the subject was primarily in connection with the determination of soluble bromide in emulsions. If there existed nonhalide silver in such quantities as were reported by Schmidt and Pretschner, this might well interfere with analysis for small amounts of bromides. Determination of nonhalide silver is also of use in any experiments on ripening and on nuclear sensitizers, although it is obvious from the available evidence (3) that the quantity is less important than its structure and relation to the silver halide grains. Being distinctly skeptical at first of the reality of the silver determined by any of the methods, we not only considered those published, but attempted independent verification by other processes which will be very briefly reported.

2. EXPERIMENTS WITH THE WEIGERT AND LÜHR METHOD

For the necessary electrometric titrations we used the apparatus which has already been described in another connection (22) measuring the emf of a cell consisting of the silver electrode in the solution to be titrated and a 0.1 N calomel electrode connected to it by a salt bridge filled with ammonium nitrate solution. While our procedure was not strictly a differential titration, the end point was always determined by a plot of $\Delta E/\Delta v$ against volume of solution. The procedure, involving the use of a potentiometer, is somewhat slower than that of Weigert and Lühr, but we found it a real advantage to be able to judge from the constancy of the potential whether the electrode was in equilibrium with the solution. Sluggishness which is completely negligible for the titration of 20 ml of 0.1 N solution is an entirely different matter when the end point comes at 1 ml of 0.00020 N KI. Like Clark (24) and Lühr (7), we found that the electrodes were more satisfactory after use; in fact, the first titration with dilute iodide solutions was quite unreliable. Unlike Lühr, we found it tended to be high rather than low; this is probably because the electrode after cleaning was usually made anode in dilute KI solution. All the experiments were made with 5 by 7 inch plates. Fixing and washing were carried on in new enameled trays, which were discarded when there was any indication of attack on the glaze, or in glass trays. In working with machine-coated experimental plates, the quantity of silver halide on the plate was determined by digesting the fixing baths with zinc. The resulting mixture of silver, silver sulphide, and excess zinc was dissolved in nitric acid and titrated with standard thiocyanate solution, using ferric alum as indicator.

We will, for convenience, refer to the quantity of silver halide per given area as the "coating thickness" of the plate; this quantity is, for a given emulsion, proportional to thickness although it is determined in terms of silver.

By presenting our results in an order quite different from that of the experiments we may develop the subject more logically and economize space. Table 1 gives the data for recent analyses of emulsions to which known amounts of colloidal silver and silver sulphide had been added. The reproducibility of the results for all but the controls was better than 5 per cent, and the values found agree with the amounts added within 12 per cent; in view of the uncertainty of measuring the volumes of emulsion used in making the knowns, the agreement with the true value may be better than this. The knowns were made by mixing the colloid with the emulsion just before coating, control batches being coated without such addition. The colloidal silver had been made by the dextrin method of Carey Lea as modified by Wiegel (25), and purified by two alcohol precipitations; the amounts given are corrected for the traces of silver salts present. Colloidal silver sulphide was prepared by adding first 2.34 ml of 0.107 M $Na_2S_2O_3$, then 5.0 ml of 0.100 M $AgNO_3$ to 170 ml of warm 1 per cent gelatin solution; the mixture was allowed to stand about an hour before use to complete the decomposition of the silver thiosulphate. The emulsions were not fully ripened, to keep down the nonhalide silver in the control; they were stabilized by adding 10 KBr per 1,000 AgBr before coating, and the analyses were made within two or three days after drying.

TABLE 1.—*Analysis by modified Weigert and Lühr method of emulsions containing known amounts of colloidal silver or silver sulphide*

Emulsion type	Colloid	Silver halide on 5 by 7 inch plate, gram equivalent $\times 10^4$	Nonhalide silver on 5 by 7 inch plate, gram equivalent $\times 10^7$	Ag/AgBr $\times 10^5$ found	Mean difference from control	Ag/AgBr $\times 10^5$ added
Ammonia process, pure bromide.	Control	13.2	0.96	7.3		0
		12.0	.52	4.3		
	Carey Lea silver	15.7	4.40	27.9	23.1	24.9
		17.5	5.24	29.9		
Neutral process, 3.4 mol per cent AgI.	Control	12.3	.48	4.2		0
		12.4	.56	4.5		
	Carey Lea silver	13.1	4.24	32.4	28.7	26.0
		12.3	4.16	33.8		
	Silver sulphide	13.7	4.88	35.6	30.4	34.5
		15.3	5.20	34.0		
	do	14.1	2.30	16.3	12.4	13.8
		13.7	2.36	17.2		

In these experiments we used a modification of the procedure recommended by Weigert and Lühr. The plates were first fixed for 10 minutes in a solution containing, per liter, 300 g $Na_2S_2O_3 \cdot 5H_2O$, 5 g Na_2SO_3 and 1 g Na_2CO_3; this was followed by two changes of a solution containing, per liter, 50 g $Na_2S_2O_3 \cdot 5H_2O$, 5 g Na_2SO_3, and 1 g Na_2CO_3, for five minutes each; the trays were rocked continuously during fixing, and all solutions were kept at less than 20° C. After fixing, the plates were washed for four hours in running tap water at 10° C., stripped, and titrated as already described.

This procedure was adopted in order to maintain at all times a high ratio of soluble thiosulphate to silver. Silver thiosulphate is very unstable unless this condition is fulfilled, and in our opinion the considerable positive errors found by Schmidt (26) and others in the analysis for nonhalide silver by a single fixation are caused more by precipitation of silver sulphide than by adsorption of silver compounds by gelatin. Kieser (27) has demonstrated that, on dissolving silver bromide in thiosulphate solutions after exposure to light, silver sulphide may be found in the residue. In some cases the results for silver may be high, indicating that in addition to conversion of the photolytic silver to sulphide, there may be a precipitation of silver sulphide on the former. Furthermore, our data (22) on the combination of silver ions with gelatin indicate that the amount of silver per gram of gelatin which was found by Weigert and Lühr after a single fixation corresponds at pH 7 to a silver ion concentration of $10^{-8} N$, which could hardly exist after four hours of washing. Adsorbed silver would at least be partly removed by extraction of the gelatin with acid, but when plates were fixed and washed by the original Weigert and Lühr procedure, then extracted three times with 0.005 N H_2SO_4 before stripping, no trace of silver could be found in the acid extract and the silver found in the stripped emulsion was not decreased.

Weigert and Lühr determined the blank on their procedure by coating plates with gelatin containing silver bromide dissolved in sodium thiosulphate. Blank emulsions for this purpose are somewhat difficult to prepare. Any emulsion in which silver nitrate solution has been even in momentary contact with gelatin may contain silver or silver sulphide. If the silver bromide is precipitated from aqueous solution with excess of bromide and then emulsified in gelatin, this objection is avoided, but the emulsion is liable to contain lumps which fix too slowly. The most satisfactory process is that originally suggested by Abegg and Hellwig (28), the silver bromide (plus iodide) being dissolved in a hot strong solution of a soluble bromide, and precipitated by diluting this with gelatin solution. The high concentration of soluble bromide liquefies the gelatin, so that we found it desirable to centrifuge the resulting emulsion and resuspend in fresh gelatin. The soluble bromide present was still much higher than normal so that the possibility of reaction of the silver halide with gelatin was minimized. Emulsions prepared by this procedure and coated in commercial thickness (15×10^{-4} g equivalent on a 5 by 7 inch plate) showed no nonhalide silver whatever in quadruplicate analyses by the modified method just described, demonstrating that the results with normal emulsions can not be ascribed to silver retained by the gelatin or to silver sulphide from decomposition of silver thiosulphate. It is necessary to specify, however, that the solutions and wash water be kept cool, and that the coating thickness shall not be excessive. Experiments with similar emulsions extracted by the original procedure and washed at higher temperatures (the tap water having been as warm as 30° C.) gave positive values for silver which increased with the temperature and time of washing.

Schmidt and Pretschner (26) reported that the nonhalide silver found after a single thiosulphate fixation and washing increased with increasing coating thickness of the plate. The original and modified Weigert and Lühr procedures were therefore tested for their dependence on this variable. The results are presented in Figures 1 and 2 by

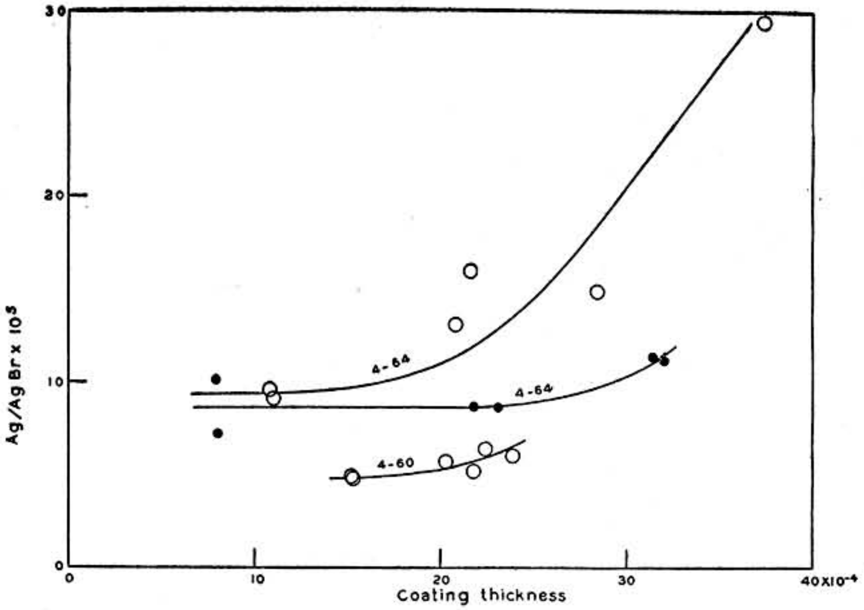

FIGURE 1.—*Variations in the results of determinations of nonhalide silver in plates with varying thickness of emulsion coating*

The data are for experimental emulsions 4-60 and 4-64
(.) Determinations by the original Weigert and Lühr method
(○) Determinations by the modified Weigert and Lühr method

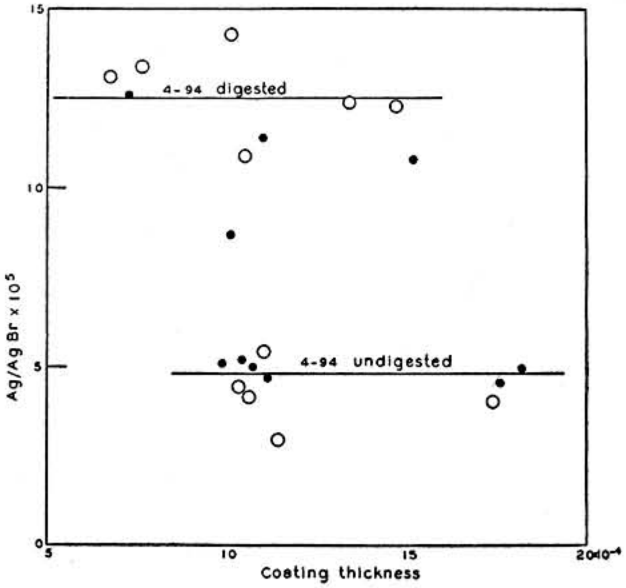

FIGURE 2.—*Variations in the results of determinations of nonhalide silver in plates with varying thickness of emulsion coating*

The data are for experimental emulsion 4-94.
(.) Determinations by the original Weigert and Lühr method
(○) Determinations by the modified Weigert and Lühr method
Note also the increase in nonhalide silver produced by digestion

plotting the nonhalide silver/silver halide ratio against the coating thickness (in terms of g equivalents of silver halide per 5 by 7 inch plate). If the results were independent of the coating thickness, the plot should be a horizontal straight line; an increase in the ratio indicates that the results are not independent of coating thickness. The scattering of the points about the curve also indicates the reproducibility of the methods. Three emulsions were analyzed by the original[3] procedure and four by the modified. Emulsion 4–94 (Fig. 2) was prepared especially for these tests; one-half was coated with the minimum of digestion after washing, the other after two hours, digestion at 55° C. Each half was coated at several thicknesses. The difference in nonhalide silver produced by digestion is obvious.

The reproducibility by the two procedures is about the same; random variations of ± 20 per cent were encountered in some cases. This is not quite as good as the results obtained by Lühr, but is of the order of the systematic errors of the method. The coating thickness did not affect the results up to a value of about 0.15 g AgBr per 100 cm^2 (18×10^{-4} g equivalent per 5 by 7 inch plate); this is the maximum which we have found on commercial emulsions. Thicker coatings, which were found on some of the experimental plates, introduce a positive error; the original procedure was the better of the two in this respect, but either one became unreliable.

Having established the order of accuracy and reproducibility of the analytical method, the next consideration is the evidence concerning the nature of the nonhalide silver in photographic emulsions which may be derived from further study.

It is interesting to find that the Weigert and Lühr procedure gives correct results for colloidal silver in an emulsion, even though the thiosulphate solutions, which are of course saturated with air, attack the same colloidal silver under other conditions. Some of our first tests of the method were made by adding colloidal silver to gelatin and coating on plates so that the gelatin and silver corresponded to the quantities of gelatin and nonhalide silver in emulsions. When these plates were put through the fixing baths and washing, the loss of silver was 30 to 90 per cent, being less for larger amounts of silver. This applied both for Carey Lea silver (the same sample used in the emulsions of Table 1) and for argyrol, losses in the latter case being corrected for the silver proteinate present. It has been suggested (27) that colloidal silver in the emulsion would be converted during fixing to silver sulphide. This would explain the failure of the fixing baths to attack colloidal silver when present in an emulsion, since, in agreement with Weigert and Lühr, we found that the attack on colloidal silver sulphide was small even when it was coated in plain gelatin.

Although the method may give correct results for colloidal silver present in emulsions, we can not agree with Weigert and Lühr that this is the main component of the nonhalide silver ("Ursilber"). We found, in agreement with Sheppard (10), that colloidal silver sulphide is attacked by persulphate. The data are given in Table 2. The silver sulphide was prepared by the decomposition of silver thiosulphate, as described on page 716, and diluted with 6 per cent gelatin solution to the desired concentrations before coating. It is evident

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[3] Except for the use of 300 g thiosulphate per liter.

from the data that this same sample was not seriously attacked by thiosulphate solurtions. The persulphate solution was 0.10 N $(NH_4)_2S_2O_8$ and 0.10 N H_2SO_4, acting for one hour at 20°, without subsequent washing.

TABLE 2.—*Attack on colloidal silver sulphide by thiosulphate and by persulphate*

(All results expressed as gram equivalents of silver $\times 10^7$ per 5 by 7 inch plate)

Original amount	Residue	
	After modified Weigert and Lühr treatment	After persulphate treatment
4.26, 4.24	3.04, 3.24	1.3, 1.0
9.76, 9.76	9.74, 9.26	1.14, 1.74

The quantity of nonhalide silver found in emulsions has been one of the principal objections to its identification with the sensitivity nuclei. Even unripened and insensitive emulsions contain amounts much larger than is necessary ((29), Tables 29, 30, 31) under favorable conditions to multiply their sensitivity manyfold. We accordingly suggested the hypothesis that most of the nonhalide silver had been formed by reactions involving silver ions or silver-gelatin complexes, while the sensitivity nuclei were formed by rearrangement of compounds first adsorbed to the grains. We have since realized that this may be tested experimentally, as the two classes can be separated by centrifuging the emulsion, and determined by analyzing the silver halide grains and the cleared gelatin. Three emulsions were made up for this purpose. Portions of each were coated unchanged. The rest of the emulsion was separated in the centrifuge, and the cleared gelatin coated in the same way, at about the same thickness, as the original emulsion. In two cases the separated silver halide was again emulsified in fresh gelatin and coated like the rest. The plates were analyzed by the modified method; the coating thickness was excessive, but there are no indications of difficulty from this source. The data in Table 3 clearly demonstrate that the nonhalide silver is associated with the grains and not dispersed through the gelatin. The data given by Sheppard (3) for the silver sulphide in emulsion grains, obtained by a different analytical method, are obviously proof of the same point. The explanation of the existence in the same emulsion of silver sulphide of widely varying effectiveness in sensitizing remains to be provided. It is obvious that some other function of the silver sulphide is overwhelmingly more important than its total quantity.

TABLE 3.—*Distribution in emulsions of nonhalide silver determined by the Weigert and Lühr method*

Type of emulsion	Coating on plate	Total silver on plate, gram equivalents $\times 10^4$	Nonhalide silver on plate, gram equivalents $\times 10^7$	$Ag/AgBr \times 10^5$
Neutral, pure bromide	Original emulsion	22.6	1.88	8.3
		21.8	1.42	6.5
	Cleared gelatin	.1	.4	----------
		.1	.3	----------
	Silver bromide in fresh gelatin	23.6	2.24	9.5
		24.0	2.12	8.9
Ammonia ripened, 1 per cent AgI	Original emulsion	17.3	4.80	27.7
		15.8	4.34	27.4
	Cleared gelatin	.2	0	----------
		.2	0	----------
	Silver halide in fresh gelatin	21.6	7.5	34.7
		21.1	6.16	29.2
	Original emulsion	34.2	2.78	8.1
		33.5	2.68	8.0
	Cleared gelatin	.3	0	----------
		.3	0	----------

3. EXPERIMENTS WITH OTHER METHODS

(a) DIRECT EXTRACTION WITH NITRIC ACID

Direct extraction with nitric acid as recommended by Schmidt and Pretschner, dissolves silver in every form likely to be present except the halides. Soluble halides must be completely removed or they will react with the dissolved silver. The extensive washing necessary to remove the halides results in the formation of silver-gelatin compounds if the washing is done with pure water, with consequent positive errors many times the quantities to be determined. As Schmidt and Pretschner have recognized this, it will be unnecessary to present all the data accumulated to prove the point.

The apparatus for electrometric titration being available, we substituted this for the gravimetric methods of Schmidt and Pretschner, and worked with the emulsion from a 5 by 7 inch plate instead of with larger quantities as "noodles." The sensitivity of the titrations was less than those for the Weigert and Lühr method; the final solution being saturated with silver bromide, it is necessary to titrate with bromide solution and the end point is less sharp because of the greater solubility of silver bromide. The uncertainty of a titration was about 2×10^{-7} g equivalent of silver, as against 0.4×10^{-7} with iodide. The coating thickness of the plates was readily determined by an application of the Liebig method for cyanides. The coagulated silver bromide was filtered off after the nitric-acid digestion, and dissolved in standard sodium cyanide solution. The excess cyanide was then titrated with silver nitrate solution, using the appearance of turbidity as the end point.

The principal systematic error in the determination of nonhalide silver in emulsions by nitric-acid extraction is caused by the formation of silver-gelatin compounds while extracting soluble bromide. This may be eliminated by extracting the bromide with dilute acid instead of with water, as will be explained in more detail in the second part of this paper. However, the sensitivity of the method is insufficient. The changes in nonhalide silver produced by after-ripening could be detected, but were little larger than the uncertainty of the titration.

Nitric acid extraction was used in the determination of silver-gelatin compounds in emulsions; these results will be given in the second part of this paper.

(b) CYANIDE FIXATION

If an unexposed and undeveloped plate is fixed in a cyanide solution under ordinary conditions, followed by adequate washing, all silver will be removed; even silver sulphide will be dissolved by complex ion formation, and small amounts of finely divided silver will be attacked by the dissolved oxygen in the solution and then dissolved by the cyanide. If oxygen were quantitatively removed from the solutions, it might be possible to fix with cyanide, thus removing silver halide and sulphide, and to determine the remaining metallic silver. An apparatus was built in which it was possible to free a liter of water from dissolved gases by refluxing in vacuum for several hours; portions of this water were then transferred to a tube containing the strip of plate to be analyzed, and solid sodium cyanide. The cyanide solution thus prepared in the absence of oxygen fixed the plate and was replaced by successive portions of water. The whole apparatus could be rocked to insure agitation. The attack on silver was tested by using a strip of plate coated with colloidal silver (free from silver salts) in gelatin, 3.3×10^{-6} g equivalent Ag. Using single fixation followed by four changes of water, no silver could be detected in the acidified extract from one run; in a second run where some leakage of air into the apparatus had occurred 3×10^{-7} g equivalent of silver was found in the extract. Complete removal of silver from the emulsion was found to require more thorough washing. Test strips of Eastman 33 plates were fixed in the apparatus in two changes of cyanide solution (a second portion of the solid salt being held out of contact with the solution during the first fixation), followed by six changes of water. No silver could be detected in the remaining emulsion. The method was abandoned at this point as too cumbersome and uncertain.

If the emulsion is freed from soluble bromide and then fixed in air, all silver is extracted, provided the amount present as metal is small. If the fixing bath was then acidified and evaporated to remove hydrocyanic acid (using a hood for this operation), it was found by experiment that silver sulphide and silver halides were precipitated quantitatively, but that traces of silver originally present as metal remained in solution. Apparently if silver cyanide was first precipitated, it was decomposed during the evaporation if the quantity was small enough. This method was of possible interest, since it might be a means of determining metallic silver but not silver sulphide. However, it is obviously dependent on removal of soluble bromide, and any silver-gelatin compounds formed in this process appear in solution and can not be distinguished from metallic silver. Attempts to apply the process to the determination of soluble bromide will be reported in the second part of this paper.

Other solvents were also considered. Sulphite unfortunately can be used only for chloride emulsions. Ammonia was reported by Schmidt (17) to give "very disturbing side reactions"; the nature of these will be discussed in a separate communication on hypersensitization by ammonia solutions.

It is possible that the nonhalide silver might be determined in the emulsion after extraction with acid solutions of thiocarbamides, or with thiocyanates, but neither of these methods were tested.

II. DETERMINATION OF SOLUBLE BROMIDE

The determination of soluble bromide in photographic emulsions is of considerable practical interest because of the effect of this constituent on the ripening and after-ripening process, the sensitivity (especially in the presence of sensitizing dyes) and the stability on storage. The analytical problem appears superficially to be very simple, and probably for this reason has received very little mention in the literature.

Since the soluble bromide is at most about 1 per cent of the total bromide, it is obvious that it can be more accurately determined if separated from the silver bromide. The extraction of the soluble bromide from the emulsion is subject to an unexpected positive error from the formation of silver-gelatin complex and consequent decomposition of silver bromide, which leads to high results. The combination of silver ion with gelatin has been quantitatively studied in this laboratory (22). Its existence was independently inferred by Mitchel and Rawling (30). They analyzed emulsions of known composition by coagulating the gelatin and silver bromide and determining soluble bromide in the filtrate. The results were high in bromide by an amount increasing as the excess of bromide over silver was decreased. Chloride emulsions gave a larger error in the same direction, while iodide emulsions were slightly low in iodide recovered, indicating adsorption. Their data are quite consistent with the formation of silver-gelatin complexes in amounts increasing with the silver ion concentration of the emulsions. If the error from this source is eliminated, the remaining problems are the completeness of extraction of the soluble bromide and its determination in small quantities such as are obtained from reasonable areas of photographic materials.

The methods here proposed are based on the use of acid to prevent the formation of silver-gelatin complexes. Electrometric titration has been used in most of the experiments for the determination of soluble bromide in the extracts, and is strongly recommended for this purpose. The acid extracts may, however, be analyzed by other methods.

As the combination of silver ion with gelatin (22) failed to disappear completely at any hydrogen ion concentration which was tested, the conditions under which it became negligible during extraction of bromide from plates were tested directly. Table 4 gives the data for the extraction of commercial plates (Eastman 33) with varying concentrations of acid. Five by seven inch plates were used in the experiments, the emulsion on each plate containing $15.4 \pm 0.4 \times 10^{-4}$ g equivalent of silver halide. Three extractions were made with 100 ml portions of acid, rocking the plate for three minutes in each. After the extractions, the emulsion was stripped off and analyzed for nonhalide silver by digestion with 0.5 N HNO_3.

Results are given in terms of the ratio of equivalents of soluble bromide or nonhalide silver per equivalent of silver halide.

TABLE 4.—*Extraction of soluble bromide from Eastman 33 plates, and nonhalide silver in plates after extraction*

Solvent used for extraction	$Br^-/AgBr$ $\times 10^3$	Nonhalide silver, after extraction Ag/AgBr $\times 10^3$	Solvent used for extraction	$Br^-/AgBr$ $\times 10^3$	Nonhalide silver, after extraction Ag/AgBr $\times 10^3$
Water	3.0	[1] 1.47	0.0050 N H_2SO_4	2.03	0.29
	2.9	[1] 1.44			.26
	3.7	[1] 1.46	0.025 N H_2SO_4	2.03	.30
	3.7	[1] 1.46		2.00	.25
0.010 N [2] acetic acid	2.06	.45	0.125 N H_2SO_4	2.05	.23
	2.10	.43		1.99	.25
0.0010 N H^2SO^4	3.80	.51	Chrome alum 10 g/liter	2.02	
	3.80	.45		2.06	.22
	2.24	[1] .29		2.06	.25
	2.31	[1] .29		1.97	.25

[1] Determined by direct electrometric titration of acidified stripped emulsion, instead of nitric acid extraction.

[2] Five extractions.

This procedure was found to give complete extraction within the limits of error of the titration of the extracts. For example, successive extracts of the Eastman 33 plates with water were found to be equivalent to the following, in ml of 0.0010 N $AgNO_3$: First, 4.18, 4.0; second, 0.5, 0.5; third, 0.0, 0.0. Using 0.010 N HAc, the combined first extracts from two plates were equivalent to 5.8 ml; the second to 0.51 ml, and the third, fourth, and fifth each to 0.0.

The data on bromide extracted and on nonhalide silver remaining show that a constant minimum is reached with solutions as acid as 0.005 N H_2SO_4 (pH approximately 2.7). The nonhalide silver remaining after extraction with the more acid solutions represents silver sulphide rather than silver-gelatin complex, since it checks the nonhalide silver in these same plates found by the Weigert and Lühr method (mean value 0.21×10^{-3}) which includes only silver and silver sulphide.

The chrome alum solution was tested because it seemed likely to be useful for extracting emulsions with a tendency to loosening from the base; electrometric titration may be made without eliminating the alum, although $\Delta E/ \Delta v$ at the end point is smaller. The pH of chrome alum solution, 20 g/liter, is 2.16 by the quinhydrone electrode.

The extraction with chrome alum solution (10 g/liter) was tested on an experimental emulsion to which soluble bromide had been added after a thorough washing. 8.0 ml of 0.111 N KBr had been mixed with half the emulsion, containing 0.16 g equivalent silver halide, giving a ratio $Br^-/AgBr$ of 5.5×10^{-3}. Extractions of plates from the half without added bromide contained 0.0, 0.0, 0.0, 0.1×10^{-3} $Br^-/AgBr$; from the half with bromide the ratios were 5.35, 5.33, 5.56, 5.41×10^{-3}. The difference is within the limits of error in making up the known.

While the above data indicate that relative amounts of soluble bromide in different portions of the same emulsion may be determined by extraction, there remained the possibility that the silver halide grains may carry appreciable amounts of alkali bromide which is irreversibly adsorbed or even in solid solution, and hence not to be removed by such extraction. This could be liberated by fixing the plate. Accordingly, the whole emulsion of Eastman 33 plates was analyzed by the method of Clark (24). After fixing in two changes of cyanide solution, followed by two changes of distilled water, the silver was reduced by digesting with zinc. The halide solution was filtered and hydrocyanic acid eliminated by boiling with acetic acid. The silver and zinc were dissolved in nitric acid and excess nitric acid driven off by gentle heating. The silver nitrate plus zinc nitrate was then dissolved and the silver and halide solutions made up to known volumes and titrated against each other electrometrically. The ratio Ag: halide thus obtained was 1.004, 1.004, 1.002:1. The error in this method is obviously of the same order of magnitude as the soluble bromide present. It indicates, however, that the adsorbed bromide left after extraction with the dilute acid can not be large.

Repeated attempts were made to determine total soluble bromide, including possible adsorbed material, by a modification of this process. The plates were fixed in 1 per cent NaCN, followed by 0.1 per cent NaCN and two changes of water. Hydrocyanic acid and dissolved silver salts were eliminated by acidifying with sulphuric acid (double the amount necessary to liberate the hydrocyanic acid) and twice evaporating to half volume on the steam bath, after which the solution was filtered and titrated electrometrically. Starting with known amounts of silver nitrate and potassium bromide, the correct value for excess bromide was obtained by this procedure. However, the results with extracts from plates were erratic; and the electrode potentials were unsteady unless the solution were strongly acidified during titration. It was found that extracts from certain samples of gelatin produced very similar results when added to controls, indicating reduction of silver bromide by the combined action of the cyanide and organic extract from the gelatin. It is interesting that other samples of gelatin caused no such trouble. Mitchel and Rawling were able to determine bromide in the presence of gelatin by the Lang method (31), which is based on oxidation of the bromine to cyanogen bromide and titration of iodine liberated by the cyanogen bromide after first removing the excess of oxidizing agent. This method was therefore applied to the solutions from the cyanide fixation. The apparent errors were not as large as those of electrometric titration of these solutions, but the results were not satisfactory by either method.

The Volhard method obviously might be used for the determination of bromide in the extracts if chloride were known to be absent, but this will seldom be the case. The adsorption indicators, such as fluorescein, can not be used for titration of halide against silver in the presence of protective colloids, such as gelatin extracts.

As the Lang method was found by Mitchel and Rawling (30) to work in the presence of gelatin, it was tested for use on the acid extracts from emulsions. The plates were extracted three times with 0.005 N H_2SO_4 and the combined extracts neutralized with Na_2CO_3 and evaporated to about 10 ml. One to three ml of sirupy phosphoric acid, 3 ml N $KMnO_4$ and 3 ml 0.5 N NaCN were rapidly added to each sample, and the flasks stoppered and left to stand for 20 minutes; no loss was caused by increasing the time to 30 minutes. After the oxidation was complete, the excess $KMnO_4$ and MnO_2 were eliminated by adding saturated $FeSO_4$ solution in slight excess, followed by about 1 g solid KI. After a minute the liberated iodine was titrated with 0.001 N $Na_2S_2O_3$ solution with starch as indicator.

It seems worth reminding the chemist who has not previously used the Lang method that the final reaction is as follows:

$$\mathrm{BrCN} + 2\mathrm{H}^{\cdot} + 2\mathrm{I}^{-} = \mathrm{HCN} + 2\mathrm{I} + \mathrm{H}^{\cdot} + \mathrm{Br}^{-}$$

In the presence of organic matter, such as gelatin or gelatin extracts, we found it necessary to increase the amounts of $KMnO_4$ and NaCN and the time of oxidation as indicated, even though Mitchell and Rawling report satisfactory results with 1 ml N $KMnO_4$ and 0.5 ml of 0.5 N NaCN, the proportions recommended by Lang. Examples are given in Table 5. Results, were slightly low in all cases and unless there is a distinct excess of $KMnO_4$ at the end of the oxidation and sufficient cyanide to insure that the Br goes quantitatively to BrCN, the error is very serious.

Comparison of the Lang and electrometric titrations of extracts from plates is given in Table 6. Values obtained by the Lang method were in all but one case lower than those found by electrometric titration. Interfering material of unknown character apparently was responsible for a loss of over 20 per cent in the determination of bromide from the second emulsion by the Lang method. Results with the other emulsions may be described as tolerable for practical use.

TABLE 5.—*Determinations by Lang method of 10.0 ml of 0.00100 N* KBr *to which was added either 1 g gelatin, or acid extracts from 1 g gelatin*

(Calculated volume of 0.0011 N $Na_2S_2O_3$, 18.2 ml)

Added material	N $KMnO_4$	0.5 N NaCN	Time of oxidation	0.0011 N $Na_2S_2O_3$
	ml	*ml*	*Minutes*	*ml*
Gelatin	2.0	0.5	5	11.7
				12.4
	5.0	.5	5	8.0
			+	14.5
	5.0	5.0	5	15.1
			10	15.1
			15	16.5
			25	17.2
Extract	1.0	.5	5	10.8
			5+	11.1
	5.0	5.0	20	17.0
			28	17.6
			35	17.3
			40	17.3

TABLE 6.—*Analysis of extracts from plates (with 0.005 N* H_2SO_4*) by electrometric titration and by Lang method*

Emulsion	$Br^-/AgBr \times 10^3$	
	Electrometric titration	Lang method
Commercial unsensitized No. 1	1.90, 1.93, 1.93	1.91, 2.01.
Commercial unsensitized No. 2	8.99, 8.90, 8.70, 8.79	6.8, 6.8.
Commercial panchromatic	0.96	0.84, 0.84.
Experimental 10-2	7.92, 7.99	7.2, 7.4.

In the case of emulsions before coating, we have found that the direct determination of bromide ion concentration by the silver-silver bromide electrode, using only the potential of the electrode in the emulsion without a titration, is quite satisfactory for control of washing, digesting, and coating conditions, and is very readily carried out if the apparatus is available. It is also possible to determine the amount of soluble bromide by acidifying the emulsion to pH 2 (approximate) and making an electrometric titration; the normality so obtained will not agree with the concentration of free bromide ions found by the electrode potential because of adsorption, and the combination of silver ions with gelatin. The accuracy of the titration may be illustrated by the figures for emulsion 10–2. This was washed thoroughly, then melted and mixed with KBr solution making it 0.00097 *N*. Electrometric titrations gave 0.000965, 0.00098, 0.00097 *N*. The concentration of the emulsion was by mistake not accurately determined but these titrations correspond to about 7.5×10^{-5} Br/AgBr, as compared to 7.9×10^{-5} by extraction of the finished plates. (Table 6.)

Mitchel and Rawling's method for determination of bromide in the emulsion before coating is based on coagulation of the emulsion by magnesium sulphate and alcohol. The error resulting from the combination of silver ion with gelatin might be eliminated if the emulsion were sufficiently acid when coagulated, but we were unable to secure a satisfactory coagulation at pH 2. The electrometric methods only can be recommended for the liquid emulsion, on the basis of our experience.

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THE PHOTOGRAPHIC EMULSION: SENSITIZATION BY SODIUM SULPHITE

By Burt H. Carroll and Donald Hubbard

ABSTRACT

Sodium sulphite, in quantities sufficient to reduce a few tenths percent of the silver bromide of a photographic emulsion, may act as a powerful sensitizer only slightly inferior to the natural sensitizers in gelatin. It acts as such only after digestion with the emulsion, insuring that it has reacted with the silver bromide. The sensitivity nuclei thus formed are of metallic silver, in amounts similar to the silver sulphide nuclei of normal emulsions. The rate of change of sensitivity increases with increasing alkalinity and decreases with increasing bromide-ion concentration. Sulphite may be added to the emulsion before washing, sensitizing only on digestion after washing. There was no indication of panchromatic sensitization (Capstaff effect).

CONTENTS

I. INTRODUCTION

It has long been known that if pure silver bromide is precipitated from water solutions and subsequently suspended in gelatin, the resulting photographic emulsion is very insensitive. While there are difficulties connected with the emulsification under these conditions, it suggested that the grains of an emulsion may not be pure silver bromide (or bromide-iodide). Further evidence was supplied by Lüppo-Cramer's discovery[1] (1), later extended by Clark, (2), (3), (4), and others, that the sensitivity of ripened emulsions was greatly reduced by treatment with oxidizing agents, such as chromic acid, which do not attack silver bromide. Statistical studies of the sensitivity of individual grains and of the distribution of the development

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[1] Numbers in parentheses here and throughout the text refer to the list of references at the end of the paper.

centers on them (5) indicated that it is highly probable that the unexposed grains of an emulsion contain nuclei which are different from the rest of the grain, and a most important factor in sensitivity. Finally, Sheppard and his coworkers (6), (7) demonstrated the existence of materials which act as powerful sensitizers for emulsions when used under conditions which insure the formation of a trace of silver sulphide by reaction between silver bromide and the sensitizer.

The hypothesis naturally suggested by the desensitizing action of oxidizing agents was that traces of silver bromide had been reduced during the ripening process to silver. It has never been definitely proved or disproved that the nuclei of ripened emulsions contain metallic silver. Clark (8) attempted to distinguish between silver and silver sulphide by means of oxidizing agents of varying potential, without conclusive results. Weigert and Lühr (9) believed that they had proved by treatment with persulphate that the "Ursilber" (silver not combined with halogen) could not be silver sulphide, but this has since been found (10), (11) to be incorrect. On the other hand, Carroll and Hubbard (12) demonstrated that colloidal silver may, under special conditions, sensitize an emulsion, apparently by functioning as nuclei after adsorption to the grains. In this paper it is shown that sodium sulphite may have photographic-sensitizing action approaching that of allyl thiocarbamide, when it is added to emulsions under such conditions that it must reduce traces of the silver bromide to metal. The hypothesis that metallic silver may act as sensitivity nuclei, therefore, appears to be proved. Reduction of the silver bromide before exposure normally causes fog, exactly analogous to the fog produced by the formation of silver sulphide from inorganic sulphides. This turns out to be fresh proof of the fact that has become increasingly evident (14) lately, that the quantity of nonhalide silver in an emulsion is much less important than what we may call its quality for want of more definite knowledge. Sheppard (6), (15) has observed that all the sulphur, selenium, and tellurium sensitizing compounds specified by him form complexes with silver halides, and that no sensitization is produced by equivalent amounts of inorganic sulphides. Sodium sulphite is closely analogous. Difficultly soluble silver salts may be dissolved in sulphite solutions by formation of a complex ion, probably $Ag(SO_3)_2^-$, similar to that formed by thiosulphate or thiocarbamide. The mechanism of reduction in one case and sulphide formation in the other is probably the same. This will be discussed in a separate paper on the kinetics of these reactions.

One hypothesis which cannot be excluded on the present evidence is that the presence of both silver and silver sulphide is essential to sensitization. Sheppard and Punnett (16) have patented the use of reducing agents such as sodium "hydrosulphite" (but not sulphite) in combination with sensitizers giving silver sulphide, and Trivelli has elaborated a theory (17) of sensitivity and the latent image based on a compound nucleus. Under the conditions of the experiments to be described in this paper, silver should have been formed in proportions greater than silver sulphide, but no gelatin emulsions can be proved to be free from the latter. Some light might be thrown on this point by testing the sensitizing action of sulphite on emulsions made up in gum arabic known to be free from labile sulphur.

The addition of sulphite to photographic emulsions is by no means new; the novelty of our results depends on the conditions of its use.

The earliest references (13) are to the combined use of sulphite and ammonia, which caused so much reduction that a mirror was deposited on the walls of the vessel, with consequent fog. Valenta (18) digested Lippmann emulsions with 1g Na_2SO_3 to 300 g emulsion at 38°. The sulphite retarded growth of grain; plates ripened up to 30 minutes could be used for the Lippmann process, while without it, the grain grew enough to give duller colors. Emulsions which were 4° Warneke after 5 minutes digestion with the sulphite were 18° after 1 hour digestion. Lüppo-Cramer (19) reports that bromine absorbents such as sulphite may increase the sensitivity of Lippmann emulsions, but the evidence in the case of Valenta's work is that the sensitization was the result of reaction of the sulphite and silver bromide, since prolonged digestion was necessary for the full effect. This feature of Valenta's work has escaped notice, although the statement about the grain size has not; in the one recent reference (20) to the use of sulphite in an emulsion formula, Valenta's experiments are said to have inspired the idea of adding sulphite to produce fine grain and high contrast.

Collodial silver in emulsions has frequently been observed to cause spectral sensitization; this effect, which has recently been reviewed by Sheppard (22), is well established, while general sensitization by silver has remained a matter of conjecture. Silver sulphide is capable of producing both effects—general sensitization when materials such as allyl thiocarbamide are added to the emulsion before digestion, and spectral sensitization when plates are bathed in the same materials, or when silver bromide and colloidal silver sulphide are precipitated together to form the analogue of the photobromide. In this case, Sheppard has concluded that the spectral sensitization is caused by larger numbers of very fine silver-sulphide particles, while the general sensitization is caused by fewer and coarser nuclei. Similar results are to be expected with silver. The analogy is apparently complete, since we have obtained general sensitization by adding sulphite to the emulsion before digestion, while Capstaff and Bullock (21) found that some emulsions (Eastman Portrait film) acquired panchromatic sensitivity by bathing in solutions of sodium bisulphite and washing in dilute alkali. The alkali was necessary to the sensitization, while soluble bromide prevented it. It was accompanied by visible discoloration of the emulsion. All this evidence indicates that the silver halide of the emulsion was reduced by the sulphite, so that the sensitization may be attributed to colloidal silver.

Investigation of photographic emulsions at this bureau has been suspended for lack of funds. The experimental data here presented are admittedly incomplete in some respects, which we have attempted to indicate, but the results seem to be quite adequate to justify publication.

II. EXPERIMENTAL

1. THE REACTION BETWEEN SODIUM SULPHITE AND EXCESS SILVER BROMIDE

Data on the kinetics of the reduction of silver bromide by dilute solutions of sodium sulphite will be given in a separate communication. The reaction may be written $2\ AgBr+Na_2SO_3+H_2O=2\ Ag+2\ NaBr+H_2SO_4$. It is retarded by the products, hydrogen and bromide ions. Under the conditions of sensitization in the emulsion, which involve reduction of not over 0.01 percent of the silver bromide, the change in concentration of these ions produced by the reaction itself is negligible.

While nothing was found in the literature to indicate that there might be side reactions, the known tendency of solutions of sulphur dioxide to form thiosulphuric and polythionic acids made it essential to test the products of the reaction for silver sulphide. Silver bromide or chloride was boiled with sodium sulphite solution, the former being in excess. The solid reaction products were oxidized with concentrated nitric acid. No sulphate was found after this treatment, although it would have been determined if as little as 0.1 percent of the silver reacting had gone to sulphide.

As the tendency for rearrangement of sulphite solutions is greatest at the boiling point, these experiments should have been an adequate test and we may say that the sensitizing action of sodium sulphite on emulsions cannot be explained by formation of silver sulphide.

The sodium sulphite used in the experiments was a c.p. product of unusually high grade, assaying 99 percent Na_2SO_3 by iodine titration. It was tested for the presence of thiosulphates or polythionates by the sensitive azide method of Feigl (24) with completely negative results. Stock solutions, about tenth normal, were kept under hydrogen, maintaining their titer unchanged for over a week.

The hypothesis that the sulphite may act simply as a bromine absorbent is satisfactorily eliminated by the complete absence of any immediate effect on sensitivity. In two cases where marked sensitizing action was developed on subsequent digestion with the sulphite (emulsions 4-124 and 125, fig. 4), the emulsion directly after its addition was, within the limits of error, no different from the controls. Using the speed number $10/E_m$ (for 6-minute development) in one case the control was 11, the batch with sulphite 10; in the other case the figures were 10 and 10.5. The sulphite-sensitized portions developed speeds of 1,400 and 300, on the same basis, on subsequent digestion.

2. PREPARATION OF EXPERIMENTAL EMULSIONS

The general methods of making experimental emulsions in this laboratory have been described in other papers. The formulas used in the experiments where sulphite was added after washing will be given in full at this point; some of the experiments with sulphite in the original mix of the emulsion will be described in a later section. Practically all the emulsions were of the neutral type. The sensitizing effect of sulphite was first tested by adding sodium sulphite or sulphur dioxide solutions to washed emulsions which had been made by the ammonia process, but no experiments have been made by adding sulphite to the original solutions of an ammonia-process emulsion. It is probable that sensitization could be produced in this way, but the sulphite would be rapidly oxidized by the air under these conditions and difficulty in reproducing results is to be anticipated.

All the emulsions were washed by the conventional method of shredding the set jelly and extracting with cold water. Except for a few otherwise noted, they were washed in changes of distilled water plus 1¼ g $MgSO_4 \cdot 7H_2O$ per liter, using the apparatus described in a recent note (25). This has been improved by the addition of a stirring device. A cam rotating about three times a minute, slowly lifts the nickel-gauze basket containing the emulsion 4 cm, then drops it suddenly through the water. This has more than doubled the rate of washing; there is very little loss of emulsion since the noodles are not scraped against the wire gauze as by rotary stirring.

The formula most used has already been described under the designation of "C" in a previous paper (27); it will be referred to as C-1 in this case. The solutions are:

NH_4Br (0.429 g equivalent)	42.0 g	$AgNO_3$ (0.353 g equivalent)	60.0 g
KI (0.0139 g equivalent)	2.30 g	Water	450 ml
Gelatin	20 g		
Water	350 ml		

With both solutions at 65° C., the silver was run into the bromide solution in a fine stream with rapid mechanical stirring in 25 ± 2 minutes. Directly after this, 80 g of gelatin, previously swelled in cold water and drained, was added in small amounts; it was completely dissolved in 8 to 10 minutes and the emulsion was then chilled rapidly. It was usually allowed to set over night before shredding and washing; even with active gelatin the ripening during this period is negligible. After washing, it was digested, this time at 55° C., and known bromide- and hydrogen-ion concentrations. At appropriate intervals, samples were taken out and test plates coated. Results with this formula, using deactivated gelatin and sensitization by allyl thiocarbamide added before digestion are recorded in figure 3.

A modification of the formula, which will be known as C-2, may be used for higher speeds with somewhat lower contrast.

NH_4Br (0.565 g equivalent)	55.3 g	$AgNO_3$ (0.47 g equivalent)	80.0 g
KI (0.0234 g equivalent)	3.90 g	Water	600 ml
Gelatin	21 g		
Water	350 ml		

In this case, the AgI has been raised to 5 mol percent. The concentration of the bromide solution has been raised in order to maintain the solubility of the silver halide and thus the grain size. The solutions were mixed in 33 ± 2 minutes at 65° C. After mixing, 110 g swelled gelatin was added in about 10 minutes and the emulsion chilled. Washing and digestion were carried out as for C-1.

One of the problems connected with any experiments on sensitizing compounds lies in the control emulsions. It is, as far as we know, impossible to prepare a gelatin which is truly inert photographically. Digestion after washing, at relatively low bromide-ion concentrations and pH of 6 or over, is apparently the most severe test of inertness; special gelatins stated by their manufacturer to be inert under other conditions were found to be quite active during digestion. As stated in a previous paper (12) some samples of gelatin can be very considerably deactivated by digestion with ammonia followed by thorough washing. About half the emulsions were made with a deactivated gelatin of this type which will be designated as "gelatin 1." "Gelatin 2", of about the same activity as the previous lot, was prepared from a batch of Nelson no. 2 gelatin. This was extracted first with dilute sulphuric acid, the pH of the gelatin being lowered to about 3, then washed thoroughly in tap water, coming out approximately isoelectric. It was then extracted with dilute ammonia, and washed again; the final pH was about 7. The control emulsions with these gelatins are recorded in figures 3 and 8.

3. SENSITOMETRY

The experimental plates were tested by the standard methods of this bureau: Nonintermittent time-scale exposure at an intensity of 1 meter candle of sunlight quality, brush development in pyrogallol without bromide for 3, 6, and 12 minutes at 20° C. and measurement of densities in diffuse illumination. The sector wheel used in this laboratory is of the conventional Hurter and Driffield pattern with 9 steps in ratio of 2. For all tests reported in this paper, 2 exposures were made, differing by 0.09 to 0.15 on the log E scale, so that 18 points on the characteristic curve were obtained. Use of the pyrogallol developer has been continued for comparison with earlier work. Some of the emulsions were also developed with the standard p-aminophenol formula (28) and with the metol-hydroquinone formula tentatively recommended by Davis and Neeland (29). As far as could be determined, the results are parallel with any of these developers; there is no indication that the sulphite sensitization introduces any peculiarities of development.

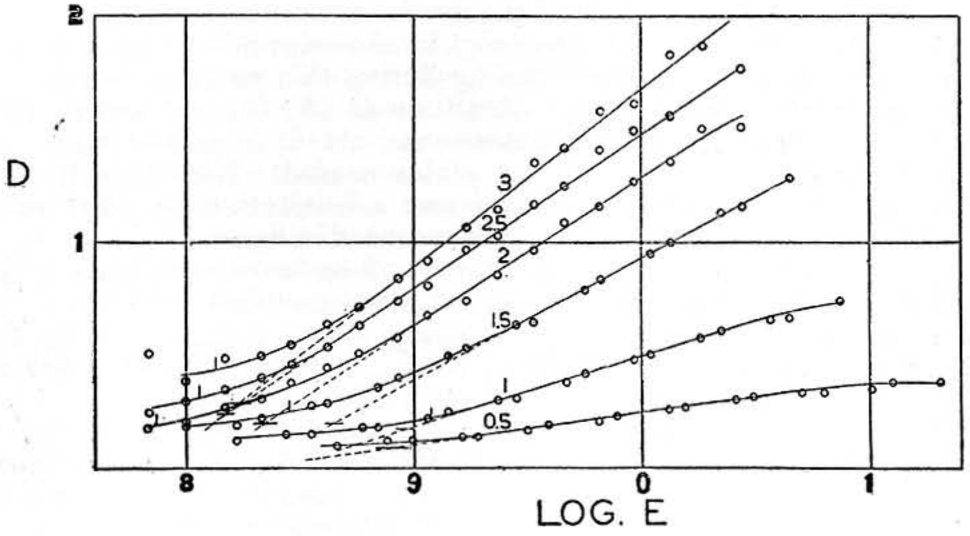

FIGURE 1.—*Characteristic curves for 6-minute development of emulsion 4-178 after digestion in vacuum with sodium sulphite for ½, 1, 1½, 2, 2½, and 3 hours.*

C-2 emulsion formula made with gelatin 2, digested with 1.7 mg sodium sulphite per g silver bromide at 55°, pH 7.4 [Br^-] 5×10^{-6}. This amount of sulphite corresponds to a ratio of 6×10^{-3} in terms of chemica equivalents.

Representation of the results without resorting to an undesirable use of tables gives the usual difficulties. The change in sensitivity on digestion with sulphite is such that the shape of the characteristic curve is altered, with changes in speed, contrast, and relative length of "toe", very much like the corresponding results on digestion of a normal emulsion (27). The type of change is illustrated by the characteristic curves plotted in figure 1 and the corresponding numerical values in table 1. After comparing different methods of plotting the results, it was decided to use the value of $10/E_m$ (where E_m is the exposure corresponding to the "minimum useful gradient" of 0.2) for 6-minute development as the best approximation to a single index of sensitivity. The characteristic curves of either type of emulsion have satisfactory straight-line portions and it would be possible in most cases to give the data in the form of $10/i$ at a constant γ. However, this would exclude a number of batches in the early stages of digestion, and would give little improvement in the accuracy of representation of the individual points. Our conclusions are, of course, in all cases based on comparison of the complete characteristic curves, and not merely on the numbers plotted in our figures.

TABLE 1.—*Sensitometric data for emulsion 4-178 at varying time of digestion with sodium sulphite; cf. figure 1, characteristic curves at 6-minute development, and figure 6, speed ($10/E_m$) vs. digestion time*

Digestion time, hours	Speed						γ			Fog		
	$10/E_m$			$10/i$								
	3	6	12	3	6	12	3	6	12	3	6	12
0.5	------	------	25	87	100	72	0.12	0.15	0.27	0.00	0.02	0.08
1.0	87	87	150	170	220	140	.24	.30	.65	.02	.03	.11
1.5	175	400	590	310	345	325	.37	.53	.77	.03	.05	.13
2.0	320	1,300	1,250	470	590	525	.44	.64	.95	.05	.07	.13
2.5	600	1,300	1,380	740	790	760	.42	.67	1.00	.08	.13	.18
3.0	460	1,000	1,400	560	580	490	.50	.82	1.26	.12	.21	.29

4. SPECTRAL SENSITIVITY OF SULPHITE-SENSITIZED EMULSIONS

No change in relative spectral sensitivity on sensitizing with sulphite has been evident in any case, but in view of the nature of the sensitizing produced by bathing in bisulphite solutions (the Capstaff effect) it was advisable to make a careful determination of this feature of the process. The effect to be anticipated is an extension of the natural sensitivity to the longer wave lengths. In order to detect this, exposures were made with a glass prism spectograph using a gas-filled incandescent lamp as light source. The instrument which was used is quite free from stray light, but in order to reduce both this difficulty and the spreading of the image by scattering of light within the emulsion itself, a Wratten "minus blue" filter was placed over the slit.[2] The plates were brush developed to insure uniformity. The plates which were compared were taken from two emulsions made by the C-2 formula under conditions which were identical within the limits of control. Having 5 percent AgI, the sensitivity extended into the longer wave lengths relatively far for emulsions containing no dye (30). Figure 2 gives curves derived from exposures of a control (unsensitized) plate and two plates sensitized with sulphite and allyl thiocarbamide, respectively. All three were developed to a γ of 0.50. Similar results were obtained in other experiments.

It is evident that, by sufficiently accurate choice of exposure, it would be possible to have close coincidence of the density-wave length curves for the batches sensitized with sulphite and thiocarbamide, but that the control emulsion shows a distinctly more abrupt decrease of density with increasing wave length. This indicates that either type of sensitivity nucleus causes a very slight extension of spectral sensitivity. Marked panchromatic sensitization such as the Capstaff effect is obviously not characteristic of sensitization by sulphite under all conditions. As all our experimental emul-

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[2] This particular filter had a transmission of 12.5 percent at 5,000 A and 1.5 percent at 4,900.

sions have been given a preliminary test exposure behind an Eder-Hecht wedge with its filter strips, any marked spectral sensitization would have been detected; none occurred.

Limited data are available on another question involving spectral sensitivity—the interrelation of sensitization by sulphite and by dyes. Sulphite, when added to the emulsion just before coating, may (31) have an appreciable hypersensitizing effect on the dye, the sensitivity to the longer wave lengths being selectively increased without a corresponding increase in the sensitivity to the blue. This is, however, distinct from the case of an emulsion which has been digested with sulphite so as to produce an increase in sensitivity independent of the action of dyes, then made color sensitive by further treatment with a dye. In such cases, the relative spectral sensitivity conferred by the dye appeared to be normal. In the most complete test of this feature of sulphite sensitization, sulphite was added to the emulsion after washing in the ratio of 2.5 g equivalents to 1,000 of silver bromide. Samples were coated directly after this and after two periods of digestion, each was sensitized with the same amount of pinacyanol. The resulting plates were tested for sensitivity to red and blue light by sensitometer exposures through Wratten A and C filters. Comparing the resulting speed numbers,[3] the ratio A/C was 3.1, 4.7, and 4.7 for the samples digested 0, 1, and 2 hours, respectively; the values for the undigested sample are the least reliable because of its low contrast. As the ratio remained approximately constant for a change in total sensitivity of 8 to 1, the evidence is that the formation of silver nuclei by sulphite sensitization is quite analogous to the action of allyl thiocarbamide in its effect on sensitization by dyes (6) (32).

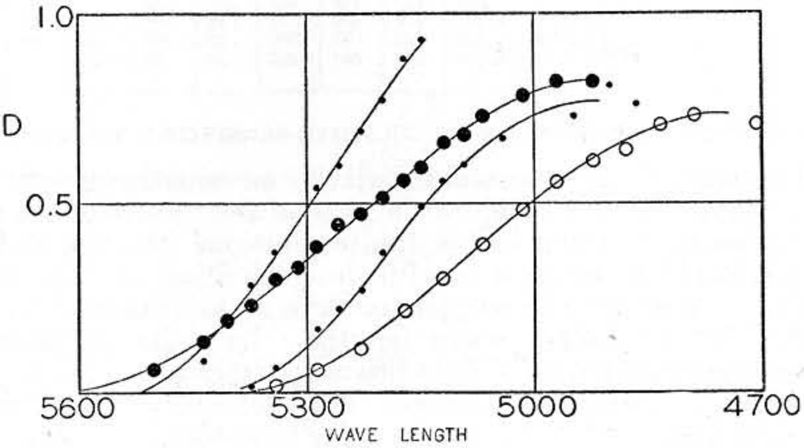

FIGURE 2.—*Densities of plates made by C-2 formula, exposed in prism spectrograph through minus blue filter, and developed to gamma of 0.5.*

● = Unsensitized control, ⬤ = sulphite-sensitized batch, ○ = allyl thiocarbamide-sensitized batch. General fog density subtracted from all image densities

The sulphite might have been expected to interfere with sensitization by reducing and decolorizing the dye. Apparently the dye is protected by its adsorption on the silver bromide, since sulphite in slightly larger quantities may even have an appreciable hypersensitizing action (31, table 8). The emulsion ripened with sulphite and

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[3] These values are arbitrary, since they are not corrected for energy distribution of the source and transmission of the filters. Comparison was made at the constant development time of 6 minutes for each plate, since the digested and undigested samples could not be compared at the same value of gamma.

sensitized with pinacyanol, and that to which sulphite was added just before coating for the tests of hypersensitizing action, were tested again (with the Eder-Hecht wedge) after 9 months' storage. There was no evident change in relative spectral sensitivity in any case, indicating that the sulphite had not reduced the dye on storage. The white-light sensitivity had increased or decreased in some cases, depending on the degree of ripening of the emulsion.

5. THE EFFECT OF CONCENTRATION OF SENSITIZER

Other conditions being constant, the rate of after-ripening would be expected to increase continuously with the sulphite concentration, and we have found this to be the case within the limits of concentration which were tested. The sensitivity, however, passes through a maximum on continued after-ripening under any conditions, and the value of this maximum is not necessarily independent of sensitizer concentration. Sheppard (33) reported that the sensitivity passed through a maximum with increasing concentration of allyl thiocarbamide, the decrease in speed being much more than would be expected simply from the increase in fog. As the conditions of his experiments were not described, we present in figure 3 the results of a similar series under the same conditions as the experiments with sulphite shown in figure 4 (C-1 emulsion formula, gelatin 1, sensitizer added after washing) for comparison with the latter. The curves of figure 3 show a progressive increase in rate of after-ripening from the control to the batch with the largest sensitizer concentration. The maxi-

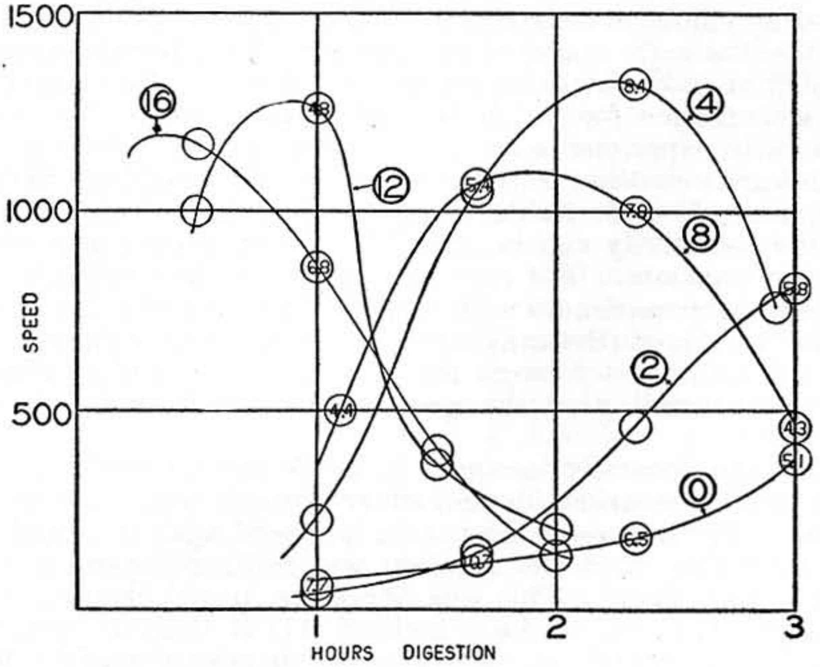

FIGURE 3.—Emulsions made by C-1 formula, gelatin 1, and sensitized by digestion with allyl thiocarbamide after washing.

The numbers of the curves indicate the ratio of allyl thiocarbamide to silver bromide in terms of chemical equivalents; for example, the figure 2 means that 2 atoms of silver per 100,000 could be converted from silver bromide to silver sulphide by the allyl thiocarbamide. Figures inside the circles representing experimental points give the nonhalide silver found in the emulsion by analysis after the digestion indicated by the location of the point; these numbers are also to be divided by 10^5 to give the ratio of the nonhalide silver to silver bromide in terms of chemical equivalents.

mum value of each curve is not much different, on this basis of representation, for the concentrations from 4 to 16×10^{-5} g equivalent of thiocarbamide per g equivalent of AgBr; the curve for 2×10^{-5} does not reach its maximum, but the value would evidently be lower. The apparent results are in this case unfortunately affected by the method of representation; using $10/i$ at a constant value of γ for the speed number instead of $10/E_m$, the maximum speed was obtained with a ratio of 8×10^{-5} and 1 hour 40 minutes digestion; the maximum for 4×10^{-5} was decreased with respect to the others, while that for 2×10^{-5} was increased. These data indicate that the sensitivity obtainable from a given emulsion is relatively independent of the amount of sensitizer over a moderate range; this in agreement with the general experience of emulsion makers that the potential sensitivity of an emulsion is largely determined by the conditions of emulsification—the early stages of the making where the composition and size-distribution of the grain are fixed. Obviously the range of sensitizer concentration for which this holds is limited. The amounts used in these experiments are in the optimum region for these conditions, but are well below the optimum ratio calculated from Sheppard's (33) figures. It is desirable to repeat that this relatively constant maximum sensitivity can be secured only by proper adjustment of digestion conditions. For constant digestion, the sensitivity passes through a sharp maximum with changing amount of sensitizer. For example, at 1 hour the maximum sensitivity was obtained with a ratio of 12×10^{-5}; at 2 hours the optimum ratio had changed to 4 or 8×10^{-5} depending on the speed number used, and at 3 hours it was 2×10^{-5}.

It has been generally assumed in the literature that the reaction between allyl thiocarbamide and silver bromide was complete during digestion. The nature of the curves for speed against digestion time makes it evident that the reaction was nowhere near complete at maximum sensitivity. This was, therefore, tested chemically, using the modified Weigert and Lühr method (11) of analysis for nonhalide silver. The results are given by the numbers in the circles locating the points of figure 3. Not all the plates were analyzed; those chosen correspond to the optimum digestion time for a given ratio (choosing the time giving the maximum $10/i$), plus all times for the control and 8×10^{-5} ratio. Analysis for these minute traces of material is subject to considerable error in the final determination, and still more in the separation of silver halide and nonhalide silver. The reliability has been tested on synthetic mixtures, however, with satisfactory results. The data indicate that the maximum sensitivity corresponded to the formation of nonhalide silver in amounts of the order of $5-8 \times 10^{-5}$ g equivalent per g equivalent of silver bromide, for all amounts of thiocarbamide. It is impossible to say how much of the nonhalide silver was silver sulphide and how much was metal. The values for the controls were disconcertingly high; similar results have been obtained with other insensitive emulsions (27). It seems probable that some of the nonhalide silver comes from the traces of colloidal silver present in the best commercial silver nitrate, or is formed during mixing from contact of the silver-nitrate solution with the gelatin, or both. This does not explain the existence of larger quantities in the control than in the batches to which thiocarbamide had been added. There are no reasons for suspecting these particular data, and they are given for what they are worth. The decrease in nonhalide silver on continued digestion has been observed before (27); oxidation of metallic silver or silver sulphide of colloidal dimensions is not improbable under the conditions of digestion, and would lead to a decrease in the silver remaining after fixation.

The data presented in figures 4, 5, and 6 show the expected increase in rate of after-ripening with increase in sulphite. For the C-1 emulsions, figure 4, the time required to reach a given sensitivity is, very roughly, inversely proportional to the sulphite-AgBr ratio. For the C-2 emulsions, figures 5 and 6, the change in rate of after-ripening is much less than the change in sulphite. It will be noted at once that the quantities of sulphite used are of the order of 20 to 50 times as great as the allyl thiocarbamide used for the same effect (both being expressed in terms of chemical equivalent). This could indicate either that the chemical reaction of silver bromide with sulphite is much slower than the corresponding reaction with allylthiocarbamide, or that larger amounts of silver are necessary to produce the same photographic effect as a given amount of silver sulphide. Our data on the kinetics of the reactions show conclusively that the reaction with sulphite is the slower. This is confirmed by analyses of the emulsions. Nonhalide silver, determined by the modified Weigert and Lühr method, is again indicated by the numbers in the circles locating experimental points, in figures 5 and 6. These indicate that about 1 percent of the sulphite reacted with the silver bromide at the most (assuming that the nonhalide silver in the undigested portions was there before addition of the sulphite). If this is correct, silver is equivalent to a larger amount of silver sulphide[4] rather than a lesser one. For either sensitizer the optimum amount of nonhalide silver present as sensitivity nuclei in our emulsions is about 1 to 5×10^{-5}, expressed in terms of its atomic ratio to silver halide. This is toward the lower limit of Sheppard's estimate (14).

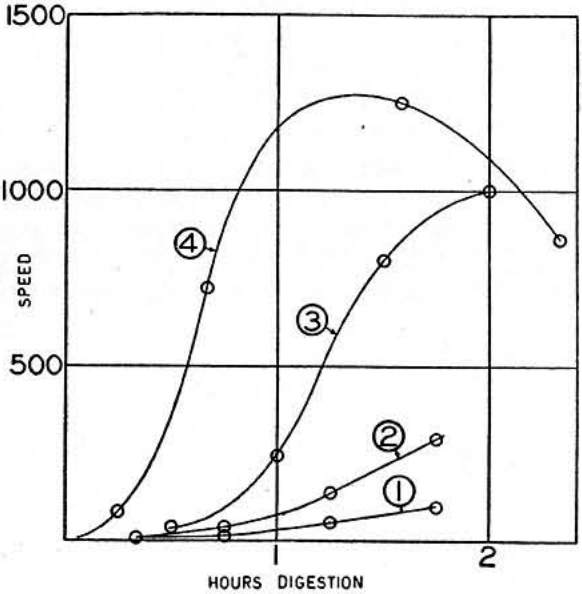

Figure 4—*Emulsions made by the C-1 formula, gelatin 1, and sensitized by digestion with sodium sulphite after washing, in vacuum at 55°,* pH *6.8* [*Br*$^-$] *3-5*$\times10^{-5}$.

Ratio of sodium sulphite to silver bromide in terms of chemical equivalents. Curve 1, 0; curve 2, 5×10^{-4}; curve 3, 1.3×10^{-3}; curve 4, 2.4×10^{-3}. That is, the sulphite added to the emulsion giving curve 4 was sufficient to reduce 2.4 atoms of silver per 1,000 from silver bromide to metallic silver.

The sensitivity of the emulsion passes through a maximum on continued digestion with sulphite, as in other methods of after-ripening. The height of the maximum is roughly constant over a moderate range

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[4] The nonhalide silver in the emulsions made with deactivated gelatin and sensitized with either allythiocarbamide or sodium sulphite was less than in emulsions made with active gelatin (27).

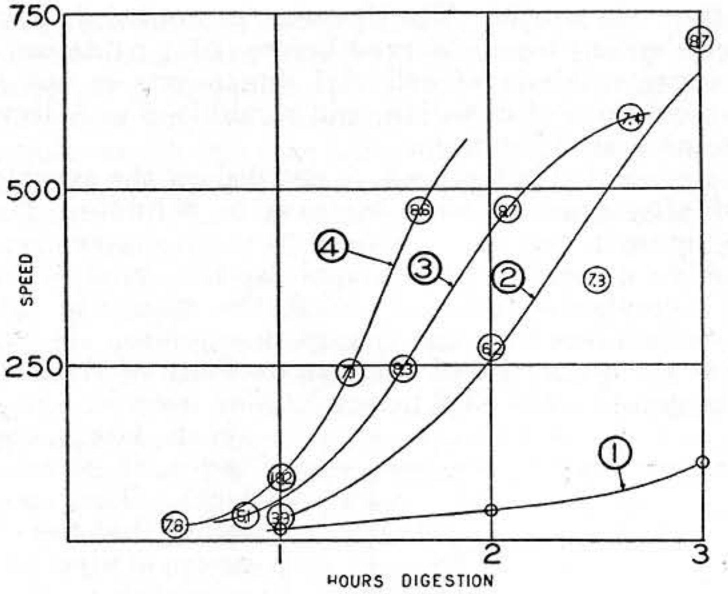

Figure 5.—*Emulsion made by the C-2 formula, gelatin 2, and sensitized by digestion with sodium sulphite after washing, in beakers at 55°,* pH *6.7 [Br⁻] 1.3×10⁻⁵.*

Curve 1, control emulsion digested under same conditions without sulphite. Ratio of sulphite to silver bromide: Curve 2, 1.9×10^{-3}; curve 3, 3.8×10^{-3}; curve 4, 7.6×10^{-3}. Numbers in the circles locating experimental points give the nonhalide silver found in the emulsion by analysis after the digestion indicated by the location of the point; these numbers are to be divided by 10^5 to give the ratio of the nonhalide silver to silver bromide in terms of chemical equivalents.

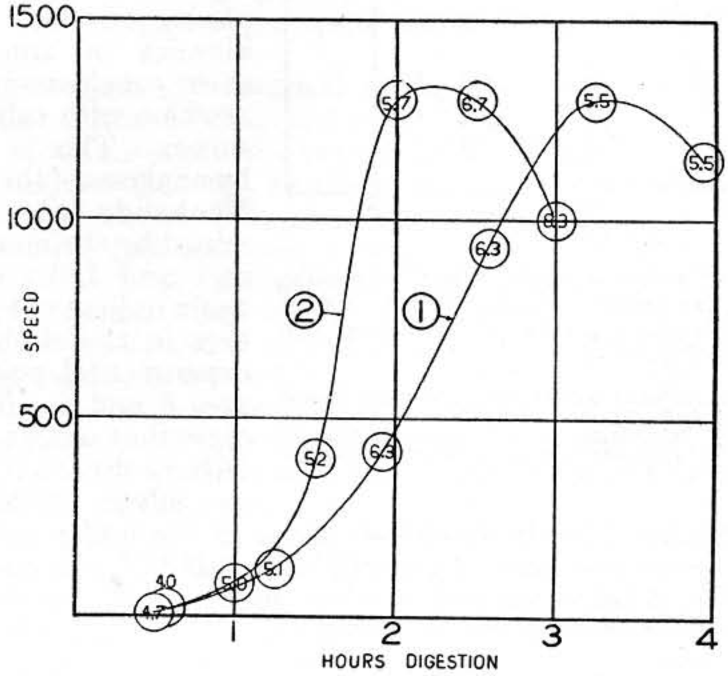

Figure 6.—*Emulsion made by the C-2 formula, gelatin 2, and sensitized by digestion with sodium sulphite after washing, in vacuum at 55°,* pH *7.4 [Br⁻] 5×10⁻⁵.*

Ratio of sulphite to silver bromide: Curve 1, 1.5×10^{-3}; curve 2, 6×10^{-3}. Numbers in the circles locating experimental points give the nonhalide silver found by analysis in the emulsion after the digestion indicated by the location of the point; these numbers are to be divided by 10^5 to give the ratio of the nonhalide silver to silver bromide in terms of chemical equivalents.

of conditions; ratios of sulphite to silver bromide of 1.5×10^{-3} or over appeared to differ mainly in the rate of change (figures 6 and 10 show well-defined maxima with different concentrations). Using the same formula, the maximum obtainable with sulphite was slightly lower than that with allyl thiocarbamide; the difference in the numerical values used for plotting the curves was very small, but it was larger on the basis of $10/i$. The results with these two essentially different sensitizers are still close enough to emphasize that the maximum sensitivity is determined more by the composition, structure, and size of the grains than by the subsequent ripening processes.

Results with the C-1 and C-2 formulas are parallel. A number of experiments were made with emulsions of pure silver bromide or with 1 percent AgI. Such emulsions have less capacity for sensitization, as judged from experience with after-ripening under normal conditions (27) and from the literature on emulsions. It is necessary to adjust the time and temperature of mixing in order to secure the same grain size and distribution in emulsions with varying iodide content (27), since the increased solubility of the silver halide with decreasing iodide results in an increase in grain size if the formula is otherwise unchanged. This was worked out quite well for the emulsions with 1 percent AgI; the few emulsions made with pure bromide had a coarser grain. The results proved difficult to reproduce and the experiments were not completed, but it was evident that under the same conditions the sensitization of these emulsions by sulphite was much less than for those with 4 to 5 percent AgI, and that the pure-bromide emulsions were the worse in this respect. Our earliest experiments with sulphite happened to be with pure-bromide emulsions made by the ammonia process. In these, increases in speed of 50 percent over the control were obtained; comparative experiments with allyl thiocarbamide gave the same results.

Oxidation of the sulphite by air during digestion is a complication of the ripening process. Our emulsions are normally digested in open beakers with stirring to prevent settling; the exposed surface is large enough so that the liquid may be expected to be saturated with air. The effect of the aerial oxidation is apparently less than would be expected, most probably because adsorption of the sulphite to silver bromide protects it. Comparative results of digestion with and without exclusion of air are given in figure 7. Digestion in vacuum was accomplished by pouring the freshly melted emulsion into a balloon flask provided with a special low-sulphur stopper [5] through which was run a stopcock. The flask was evacuated repeatedly, usually with small additions of alcohol, until the froth was broken and the warmed emulsion boiled vigorously under the reduced pressure. The sulphite solution was then introduced through the stopcock without breaking the vacuum. The samples for coating were removed by inverting the flask over a bottle with a 2-hole stopper, through which the stopcock passed tightly, evacuating the bottle and opening the stopcock when the pressure was below the vapor pressure in the flask. The flask was shaken violently before taking a sample, or every half hour if the sampling was less frequent; settling was negligible. Comparing curve 1 with curve 2, and curve 3 with curve

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[5] We are indebted to the rubber section of this bureau for making these stoppers; comparison of control batches digested in flasks fitted with them with those digested in the usual way demonstrated that they did not cause fog or sensitization.

4, the indications are that the loss of sulphite by oxidation was relatively small. The rate of after-ripening in vacuum was definitely faster in curve 4 than in curve 3; in this emulsion 4-127, the concentration of sulphite was less than in 4-124, curves 1 and 2, so that the effect of oxidation might be larger. Curves 1 and 2 might legitimately be drawn in practical coincidence, although the form chosen for curve 2 is the most probable considering its points alone. Later experiments were generally made in vacuum, although in some cases, which are indicated, the open beakers were used for convenience. It was later decided to make experiments with more careful exclusion of oxygen. In these, the same apparatus was used as for the vacuum digestion, but the flask was repeatedly evacuated and flushed out with nitrogen or hydrogen. Digestion under hydrogen was found to cause heavy fog, accompanied by an increased rate of after-ripening in the early stages of the process. It was at first thought that this indicated extensive oxidation of the sulphite even in the vacuum digestion, but direct comparison with nitrogen proved that the fog came from the hydrogen.[6] It is possible that the colloidal silver formed by the sulphite catalyzed further reduction of the silver bromide by the hydrogen. Curves 5 and 6 compare the digestion of C-2 emulsions in vacuum and nitrogen; the other halves of these emulsions were digested under hydrogen. The results indicate a considerable oxidation of the sulphite in the vacuum run, but are less reliable because curves 5 and 6 are for different emulsions.

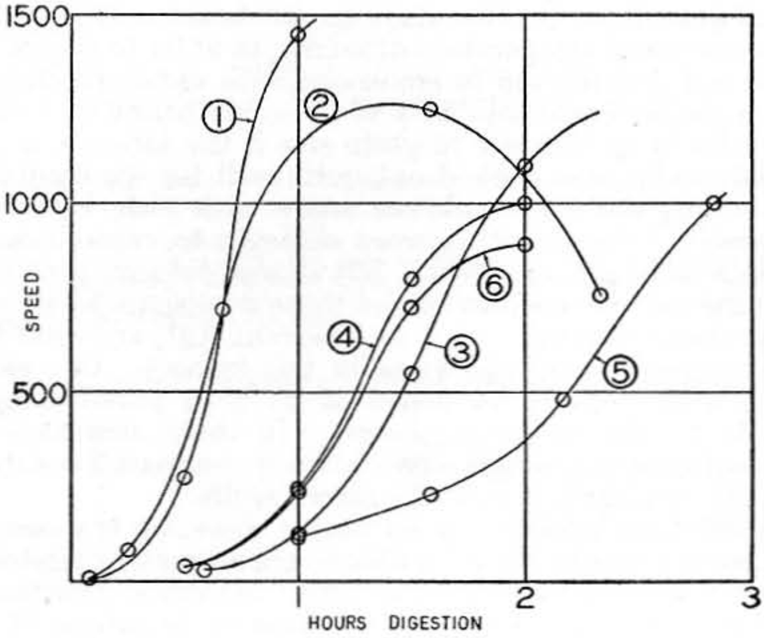

Figure 7.—*Comparison of sensitization of emulsions digested with sulphite after washing with and without free access of air.*

Curves 1 and 2, emulsion 4-124, C-1 formula, gelatin 1; digested at 55° pH 6.8 [Br$^-$] 5.6×10^{-5}, sulphite-silver bromide ratio 2.4×10^{-3}; curve 1 in beaker, curve 2 in evacuated flask. Curves 3 and 4, emulsion 4-127, C-1 formula, gelatin 1; digested at 55°, pH 6.7, [Br$^-$] 2.9×10^{-5}, sulphite-silver bromide ratio 1.3×10^{-3}; curve 3 in beaker, curve 4 in evacuated flask. Curve 5, emulsion 4-180, C-1 formula, gelatin 2; digested at 55°, pH 6.5 [Br$^-$] 2.6×10^{-5}, sulphite-silver bromide ratio 1.5×10^{-3} in evacuated flask. Curve 6, emulsion 4-186; conditions identical with 4-180 except that flask was filled with nitrogen.

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[6] Both gases were freed from oxygen by passing slowly through a spiral wash bottle filled with fresh alkaline pyrogallol.

6. FOG AND STABILITY OF SULPHITE-SENSITIZED EMULSIONS

Fog densities corresponding to the maximum sensitivities shown in the figures were from 0.06 to 0.13 corrected for the density of the support. The fog densities of emulsions sensitized with allyl thiocarbamide to the same range of sensitivity fell within the same range; using active gelatins, the values were about the same for the best samples. It is a distinct practical advantage for the sulphite that the effect of concentration is not so critical as with other sensitizers. For example, the longest time of digestion of emulsion 4-178 with the higher concentration, 6×10^{-3}, was ⅓ more than the optimum, and the decrease in sensitivity was about ¼; the corresponding fog was only 0.21. Under corresponding conditions with thiocarbamide or active gelatin, the fog has usually been 0.3 to 0.4.

Adding the amounts necessary to give a reasonable digestion time, only a small percentage of the sulphite is utilized, so that it was feared that the plates would fog rapidly on storage. This has not been the case; the stability has been rather better than normal on the plates which have been tested. The tests were made after 1 year storage, repeating the Eder-Hecht wedge exposure used for the preliminary test, with tank development in pyro giving fog about the same as 6-minute brush development. Fog densities after 1 year for the plates corresponding to the maximum speeds on the curves are as follows: Figure 4, curve 3, fog 0.21; figure 4, curve 4, fog 0.18; figure 7, curve 1, fog 0.14; figure 10, curve 4, fog 0.27. Speed was in all cases constant as closely as could be determined by Eder-Hecht exposures. These are satisfactory values after 1 year in the climate of Washington. In all 4 cases cited, the emulsion had been given a thorough washing, digested, and coated without addition of soluble bromide, the bromide-ion concentration being 2 to $3 \times 10^{-5} N$. For practical use, bromide would have been added after digestion in the ratio of about 3 KBr:1,000 AgBr, raising the bromide-ion concentration to 5 to 8×10^{-4} N; this would avoid the edge fog which was obvious for a few mm from uncut edges of the plates, as well as increasing the time of stability. The unexpectedly high stability is probably explained by oxidation of the sulphite by air during drying which eliminates the excess sensitizer. Analytical data in proof of this have not been obtained, as time was not available to attempt a test of such obvious difficulty.

7. HYDROGEN-ION CONCENTRATION

The rate of after-ripening with sulphite is less sensitive to hydrogen-ion concentration than the corresponding process in active gelatin; the data in figure 8 illustrating the variation with pH may be compared with the corresponding figures 2 and 3 of B.S. Research Paper No. 430. Control batches for each value of pH have been included in figure 8, as the activity of treated gelatins has been found to be liable to be highly dependent on this variable. The data on sulphite sensitization which are illustrated were obtained by vacuum digestion. Two sets of experiments by digestion in beakers gave results less dependent on pH and falling in no regular order, although in both cases the batch at 6.7 gave a minimum rate. The most probable explanation of this behavior lies in competition for the sulphite between the silver bromide and the oxygen of the air; oxidation by the air being highly dependent on hydrogen-ion concentration, the reaction between silver bromide and sulphite might actually assume a minimum at some pH. Our data show no indication of systematic difference in the maximum sensitivity obtainable at different hydrogen-ion concentrations within the range tested.

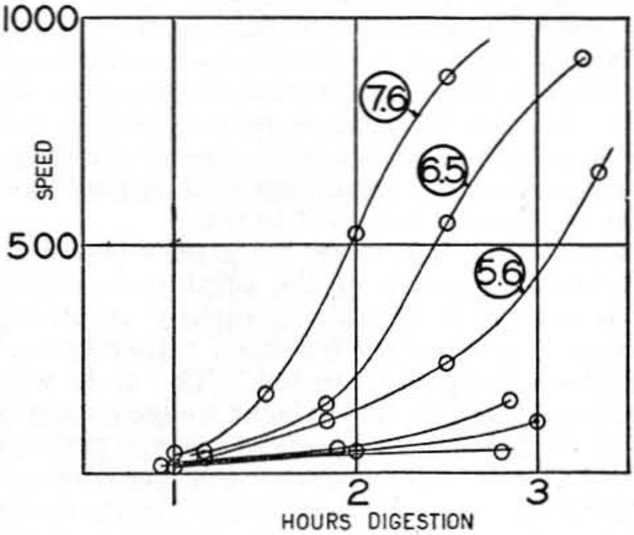

Figure 8.—*Comparison of sensitization of emulsion digested with sodium sulphite in vacuum after washing, at varying* pH.

Emulsion 4-177, C-2 formula, gelatin 2; [Br⁻] as washed 4.6×10^{-5}. Numbers on the curves indicate pH of digestion. The lower curves are for digestion of a control emulsion without sulphite at the same values of pH.

8. BROMIDE-ION CONCENTRATION

After-ripening with active gelatin or with pure sensitizers such as allyl thiocarbamide is retarded by increase in bromide-ion concentration, but the sensitivity reaches its maximum value by digestion at a bromide-ion concentration which may be as high as $1\times10^{-3}\,N$ (27). Since bromide ions are also a product of the ripening with sulphite, similar relations may be expected to hold. Data obtained with C-2 emulsions are presented in figure 9, those from C-1 emulsions in figure 10. The reaction rate is more sensitive to bromide-ion concentration than to hydrogen-ion concentration, but the factor is less than 2 as far as it can be estimated from the time required to reach a given sensitivity. Neither approaches the effect of the concentration of sulphite; the time for a given effect was not more than doubled when the bromide-ion concentration was multiplied by 10. The effect of bromide-ion concentration on the sulphite sensitization is at least as large as on the corresponding process with allyl thiocarbamide, and is much greater than when sodium thiosulphate or active gelatin is used (27). Contrary to the case of normal after-ripening (with active gelatin), the maximum sensitivity is not improved by addition of soluble bromide to a thoroughly washed emulsion before digestion; with sulphite the more rapid after-ripening led to results which were always as good and in some cases better. This may possibly be explained by the oxidation of sulphite by air from leakage into the flask with consequent serious loss before the end of a long digestion, but it seems more likely to be characteristic of the process. As bromide may be added after digestion as a preservative, it is obviously better practice to digest the emulsion after thorough washing ([Br$^-$] around 2×10^{-5}) and add the preservative before coating.

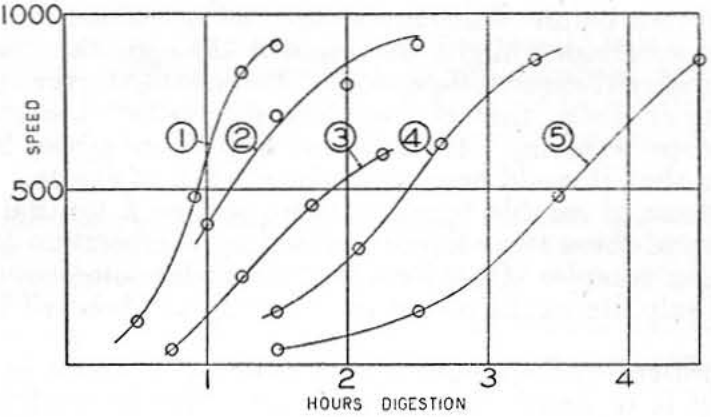

FIGURE 9.—*Comparison of sensitization of emulsions digested with sodium sulphite after washing in vacuum at varying bromide-ion concentrations.*

Curves 1 and 3, emulsion 4-194, C-2 formula, gelatin 2 pH 6.7, sulphite-silver bromide ratio 3.0×10^{-3}. curves 2, 4, and 5, emulsion 4-179; digested under same conditions except pH 7.7. Bromide-ion concentrations [Br$^-$]: Curve 1, 3.1×10^{-6}; curve 2, 1.0×10^{-5}; curve 3, 2.6×10^{-5}; curve 4, 1.2×10^{-4}; curve 5, 4.8×10^{-4}.

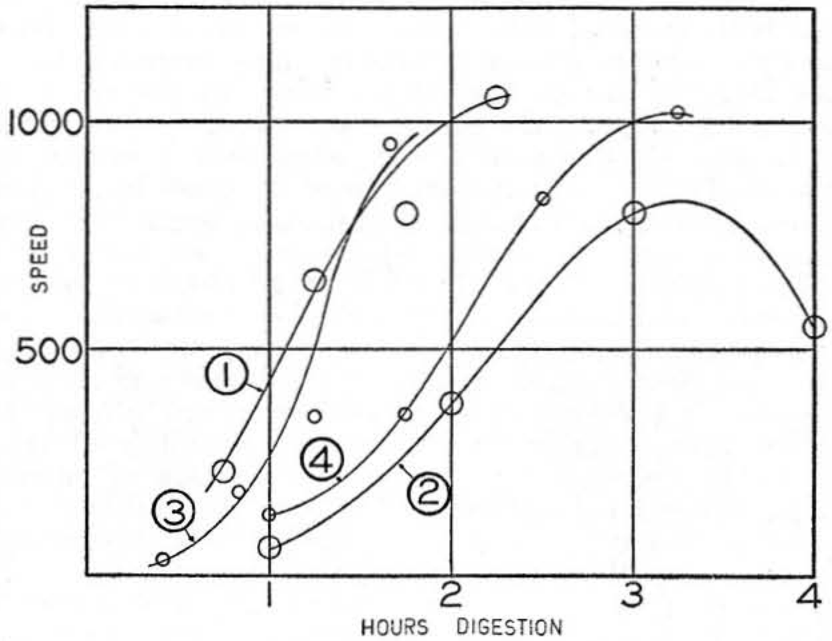

FIGURE 10.—*Comparison of sensitization of emulsions digested with sodium sulphite after washing at varying bromide-ion concentrations.*

Emulsion 4-140, C-1 formula, gelatin 1; digested in beakers at 55°, pH 6.6, sulphite-silver bromide ratio 3×10^{-3}; curve 1, [Br$^-$] 3.1×10^{-5}, curve 2, 9.4×10^{-4}. Emulsion 4-134, C-1 formula, gelatin 1; digested in evacuated flasks at 55°, pH 6.5, sulphite-silver bromide ratio 1.3×10^{-3}; curve 3 [Br$^-$] 1.5×10^{-4}, curve 4, 2.4×10^{-5}.

9. EMULSIONS WITH SULPHITE ADDED BEFORE WASHING

Most of the experiments were made by the additions of sulphite to the washed emulsion, since this permitted control of the sulphite concentration and made the observation of its effect simpler than when change in grain size or other processes may be taking place. For practical use, it might be preferred to add the sulphite to the emulsion before washing (although on washing with hard water there might be difficulty with precipitation of calcium sulphite). There would then be the alternatives that the silver nuclei might be formed during the ripening process before washing, or that adsorbed sulphite (like adsorbed thiocarbamide) might be retained through the washing and function during subsequent digestion. There is the further possibility, independent of these, that the sulphite may affect the grain size if present before washing. Its solvent action on silver bromide is sufficient so that it could accelerate the growth of grains. However, in the presence of soluble bromide there will be a mutual reduction in the action of these two solvents caused by competition to form the corresponding complex silver ions, so that under some conditions the addition of sulphite might retard the ripening as observed by Valenta (18).

In the presence of ammonia, reduction by sulphite is relatively rapid and it is reported (13) to cause fog. While conditions might be adjusted to avoid this, the limited number of experiments which we were able to make were all with neutral emulsions, appropriately modified from the type formulas given on page 747. In all but one case, the sulphite was added to the bromide solution before mixing. Photomicrographs of the grain of these emulsions were compared with those of other emulsions in which conditions were the same except for the presence of the sulphite; there was no evident difference in grain size or size distribution. In the one exception (emulsion 4-138, table 2), the sulphite was added directly after completing the mix and the emulsion digested with it for an hour at 65° before washing. Photomicrographs of the grain before and after this process showed little change in grain size, apparently less than from digestion with the same concentration of soluble bromide without the sulphite. The evidence from the characteristic curve—contrast, scale, and underexposure region—confirms that from the photomicrographs, since these characteristics are practically the same as in emulsions mixed without the sulphite and sensitized by other means. It had been expected that when sulphite was present in quantity during mixing, the increase in solubility of the silver bromide would decrease the contrast. The time of mixing was accordingly reduced for emulsion 4-134, but the contrast both for this and for 4-136 was very nearly the same as for emulsions made by the same formula without the sulphite.

There was no indication of reduction of the silver halide by the sulphite before washing in any case; portions of the emulsion coated without digestion were invariably of low sensitivity, practically indistinguishable from controls. In the case of emulsions 4-189 and 4-190, the excess of bromide over silver had been reduced so that the bromide-ion concentration was only 5.6×10^{-3} N after adding all the silver solution. During addition of the secondary gelatin before chilling, the emulsions were held at 65° C., pH 7.3 and the above bromide-ion concentration for 10 minutes, but the undigested emulsions were as insensitive as others with more bromide and less sulphite. It is probable that continued digestion under these conditions would have produced some sensitization. While we were unable to test this, there is little reason to expect that the results would be superior to those which we obtained by digestion of the emulsions after washing. In this case, the after-ripening is best explained by adsorbed sulphite left after washing. A less probable hypothesis, concerning which we have no evidence, is that some new sensitizing compound has been formed by digestion of the sulphite with the deactivated gelatin during mixing of the emulsion. The after-ripening was of the normal type, the results being very similar to those where sulphite was added to the emulsion after washing. The nature of the data is such that they must be tabulated, and for economy of space we present only the optimum results for each digestion.

TABLE 2.—*Emulsions with sodium sulphite added to bromide solution before mixing. Volumes of solutions as for C-1 or C-2 formulas. Mixed in 26–29 minutes at 65° except as otherwise stated; digested after washing at 55°*, pH *7.1±0.3*, $[Br^-]$ $2.5 \pm 1 \times 10^{-5}$

Emulsion number	Gelatin	Percent AgI	Percent excess NH_4Br	G equivalents Na_2SO_3, per g equivalent AgBr	Digestion conditions	Optimum digestion time, minutes		Characteristics at digestion time nearest optimum									
								Speed						γ			Fog
								10/E_m			10/1						
						Interpolated	Nearest experimental value	3	6	12	3	6	12	3	6	12	6
4-188	2	4	25	0.10	Air	95	90	330	770	920	320	370	315	0.57	0.90	1.33	0.05
4-189	2	4	2	.10	do	100	90	290	740	1,400	245	230	230	.61	.94	1.42	.10
4-193	2	5	25	.15	do	120	115	155	500	690	200	315	250	.46	.64	.95	.02
4-196[a]	2	5	25	.15	Vacuum	100	90	460	950	1,400	630	620	500	.41	.70	1.16	.09
4-190	2	4	2	.40	Air	35	30	315	------	1,150	260	260	390	.54	.82	1.19	.26
4-136	1	4	10	.50	do	35	30	730	1,380	1,500	630	490	415	.50	.90	1.29	.11
4-138	1	4	25	[b] 0	do	65	60	480	1,150	1,100	640	730	480	.40	.64	.95	.08
4-134[c]	1	4	10	.50	do	80	80	180	330	470	100	100	100	1.06	1.61	2.20	.09

[a] Mixed at 70° C. instead of 65°.

[b] No sulphite in mix; directly after mix added Na_2SO_3 in 0.50:1 ratio and digested 1 hour at 65° before adding secondary gelatin and chilling.

[c] Mixed in 14 instead of 26 minutes.

As would be expected, the rate of after-ripening increased with increasing amounts of sulphite (compare 189 with 190, and 188 with 136). The emulsions in which the excess bromide in the original mix had been reduced to its lowest value (189 and 190) had appreciably more fog than those with normal excess bromide; an increase in adsorption of the sulphite under these conditions is theoretically possible, but there is no evidence for it in the form of increased rate of after-ripening. The 2 emulsions with 5 percent AgI after-ripened slower than those with 4 percent, as is to be expected. Indications from the results with emulsions 4-193 and 4-196 are that still faster emulsions might have been obtained by increasing the amount of sulphite in the same basic formula.

Results with emulsions of this type were quite similar to those when the sulphite was added after washing. This process might be preferred for practical use. As already stated, the digestion could probably be eliminated by using a small excess of soluble bromide in the original solutions and ripening after mixing, but this is less likely to be satisfactory than the after-ripening.

This type of formula appears to have the practical disadvantage of less stability on storage. After 1 year, the fog was about 1.0

for emulsions 4-134 and 4-136, and 0.6 for 4-138. Data on the others are not available; the fog may be expected to be less in those with less sulphite. These values could undoubtedly be much reduced by adding bromide before coating.

The experiments completed were all made with deactivated gelatin in order to study as simple a system as practicable. The important practical question of the combination of sulphite with a gelatin having normal activity was not covered. A few data were obtained on the related question of the sulphite content of emulsion gelatins. Three gelatin samples which had recently been tested in the C-1 formula were analyzed for SO_2 by the method of Poetschke (34); this procedure, based on weighing $BaSO_4$ derived from oxidation of volatile material by iodine, should be free from positive errors caused by the presence of other compounds in gelatin. The results were, respectively, 0.11, 0.15, and 0.007 percent SO_2. Correlation between SO_2 content and photographic characteristics of gelatins obviously should not be attempted without a large number of samples, and might then be impossible without analysis for other variables with an accuracy not now available. In the C-1 formula, the above amounts would correspond to ratios of 10, 13, and 0.3×10^{-3} g equivalent of SO_2 to 1 of AgBr. In this formula, where all the gelatin is added before washing, such amounts of SO_2 would be negligible. If, however, gelatin were added after washing, as in many formulas, the ratio with the second of these gelatins might reach 4×10^{-3} under conditions which would make its effect quite appreciable. Whether it would be desirable or undesirable would obviously depend on conditions in the emulsion, as it might lead either to increased sensitivity or to the increase in fog and decreased sensitivity characteristic of excessive amounts of sensitizer. Sheppard (35) mentions sulphur dioxide as undesirable in photographic gelatins to which dyes are to be added, but makes no specific reference to any effect on the emulsion. Wentzel (36) and Wall (20) list it as an undesirable impurity, placing the limit at 0.01 percent and 0.1 percent, respectively, without giving reasons for this limitation. The lower limit is to be recommended on the grounds of reproducibility of results with the gelatin, but attention should be called to the possibility of sensitization by amounts which are to be found in emulsion gelatins.

10. EXPERIMENTS WITH OTHER REDUCING AGENTS

It is obvious that other reducing agents might be found which would satisfy the condition of forming a molecular compound or complex ion with silver salts. A low rate of reaction is probably a further requirement for sensitization. Experiments were made with only two other materials: hydrazine and sodium arsenite. These were added to portions of an emulsion in amounts sufficient to reduce 1 atom of silver per 1,000, and digested with it at 55°, pH 6.5, $[Br^-]$ 2×10^{-5}. The hydrazine produced neither sensitization nor fog in 2 hours. The sodium arsenite in the same time produced an increase over the control which was close to the limit of error.

III. CONCLUSIONS

The data presented in this paper appear to be adequate proof that metallic silver may function as sensitivity nuclei. Silver is very probably formed during digestion with active gelatin; if formed it may increase sensitivity and the results with sulphite indicate, but do not prove, that it does.

The analytical results must be used with some caution but they indicate that the quantity of the nonhalide silver is not satisfactorily related to its sensitizing effect and that, therefore, part of it fails to function as sensitivity nuclei. Chemically equivalent amounts of silver and silver sulphide appear to have roughly the same sensitizing effect. The evidence is not sufficient to decide whether the superior results obtainable with allyl thiocarbamide are to be ascribed to the formation of silver sulphide or to the mechanism of the reaction by which it is formed. Sulphites fall into the same class with the other nuclear sensitizers in that they form a molecular complex with silver salts. Further investigation of reducing agents as sensitizers is desirable to establish how general this rule may be.

The relatively high concentration of sulphite necessary to produce a given rate of reaction, and the marked effect of bromide-ion concentration on the rate, are both in accordance with the low reduction potential of the sulphite. The effect of hydrogen-ion concentration is of the right order of magnitude for any oxidation-reduction reaction.

While many of the emulsions sensitized with sulphite were of commercial quality, none were equal to the best obtainable by standard methods from the same type formulas. The experiments which have been made by no means exhaust the possibilities of improvement. In general, the best results were obtained by rapid after-ripening, with high pH and low bromide-ion concentration; as there was little tendency to cause fog, the digestion could be carried out in this way, and the emulsion then stabilized by addition of soluble bromide and possibly acid with little loss of sensitivity. The presence of sulphur dioxide in emulsion gelatins assumes a new importance since, under certain circumstances, it may cause sensitization as well as fog.

IV. ACKNOWLEDGMENTS

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KINETICS OF REACTION BETWEEN SILVER BROMIDE AND PHOTOGRAPHIC SENSITIZERS

By Burt H. Carroll and Donald Hubbard

ABSTRACT

The kinetics of the reactions of silver bromide with sensitizing materials have been studied for comparison with the process of photographic sensitization by the same compounds. Sodium sulphite, reacting with silver bromide to give metallic silver, and allyl thiocarbamide, reacting with it to give silver sulphide, were chosen. The reactions were followed by change in bromide ion concentration. Data on solubility and adsorption were obtained to assist in interpretation of the results. The reaction with allyl thiocarbamide is autocatalytic; under the conditions of the experiments it appears to take place by decomposition of dissolved material at the surface of the silver sulphide. The sulphite reaction is also autocatalytic, and it seems probable, on theoretical grounds, that this is an essential characterist of the sensitization process.

CONTENTS

I. INTRODUCTION

It is now generally conceded that gelatin suitable for making photographic emulsions contains traces of materials which have a specific sensitizing effect. All of those which have been isolated (1)[1] react with silver halides to form silver sulphide, and the numerous compounds which have been patented (2) for use as sensitizers of silver bromide-gelatine emulsions all have this characteristic or else form the analogous silver selenide or telluride. We have recently found (3)

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[1] Numbers in parentheses here and throughout the text refer to the references at the end of the paper.

that sodium sulphite is a sensitizer approaching allyl thiocarbamide in effectiveness. The product of its reaction with silver bromide is metallic silver, instead of silver sulphide. While no sensitizers which reduce silver halides to metal have been isolated from gelatin, it is probable that some silver is formed during the normal ripening process.

All these compounds almost certainly function by reacting with the silver halide of the emulsion, since they become effective only after digestion of the emulsion with the sensitizer under conditions favoring reaction between them. The silver sulphide or silver which is formed becomes the material of the sensitivity nuclei on the grains. It has been evident from the first discovery of the sensitizers, however, that the formation of silver sulphide or silver in the emulsion is not a sufficient condition for sensitization. It frequently causes only fog, as when silver sulphide is formed by addition of alkali sulphides (1) or when most reducing agents are used. Sheppard (1) pointed out that the compounds covered by his patents all have the common characteristic of forming molecular compounds with silver halides, and postulated that the silver sulphide must be formed by rearrangement of such compounds in order to act as a sensitivity nucleus. Sodium sulphite falls under this classification, since the well-known solubility of silver halides in a solution of sodium sulphite indicates the formation of a complex silver-sulphite ion.

We have studied the kinetics of the reactions between silver bromide and sensitizers with the two-fold purpose of correlating the results with the photographic data and of attempting to find whether a particular reaction mechanism is common to sensitizers. Experiments on this subject have been suspended for lack of funds with the investigation incomplete, but the results which have been obtained are sufficiently promising to warrant publication.

Two sensitizers have been used: sodium sulphite and allyl thiocarbamide. The experiments were carried on under conditions approaching those existing in the emulsion, using a large excess of silver bromide and a low concentration of sensitizer. The progress of the reaction was followed, in both cases, by the change in bromide-ion concentration of the solution. This was determined by the silver-silver bromide electrode, using the apparatus described in a previous communication (4). The method is rapid, convenient, and sensitive. The relative values of bromide-ion activity obtained during a run were correct to about 1 percent, this sensitivity being practically independent of the concentration. The presence of solvents for silver bromide, such as sodium sulphite, allyl thiocarbamide, or ammonia, does not interfere with the working of the electrode provided the solution is saturated with silver bromide. The least unsaturation causes serious error, but the conditions of the reactions, with a large amount of finely divided silver bromide in suspension, insured saturation, and it was found that the electrode responded rapidly enough to give reliable readings even during the progress of the reaction.

II. THE REACTION OF SILVER BROMIDE WITH SODIUM SULPHITE

Sodium sulphite apparently reacts with silver bromide according to the equation

$$2AgBr + Na_2SO_3 + H_2O = 2Ag + 2NaBr + H_2SO_4$$

The solid reaction product is silver, and contains no silver sulphide. All experiments were carried out with exclusion of oxygen by passing a current of nitrogen or hydrogen through the solution.[2] The apparatus was provided with three-way cocks on the inlet and outlet tubes so that sulphite could be introduced and samples removed without admitting air. Samples were caught in thin-walled weighing bottles packed in ice, and rapidly chilled to 30 C, the temperature of the thermostat used for electrode readings of bromide-ion concentrations; at this temperature the rate of reaction was negligible. All reactions were run in the dark room under a Wratten no. 0 safelight, although this precaution was apparently unnecessary.

The first series of reactions was run at 73.4 ± 0.2° C, in unbuffered solutions. All the suspensions contained 0.03 mol AgBr per liter, either without protection or in 1 percent gelatin or 2 percent gum-arabic solution. When unprotected silver bromide was used, it was precipitated and washed just before the reaction. The fresh material was considerably peptized by the sulphite, in the absence of other electrolytes. The results of this series are summarized in table 1. All the reactions were characterized by an induction period, followed by a constant rate of reaction. This constant rate persisted up to a bromide-ion concentration of about $6 \times 10^{-4}\,N$. The rate of reaction decreased slowly after this in the gelatin suspensions and more rapidly in the unprotected ones. The maximum rate given in the sixth column of the table was characteristic of the reaction over most of the period of a 6-hour run and has accordingly been given as the best measure of the reaction velocity. These rates of reaction are of the right order of magnitude to agree with the analytical data (3, figs. 5 and 6) on the extent of the reaction of sulphite with silver bromide during sensitizing.

Unless the constant rate is entirely the result of compensation changes, which is rather improbable for the range of conditions used, it indicates that the rate is relatively independent of bromide-ion concentration when the latter is low enough. The experiments in which bromide was added to the reaction mixture before the start of the reaction confirm this. Inspection of table 1 shows that in reactions with unprotected silver bromide and $0.010\,N\,Na_2SO_3$, the maximum rate was 0.48 for an initial $[Br^-]\ 7 \times 10^{-7}$ and 0.57 for an initial $[Br^-]\ 7.7 \times 10^{-5}$. In the presence of gelatin, with the same sulphite concentration, an increase in initial $[Br^-]$ from 4×10^{-6} to 3.8×10^{-4} decreased the rate only from 0.19 to 0.10. At $10^{-3}\,N$, however, reaction was practically stopped. This agrees with the photographic evidence (3), that ripening was very slow even at 65 C pH 7.3 and $0.15\,N\,Na_2SO_3$ when the bromide-ion concentration was $5.6 \times 10^{-3}\,N$.

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[2] A sulphite solution held in the apparatus for 4½ hours under the conditions of a reaction decreased in titre from 0.00095 to 0.00090 N in that time, indicating that the protection from air was adequate. A suspension of silver bromide in the (deactivated) gelatin was held under hydrogen at 73.40 C for 5½ hours; the reaction in the absence of sulphite increased the bromide-ion concentration only from 2.0×10^{-5} to $3.4 \times 10^{-5}N$.

The rate of reaction increased less rapidly than the concentration of sulphite, which is in agreement with the photographic results (3, figs. 4, 5, 6). The data on the effect of hydrogen-ion concentration are approximate only, but indicate that it was of the same order as its effect on photographic sensitization by sulphite (3, fig. 8). This is less than for after-ripening with active gelatin (5) and much less than for the thiocarbamide reaction (next section).

TABLE 1.—*Reaction of sodium sulphite with silver bromide at 73.4 C*

[The induction period is the time required to reach the maximum reaction rate]

Na_2SO_3 concn. *N*	Colloid	pH	[Br] ×10⁴ at start	Induction period	Maximum rate, milli-equivalents Br^- formed per hour per liter	Remarks
				Hours		
0.0102	None	9.0	0.007	1/4	0.38	
.0102	do	9.0	.007	1/4	.48	
.0105	do	9.0	.004	1/4	.47	Exposed to light.
.00089	do	8.7	.006	1/8	.15	
.0103	do	9.0	.77	1/4	.57	
.0102	do	9.0	9.4	>2	.0	
.0112	Gum arabic	8.5+	0.24	1/4	.24	
.0103	Gelatin	8.5	0.024	1 1/2	.17	
.0105	do	7.8	.037	1 3/4	.17	pH determined at end of reaction.
.0101	do	------	.045	3/4	.20	Made with different gelatin from others; portions of same emulsion; second portion exposed to light.
.0098	do	------	.040	3/4	.18	
.0030	do	8.0	.034	1 1/2	.091	
.0012	do	8.4	.31	1 1/2	.031	Emulsion incompletely washed.
.0101	do	6.8	.12	1 3/4	.13	pH determined at end of reaction.
.0102	do	6.2	.06	1 1/2	.11	Do.
.0099	do	8.6	3.8	2 1/4	.10	

The induction period of the reaction was lengthened by protective colloids. Gum arabic was less effective than half the amount of gelatin, which is in accordance with their relative ratings as protective colloids. At 73.4 C the colloids appeared to decrease the maximum rate of reaction; the reaction mixtures with and without colloids unfortunately were not otherwise identical, but the differences in bromide and hydrogen-ion concentrations do not appear sufficient to explain the differences in rate.

The existence of the induction period indicates that the reaction is autocatalytic, and therefore presumably takes place at the surface of the new solid phase. It should, then, be accelerated by adding silver. The data of table 1 show that exposure of the silver bromide to light was not sufficient to accelerate the reaction. A new series [3] of experiments were made with special reference to the autocatalysis. The temperature was raised to 88.2 C so that the reactions could be carried nearer completion in the time available for each run. The reaction mixtures were buffered to pH 6.7 with *N*/2 sodium acetate-acetic acid mixture (see table 2) to simplify the kinetics by minimizing the change in pH during the reaction; this, however, tended to coagulate the silver bromide. The data were less regular, probably for this reason.

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[3] The first series was intended as a preliminary survey, which would be continued after obtaining comparative results with allyl thiocarbamide. This became impossible so the second series was limited as indicated.

TABLE 2.—*Buffer solutions used for reaction mixtures of allyl thiocarbamide and silver bromide*

[410 ml water and 62.5 ml of 4 *M* sodium acetate, to which was added 0.050 *N* acetic acid, as follows. pH determined with hydrogen electrode at 30.0 C]

Ml HAc solution	5.0	10.0	15.0	23.0	27.5	40.0	60.0
pH	7.64	7.29	7.11	6.92	6.84	6.67	6.48

The tenth-normal sodium acetate buffer contained 5.0 ml of 0.050 *N* HAc and 12.5 ml 4 *M* NaAc in 500 ml; pH 6.77.

Figure 1 represents the results of these experiments. Curves 1 and 4 show the typical course of the reaction without catalyst. In the other experiments, colloidal silver was added before the sulphite. It was prepared by allowing the silver bromide to react with sodium sulphite, then washing thoroughly by decantation before using it for the kinetic experiment.[4] Approximately one half milli-equivalent

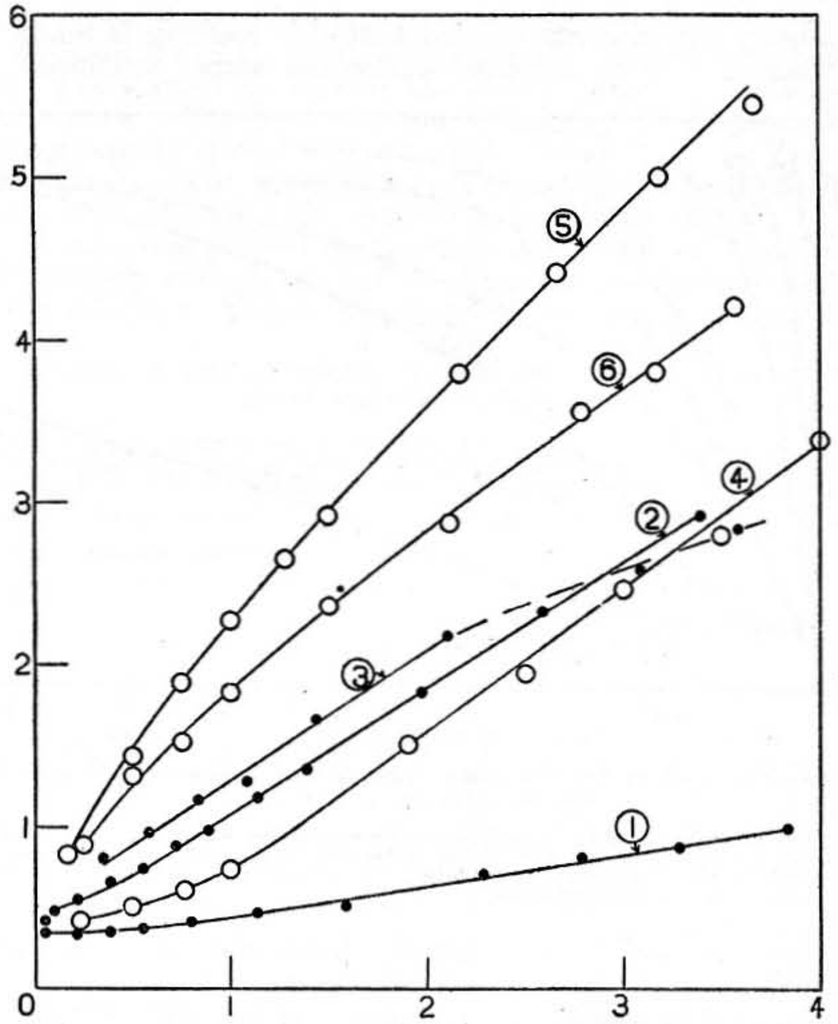

FIGURE 1.—*Rate of reaction between silver bromide and sodium sulphite solutions at 88.2 C.*

Abscissas, time in hours; ordinates, bromide-ion concentration of solution, $\times 10.^{4}$ Curves 1, 2, and 3 for 0.0012 *N* Na_2SO_3, curves 4, 5, and 6 for 0.0033 *N* Na_2SO_3. Curves 1 and 4, silver bromide suspended in 1 percent gelatin. Curves 2 and 5, silver bromide plus silver, suspended in 1 percent gelatin. Curves 3 and 6, silver bromide plus silver, without protective colloid.

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[4] The product was a brown absorption compound, from which the silver could not be removed completely by nitric acid.

of metallic silver was added to one half liter of reaction mixture. The curves show clearly that the induction period was completely eliminated by the addition of the silver. The order of the reaction remained less than one. As in the other series, the rate began to decrease irregularly in the unprotected mixtures after a relatively short interval. In the presence of sufficient silver, the maximum rate was apparently the same with and without gelatin.

III. THE REACTION OF SILVER BROMIDE WITH ALLYL THIOCARBAMIDE

1. EXPERIMENTAL METHODS

Preliminary experiments showed that this reaction is many times faster than that with sulphite under the same conditions. The temperature of 30.0 C used for the determination of bromide-ion concentrations with the silver-silver bromide electrode proved to give convenient reaction velocities, and the electrode adapted itself so rapidly to the solution that it was found possible to run the reactions in the air thermostat used for the electrode measurements, the silver electrode and salt bridge being left in place throughout the reaction. This arrangement had the great advantage that readings could be taken almost continuously when needed.

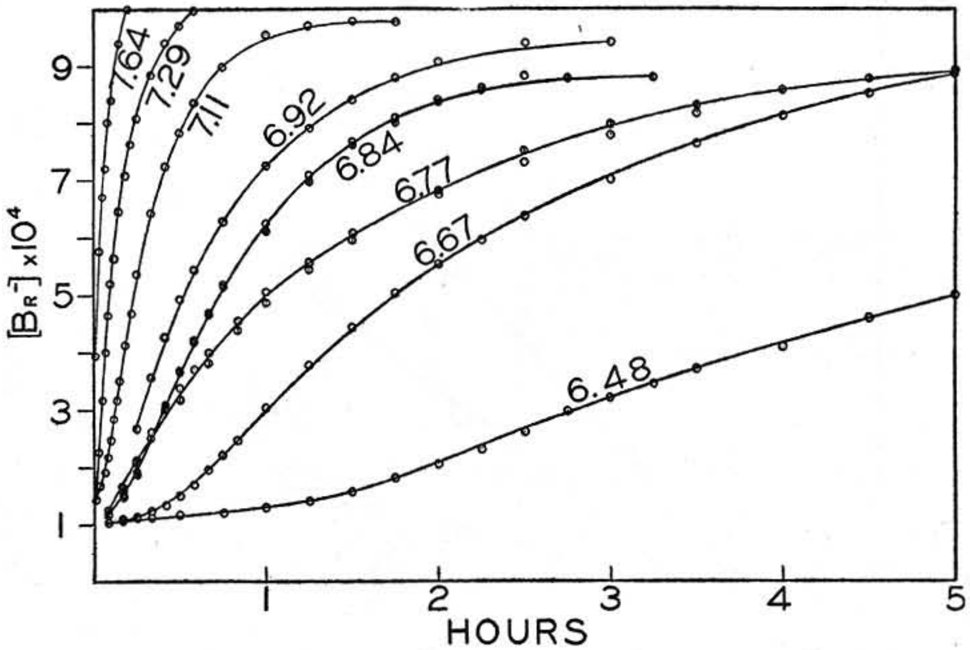

Figure 2.—*The reaction between silver bromide and 1.00×10^{-3} N allyl thiocarbamide solutions at 30.0 C.*

Abscissas, time from start of reaction; ordinates, bromide-ion activities, which are a direct measure of the reaction which has taken place. Numbers on the curves give the pH. All buffered with NaAc−HAc mixtures; 0.1 *N* for pH 6.77 and 0.5 *N* for the others. No protective colloid except for the runs at pH 6.84 which were made in a gelatin emulsion.

The electrode was coated with silver sulphide at the end of a run, but continued to give normal readings in known bromide solutions. In the few cases where the electrode gave trouble it was quite obvious from the erratic nature of the potential. The window of the thermostat was coated with orange lacquer which excluded practically all light of less than 500m μ wave length, but as a further precaution a black curtain was kept over it. The silver bromide was necessarily exposed to light in setting up the apparatus, but the results with sulphite indicate that this was not likely to affect the reaction.

As this reaction was known in advance to be sensitive to hydrogen-ion concentration, all the reaction mixtures were buffered. Tenth normal ammonium acetate was used in some of the runs; the pH was 6.68 at first, falling to about 6.5 on completing reaction with 0.001 *N* allyl thiocarbamide. Acetic acid-sodium acetate mixtures were adopted later; compositions of the mixtures and pH determined at 30.0 C with the hydrogen electrode are given in table 2. In using these, the acetic acid was first added to the silver bromide suspension, then the thiocarbamide; no reaction took place in the presence of the acetic acid and the mixture could be brought to equilibrium before the reaction was started by adding the concentrated (4 *M*) solution of sodium acetate. The final addition took about 60 seconds, the mixture being rapidly stirred with a turbine stirrer.

The original data on the effect of pH on reaction velocity are plotted in figure 2 to illustrate the general form of the curves. After an extended induction period, the reaction usually follows the first order equation closely enough so that the constant can be used to characterize the velocity. This is illustrated by the data given in table 3.

TABLE 3.—*Original data of reaction between silver bromide (with no protective colloid) and allyl thiocarbamide*

[0.03 mol AgBr suspended in 477 ml water at 30.0 C, plus 5.0 ml 0.050 *N* HAc. Then added 5.0 ml 0.100 *N*[1] allyl thiocarbamide solution and allowed mixture to reach equilibrium with electrode. Reaction started by adding 12.5 ml of 4.0 *M* NaAc solution, raising pH to 6.77; time taken from this. Velocity constants calculated from the equation $K=\frac{2.303}{t}\log\frac{a}{a-x}$ where a is the initial concentration of allyl thiocarbamide and x is the concentration at time t]

Time		emf of cell	Bromide-ion activity *N*	Reaction	$k\times10^3$
	Minutes			*Percent*	
Before addition	atc	−0.0968	1.08×10^{-6}	----------	----------
After addition	atc	+.0125	7.09×10^{-5}	----------	----------
After addition NaAc	0	.0221	1.02×10^{-4}	0.	----------
	5	.0258	1.18×10^{-4}	2.1	4.
	10	.0345	1.65×10^{-4}	8.1	8.7
	15	.0411	2.12×10^{-4}	14.3	10.4
	20	.0467	2.63×10^{-4}	20.8	11.7
	25	.0502	3.01×10^{-4}	25.8	12.0
	30	.0533	3.38×10^{-4}	30.6	12.2
	35	.0557	3.71×10^{-4}	34.9	12.2
	40	.0577	4.00×10^{-4}	38.7	12.2
	50	.0611	4.56×10^{-4}	45.9	12.3
	60	.0638	5.06×10^{-4}	52.2	12.3
	75	.0664	5.59×10^{-4}	59.0	11.9
	90	.0686	6.08×10^{-4}	65.5	11.9
	120	.0713	6.75×10^{-4}	74.1	11.3
	150	.0734	7.31×10^{-4}	81.3	11.3
	180	.0750	7.80×10^{-4}	87.9	11.8

[1] Concentrations of allyl thiocarbamide have been expressed in terms of normality with respect to silver. Thus, 0.10 *N*=0.05 *M*. This does not affect the velocity constant, but comes into the equilibrium equations.

Independent evidence of the influence of some of the variables was obtained by a different method of following the reaction. In these experiments the bromide-ion activity was held constant by addition of 0.0100 *N* silver nitrate solution and the rate of reaction measured by the necessary rate of addition of the silver. A turbine stirrer operated as rapidly as possible without splashing was used to mix the silver solution with the suspension. If the flow of solution was temporarily interrupted it was very evident from the rate of change of electrode potential that the rate of reaction with the silver bromide corresponded to the rate of addition of solution which had been required. These experiments gave particularly clear evidence of the autocatalytic nature of the reaction. For example, the data of curve 4, figure 3, were plotted on a large scale and the slope of the curve, giving the instantaneous rate of reaction, carefully measured at each ml addition. Up to 10 ml, 20 percent reaction, the rate of reaction was proportional within 5 percent to the percentage reaction, after which it rapidly approached a constant value.

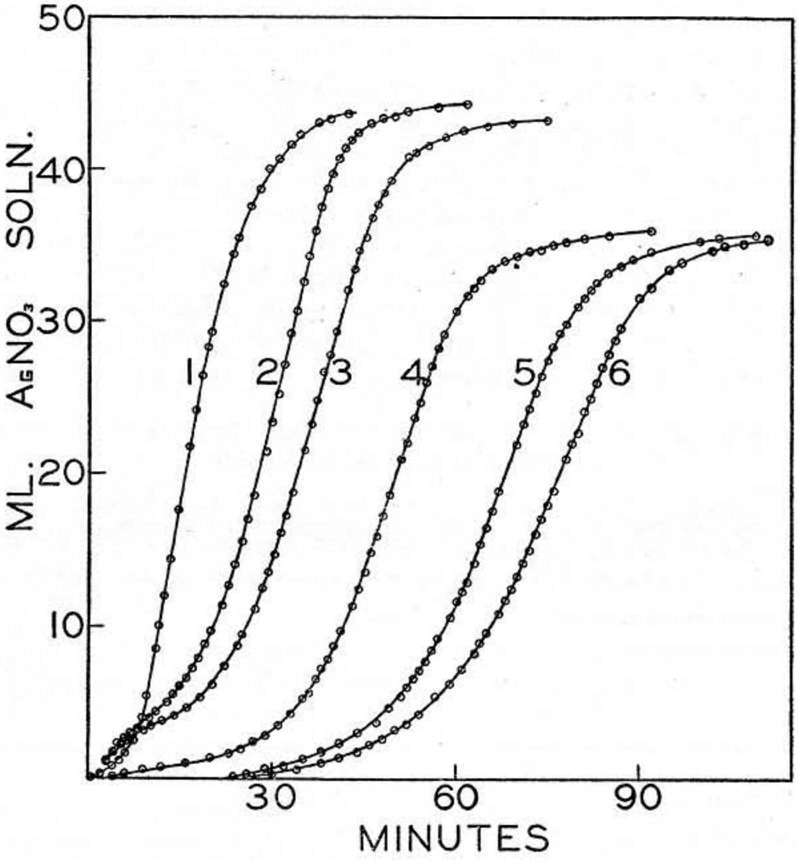

Figure 3.—*The reaction between silver bromide and allyl thiocarbamide at 30.0 C and constant bromide-ion concentration.*

pH maintained at 6.84 by 0.5 N NaAc—HAc buffer. Conditions for the runs are given under the corresponding numbers in table 5. As all those illustrated were made with 0.5 liter of 1.00×10^{-3} N allyl thiocarbamide, 50 ml of the AgNO, solution would represent complete reaction.

The results of this series were obviously not as reproducible as the others; they were probably much more dependent on mechanical details such as the mixing of the solution. It will be noted, however, from table 5 that the maximum rate of reaction and the fraction of the total occupied by the induction period were reasonably constant for given conditions; the greatest variation was in the time of the induction period which appears to be less significant. It will also be noted that these reactions did not run to completion like the others, and that the reactions in the emulsion were the least complete.

2. VARIABLES AFFECTING THE RATE OF REACTION

The curves shown in figure 3 indicate that the reaction is autocatalytic. It was readily demonstrated that silver sulphide is the catalyst. The mixture of silver bromide and silver sulphide left from a previous reaction was thoroughly washed and used to make up the suspension for a new experiment, the conditions otherwise being the same as those given in table 3. The reaction between the allyl thiocarbamide and the silver bromide-silver sulphide mixture started at the maximum rate (3 percent per minute) with no induction period, and followed approximately the equation

$$\frac{d[Br]}{dt}=k.\frac{a-x}{[Br^-]}$$

In another experiment, colloidal silver sulphide was prepared by decomposition of sodium thiosulphate in the presence of gelatin. This was added to a Lippmann emulsion which had previously been found to react with allyl thiocarbamide in the absence of catalyst only after a long induction period. With the addition of the colloidal silver sulphide, there was no induction period and the reaction was even more rapid than in the previous experiment with unprotected silver bromide-silver sulphide mixture. It should be noted that in this second case it is very improbable that the silver bromide and silver sulphide were in contact. Silver bromide carrying colloidal silver from a previous reaction with sodium sulphite reacted at a normal rate with allyl thiocarbamide, indicating that the catalysis by silver sulphide is specific.

Calculation from the data given in figure 2 indicates that the rate of reaction varies inversely as the square of the hydrogen-ion concentration, as a first approximation. Velocity constants could not be calculated for the more rapid reactions, so the slopes of the curves at $[Br^-]$ 3.5×10^{-4} were taken as the rate for this estimate. At pH 4.7 no reaction can be detected for several hours; the practical limit lies about at Sheppard's original figure of pH 6. The effect of acid on the reaction is therefore even greater than on after-ripening with active gelatin (5). After-ripening is quite appreciable at pH 5, which indicates the presence of sensitizers other than allyl thiocarbamide in gelatin.

The reaction velocity varied approximately as $\frac{1}{[Br^-]^{3/2}}$.

This relation may be obtained either from the maximum velocities of the reaction at constant $[Br^-]$, or from the constants of table 4. This is much greater than the effect of bromide-ion concentration on photographic after-ripening (6).

The last three experiments listed in table 5 indicate that the rate of reaction is directly proportional to the concentration of allyl thiocarbamide, the maximum rates corresponding to about the same percentage of the original concentration in each case. The run with 3×10^{-3} N allyl thiocarbamide, corrected for the increased bromide-ion concentration, comes within 20 percent of the same ratio.

TABLE 4.—*Velocity of reactions of silver bromide with allyl thiocarbamide, buffered by 0.10 N ammonium acetate, without protective colloid, at 30.0 C.*

[0.03 mol silver bromide per liter of reaction mixture. Initial pH 6.68]

Initial concentration of allyl thiocarbamide *N*	Initial bromide-ion activity *N*	$k \times 10^3$	Initial concentration of allyl thiocarbamide *N*	Initial bromide-ion activity *N*	$k \times 10^3$
3.00×10^{-4}	6.5×10^{-5}	20.1	1.00×10^{-3}	1.66×10^{-4}	6.4
1.00×10^{-3}	9.7×10^{-5}	9.6	1.00×10^{-3}	1.6×10^{-4}	6.3
1.00×10^{-3}	9.6×10^{-5}	10.5	1.00×10^{-3}	2.4×10^{-4}	2.25
1.00×10^{-3}	9.6×10^{-5}	11.3	1.00×10^{-3}	3.1×10^{-4}	1.57
3.00×10^{-3}	2.7×10^{-4}	1.41	1.00×10^{-3}	3.4×10^{-4}	1.6

TABLE 5.—*Reaction velocities at constant bromide-ion concentration*

[All experiments at 30.0 C, pH 6.84 (0.5 *N* HAc—NaAc buffer), 0.03 g equivalent of silver bromide per liter of reaction mixture]

Curve number in fig. 3	$[Br^-]$	Allyl thiocarbamide concentration *N*	Maximum velocity milliequivalents per hour per liter	Induction period		Remarks
				Percent of reaction	Minutes	
1	3.1×10^{-4}	1.00×10^{-3}	2.8	10	9½	No protective colloid.
	2.4×10^{-4}	1.02×10^{-3}	7.7	30	12½	Do.
2	3.1×10^{-4}	1.00×10^{-3}	2.05	28	24	Silver bromide precipitated and washed before suspending in gelatin.
3	3.1×10^{-4}	1.00×10^{-3}	1.75	30	30	
	3.1×10^{-4}	1.00×10^{-3}	3.0	35	29	Emulsion made by adding silver nitrate solution rapidly in small portions.
	3.1×10^{-4}	1.00×10^{-3}	1.75	40	40	
	3.1×10^{-4}	1.00×10^{-3}	.02	---------	>1,000	Lippman type ("grainless") emulsion.
4	3.1×10^{-4}	1.00×10^{-3}	1.45	24	35	Emulsion, made by adding silver nitrate solution in continuous fine stream for 10 minutes.
5	3.1×10^{-4}	1.00×10^{-3}	1.35	26	59	
6	3.1×10^{-4}	1.00×10^{-3}	1.15	27	70	
	1.2×10^{-4}	1.00×10^{-3}	5.5	35	12	
	3.6×10^{-4}	3.00×10^{-3}	2.6	23	45	
	2.6×10^{-4}	0.51×10^{-3}	0.98	40	36	Emulsion made by adding silver nitrate in continuous fine stream.
	2.5×10^{-4}	1.02×10^{-3}	1.93	30	40	
	3.0×10^{-4}	2.04×10^{-3}	3.36	30	54	

The rates of reaction for the experiments listed in table 4 have been characterized by the "constants" obtained from the first order equation, as in table 3. These were found to be dependent on the initial bromide-ion concentration; it will be noted that the constant was practically the same for an initial $[Br^-]$ of 3×10^{-3} in the cases where this represented simply the solubility of AgBr in 3×10^{-3} *N* thiocarbamide, and where the reaction mixture contained 1×10^{-3} *N* thiocarbamide plus soluble bromide.

The apparent first order of the reaction was obviously the result of compensation between the autocatalysis and the factors decreasing the rate of reaction. The rate of reaction during the period of autocatalysis may possibly be expressed by thus:

$$-\frac{dx}{dt} = k\frac{(a-x).x}{[Br^-]^n},$$

the x in the numerator corresponding to the autocatalytic factor. If n is close to 1, and $[Br^-]$ is proportional to x, as in reactions starting with pure silver bromide and allyl thiocarbamide, this reduces to a pseudo first order. If soluble bromide had been added to the reaction mixture before starting, [Br$^-$] was no longer proportional to x and it was observed that the first-order equation fitted less closely.

An unexpected and important feature of the data was that the reaction velocity proved to be independent of the amount of silver bromide present. Ordinarily the silver bromide was equivalent to nearly 30 times the allyl thiocarbamide. When this ratio was reduced to 2.6, the results of a run without gelatin, buffered with ammonium acetate, checked the previous data within the limit of reproducibility. The experiment was repeated using an "emulsion" of silver bromide in gelatin. The excess in one case was reduced to 5 percent, gelatin being added to keep the concentration 1 percent both in this run and in the control with 2,600 percent excess AgBr. The difference between the two was so small as to be doubtful.

The effect of gelatin is not as large in this reaction as in the one with sulphite. It is most evident as an increase in the induction period. In the extreme case of the "grainless" emulsion recorded in table 5 there was no measurable reaction in 15 hours. Another very fine-grained emulsion required 30 minutes to react as much as a normal emulsion in 5 minutes under the same conditions; once under way, the "constants" were about the same as in the normal emulsion.[4] The curve for pH 6.84 in figure 2 was obtained with gelatin emulsions, and falls in well with the others which were made with unprotected silver bromide, although there is a possible difference in induction period. The effect of the gelatin on induction period is also evident in the curves for reaction at constant [Br$^-$], figure 3; here there is also a definite effect on the rate of reaction after the induction period.

IV. ADSORPTION AND SOLUBILITY DATA

1. ADSORPTION OF POTASSIUM BROMIDE TO SILVER BROMIDE

Silver bromide was known to adsorb soluble bromides, but no quantitative data were available for the region involved in these reactions. They were obtained by the use of the electrode, the bromide-ion concentration in suspensions of silver bromide being determined after successive additions of potassium bromide solution. The silver bromide used for the experiments was precipitated at room temperature from 0.5 N solutions of silver nitrate and potassium bromide, the latter being 10 percent in excess to prevent precipitation of the trace of chloride which persists through repeated recrystallization of the bromide. The precipitate was washed with 15 portions of hot distilled water; its suspension before adding soluble bromide gave a bromide-ion concentration within ±5 percent of the value calculated from the solubility product of silver bromide at 30 C. The data are presented graphically in figure 4 as g mols of KBr per g mol of AgBr; this ratio may be converted to the weight basis by multiplying by 0.58.

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[4] It was not possible to determine whether a "grainless" emulsion would react normally with sulphite, as a highly transparent washed emulsion of this type became opaque after a few minutes at 88 C, indicating a coagulation.

2. SOLUBILITY OF SILVER BROMIDE IN SODIUM SULPHITE SOLUTIONS

The solubility of the silver bromide in the sodium sulphite solutions at 30.0 C could be estimated from the original electrode readings in the reaction mixtures, since the bromide-ion concentration (corrected for the solubility of silver bromide in pure water) was equal to the dissolved silver bromide. In 0.010 N Na_2SO_3 (pH 8.5) the silver bromide was $7.5 \pm 0.5 \times 10^{-5}$ N; this was reduced to 3.5×10^{-5} N in a gelatin emulsion at pH 6.2 with the same sulphite concentration, and to 4×10^{-5} N by the addition of 4×10^{-4} N KBr at pH 8.5. The solubility in 0.0030 N Na_2SO_3 was 2.9×10^{-5}, and in 0.0012 N, 2.0×10^{-5}. These figures are about double the values of Mees and Piper (7) obtained by analysis at room temperature. At the reaction temperatures the solubility was probably several times as great, but the variation with concentration of sulphite, and hydrogen and bromide ions may be expected to be parallel to the results at lower temperature.

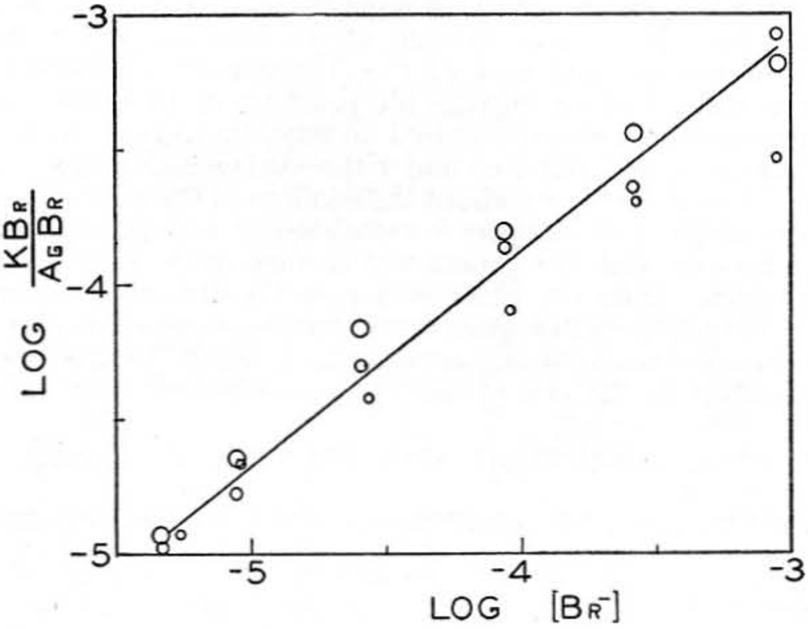

FIGURE 4.—*Adsorption of* KBr *by* AgBr, *in the absence of gelatin, at 30.0 C. The different size circles indicate separate series of measurements.*

No data on the adsorption of sulphite to silver bromide were obtained.

3. SOLUBILITY OF SILVER BROMIDE IN ALLYL THIOCARBAMIDE SOLUTIONS

The available data on the solubility of silver bromide in allyl thiocarbamide solutions do not cover the range of concentrations used in our experiments or the equilibrium relations. Pawelka (8) measured the equilibrium between silver ion and thiocarbamide electrometrically and found that the complex ion consisted of three molecules of the latter to one silver ion. The data of table 6 indicates that when there is a sufficient excess of allyl thiocarbamide over silver, the complex ion is $Ag(atc)_2^+$, but that as the concentration of silver is increased more and more of the 1 : 1 ion is formed.

In dilute solutions of allyl thiocarbamide saturated with silver bromide the thiocarbamide-silver ratio is such that the 1:2 ion is still the principal form. When silver bromide goes into solution in a solution of allyl thiocarbamide, bromide ions and complex silver-thiocarbamide ions must be formed in equal numbers. Their normalities will therefore be equal, provided the solubility of silver bromide in pure water may be neglected. The concentration of dissolved silver bromide may thus be determined simply by electrometric measurement of [Br^-] in the solution.

TABLE 6.—*Equilibrium in allyl thiocarbamide. silver-nitrate mixtures at 30.0 C, pH 3.34*

[Constants calculated from the equation $K=\frac{[Ag^+]\times[atc]^2}{[Ag(atc)_2{}^+}$]

$AgNO^3$, *N*	Allyl thiocarbamide *N*	[Ag^+]	*K*
2.71×10^{-5}	2.17×10^{-2}	2.47×10^{-12}	4.24×10^{-11}
5.42×10^{-5}	2.16×10^{-2}	4.68×10^{-12}	4.00×10^{-11}
1.07×10^{-4}	2.15×10^{-2}	9.71×10^{-12}	4.15×10^{-11}
2.13×10^{-4}	2.13×10^{-2}	2.10×10^{-11}	4.32×10^{-11}
4.17×10^{-4}	2.08×10^{-2}	5.49×10^{-11}	5.25×10^{-11}
8.00×10^{-4}	2.00×10^{-2}	1.21×10^{-10}	5.10×10^{-11}
1.48×10^{-3}	1.85×10^{-2}	4.50×10^{-10}	7.20×10^{-11}
1.86×10^{-3}	1.77×10^{-2}	9.40×10^{-10}	9.9×10^{-11}
2.21×10^{-3}	1.70×10^{-2}	2.00×10^{-9}	14.2×10^{-11}
2.52×10^{-3}	1.63×10^{-2}	4.02×10^{-9}	20.2×10^{-11}

Under conditions where only a single species of complex ion is formed, the solubility relations are quite simple. We have, first, that

$$[Ag(atc)_2^+]=[Br^-]. \tag{1}$$

Since

$$[Ag^+]\times[Br^-]=S_{AgBr}, \tag{2}$$

we may make the substitutions

$$\frac{[Ag^+]\times[atc]^2}{[Ag(atc)_2^+]}=K=\frac{S\times[atc]^2}{[Br^-]\times[Ag(atc)\ _2^+]} \tag{3}$$

$$\frac{[atc]^2}{[Ag(atc)_2^+]}=\frac{K}{S}\text{ or }\frac{[atc]}{Ag(atc)\ _2^+}=K^1 \tag{4}$$

Thus the ratio of free allyl thiocarbamide to the complex ion is a constant and, as a first approximation, the solubility of silver bromide is directly proportional to the total concentration of allyl thiocarbamide. Figure 5 shows how well this relation holds for the range of concentrations used in the velocity experiments. At pH 3.3 (0.005 N HAc), the solutions were quite stable, so that the equilibrium measurements could be made without difficulty. The upper limit at which solubility could be measured was about pH 6.8, and the data in figure 5 at pH 6.49 and the lower concentrations are possibly in error from reaction in the solution. As already mentioned, the more concentrated solutions are the slower to react because of their higher bromide ion concentration.

The solubility increased rapidly with pH. K in equation 3 fell from 15.4×10^{-11} at pH 3.34 to 3.0×10^{-11} at pH 6.77. Assuming that the formation of the complex ion is dependent on the presence of free amino groups in the allyl thiocarbamide, this is evidence for the "zwitterion" theory of its structure.

In mixtures of allyl thiocarbamide and soluble bromide, equation 3 should hold, but not equation 4. Mixtures of allyl thiocarbamide and soluble bromide, in buffer solution at pH 6.77, were made up and saturated with silver bromide. It was found that the solubility was roughly proportional to the thiocarbamide concentration, in spite of the addition of soluble bromide. (The measurements of solubility in this case were less accurate, since the solutions were unstable and the increase in [Br⁻] on adding the AgBr was small.) Since part of the bromide-ion concentration in the reaction mixture came from dissolved silver bromide, it was necessary to subtract this amount from the total in order to get the amount which came from the product of the reaction; the amount subtracted being under 10 percent, an approximate correction was satisfactory.

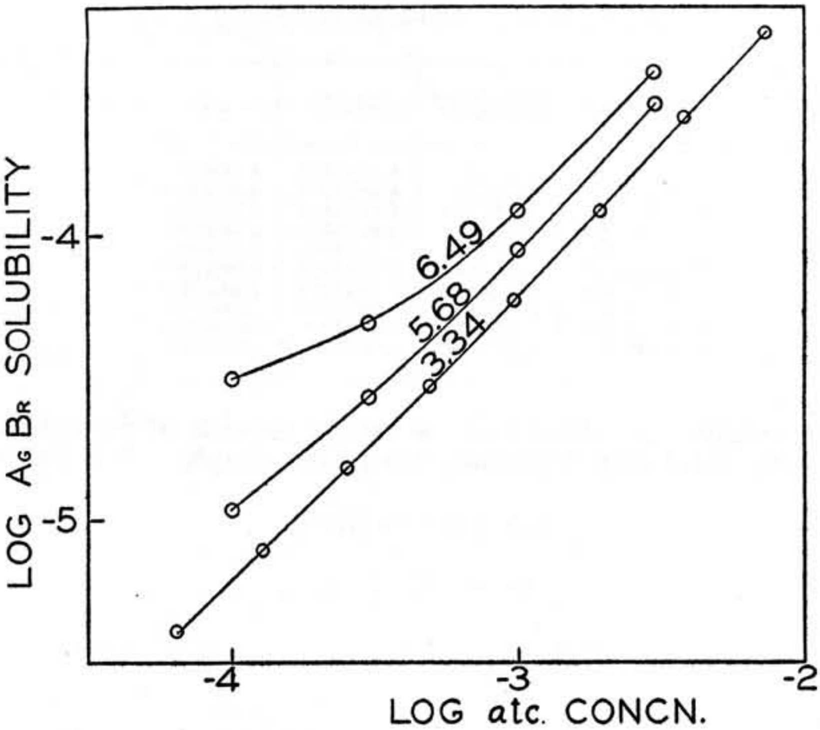

FIGURE 5.—*Solubility of silver bromide in solutions of allyl thiocarbamide at 30.0 C.*

Numbers on the curves give the pH; 0.005 *N* HAc only was used for pH 3.34 and 0.5 *N* NaAc—HAc mixtures for the others.

A few experiments were completed on the adsorption of allyl thiocarbamide on silver bromide. The thiocarbamide solutions (in 1.0×10^{-4} *N* H_2SO_4, pH 4.7) were stirred with silver bromide prepared as for the experiments on adsorption of soluble bromide, and the change in concentration determined. The conditions chosen were not satisfactory, but in 5.0×10^{-4} *M* allyl thiocarbamide (1.00×10^{-3} *N*), 1×10^{-3} mol was adsorbed on 1 mol of AgBr; at 2.9×10^{-4} *M*, the adsorption per mol AgBr was 4×10^{-4}. These values are approximately double the corresponding ratios for *K*Br on AgBr.

V. DISCUSSION

To the best of our knowledge the only other studies of the kinetics of reactions in which a solid phase reacts with a solution to form a new solid phase have also been in connection with a photographic problem, that of development (9). Our experimental methods show promise of being applicable to development as well as to sensitizer reactions.

Complete mathematical analysis of the kinetics of the reactions which we have studied would be extremely difficult in any case, but even with the limited data available it is possible to draw a few definite conclusions. The reaction with allyl thiocarbamide will be considered first because more information is available. Under the conditions of our experiments the first step must have been the formation of the complex ion in solution. It could not have proceeded by adsorption of allyl thiocarbamide to silver bromide followed by a slower rearrangement of the adsorption complex, since the rate was practically independent of the amount of silver bromide. Furthermore, colloidal silver sulphide, added separately from the silver bromide under conditions which preclude its adsorption by the latter, catalyzed the reaction so strongly that it evidently takes place at the silver sulphide surface and is not restricted to the silver sulphide-silver bromide interface. These statements are for the conditions of our experiments, and do not necessarily apply to conditions in the emulsion with a much lower concentration of allyl thiocarbamide. In the emulsion, the ratio of adsorbed sensitizer to sensitizer in solution is probably greater than one; in our experiments it was less than one. However, it seems probable that the reactivity of the material in solution is considerably greater than that of the material adsorbed on silver bromide. Solutions of silver halides in allyl thiocarbamide, like those in sodium thiosuplhate, are stable only in the presence of a large excess of the solvent. Under the conditions of sensitization, the solution is continually saturated with silver bromide and hence at its minimum stability. It seems possible that even in the emulsion the reaction may go on by decomposition of the solution.

The data on kinetics are not sufficient to formulate any mechanism consistent with the chemistry of the system. It may be noted that two hydrogen ions must be liberated by the decomposition of the silver bromide-thiocarbamide complex to form one Ag_2S, so that the reaction would be expected to be highly sensitive to hydrogen-ion concentration. The bromide ions, liberated when the complex ion was formed, affect the velocity through their effect on the solubility equilibrium.

The effect of the gelatin on the catalysis of the reaction by silver sulphide cannot be satisfactorily explained. If there were only the case of the "grainless" emulsions, it would appear that the gelatin simply retarded the crystallization of silver sulphide. The effect of the gelatin, however, nearly vanished in the normal emulsions, although the total gelatin concentration was the same.

The kinetic data on the sulphite reaction leave its mechanism in doubt. The low apparent order is rather remarkable, since by any conceivable mechanism hydrogen ions must be formed in the final step, and the equilibrium in solution must be dependent on bromide-ion concentration. The effect of gelatin on reaction velocity is consistent with its known tendency to retard the crystallization of silver from solution. The reaction was catalyzed by metallic silver. This has already been observed (10) (11) in the precipitation of silver from solutions of silver sulphite in sodium sulphite. The probability that the reaction takes place at the solid silver bromide in preference to the dissolved silver salts seems small; there was no evidence that the rate of reaction was dependent on the amount of solid silver bromide. Since photographic sensitization was obtained under conditions only slightly removed from those of our kinetic experiments, it appears very probable that sensitization was produced by precipitation of silver on the silver bromide from the solution phase.

We have already pointed out (6) that the photographic evidence on after-ripening suggests that the formation of sensitivity nuclei is an autocatalytic process. The data in this paper show that this is actually the case. Furthermore, it seems possible that the autocatalysis is a necessary condition for sensitization. If it exists, the silver sulphide or silver will tend to build up on the first particles formed, decreasing the number and increasing the average size of the nuclei. Reinders and Hamburger have recently calculated the probabilities of a purely random distribution of silver sulphide over the surface of silver bromide grains in the quantities involved in sentitization, showing that aggregates as large as 3 or 4 molecules would be of very infrequent occurrence. They have presented evidence which they have interpreted to show that, under favorable conditions, aggregates of this size may serve as centers for physical development. However, the random distribution seems probable only for instantaneous ionic reactions such as that with sodium sulphide, which does not produce sensitization. We therefore suggest that autocatalytic reactions, such as those with allyl thiocarbamide or sodium sulphite, favor sensitization because they avoid the relatively uniform distribution of silver sulphide or silver which is characteristic of instantaneous ionic reactions. Sheppard's observation that the sensitizers must form molecular complexes with the silver halides has been supported by the discovery of the sensitizing property of sodium sulphite. Our interpretation of the necessity for this condition is different from that of Sheppard. We believe that it is characteristic of sensitizers because it is characteristic of slow, autocatalytic reactions as contrasted to instantaneous ionic reactions.

We are indebted to Dr. P. H. Emmett, of the Bureau of Chemistry and Soils, for advice and suggestions used in interpreting the data and in planning some of the experiments.

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(1) Sheppard, Third Colloid Symposium Monograph, p. 1, 1925; Phot. Jour., vol. 65, p. 380, 1925.
(2) U.S. Patents nos. 1,574,944, 1,602,591, 1,602,592, 1,678,832, 1,742,042.
(3) Carroll and Hubbard, B.S. Jour. Research, vol. 11 (RP622), p. 743, 1933.
(4) Carroll and Hubbard, B.S. Jour. Research, vol. 7 (RP376), p. 811, 1931.
(5) Carroll and Hubbard, B.S. Jour. Research, vol. 8 (RP430), p. 481, 1932.
(6) Carroll and Hubbard, B.S. Jour. Research, vol. 7 (RP340), p. 219, 1931.
(7) Mees and Piper, Phot. Jour., vol. 36, p. 234, 1912.
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(9) Sheppard and Mees, Investigations of the Theory of the Photographic Process; Dzisko and others, Ukrainskii Khur, vol. 5, p. 293, 1930.
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WASHINGTON, D.C., December 27, 1933.

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U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP646

Part of Bureau of Standards Journal of Research, Vol. 12, February 1934

THE PHOTOGRAPHIC EMULSION: NOTES ON STABILITY OF FINISHED PLATES

By B. H. Carroll, Donald Hubbard, and C. M. Kretchman

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.

CONTENTS

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

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[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

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[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

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[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 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

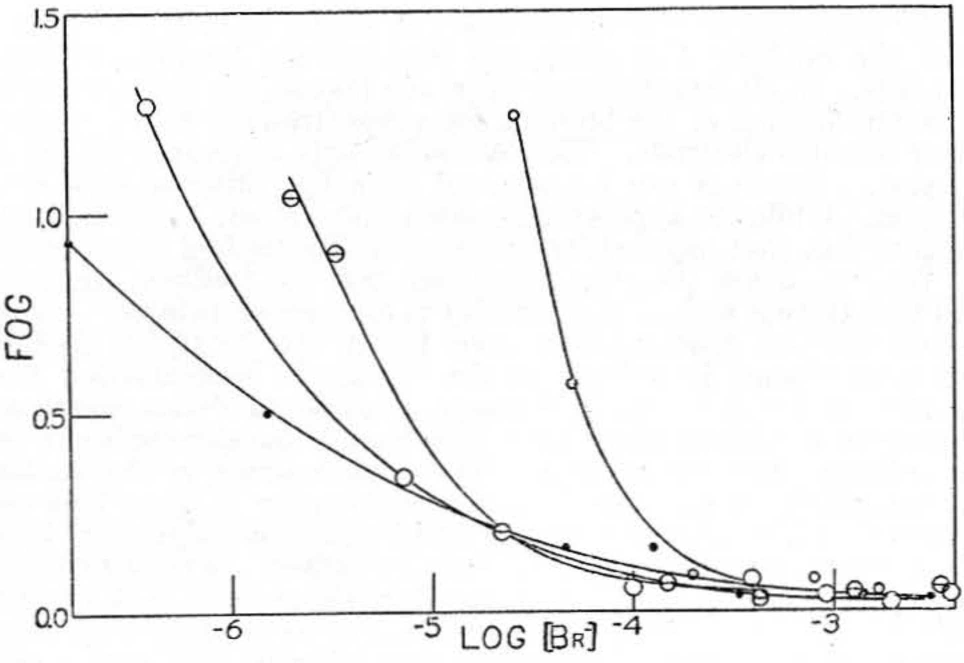

FIGURE 1.—*Stability of emulsions with varying bromide ion concentration.*

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).

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[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 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

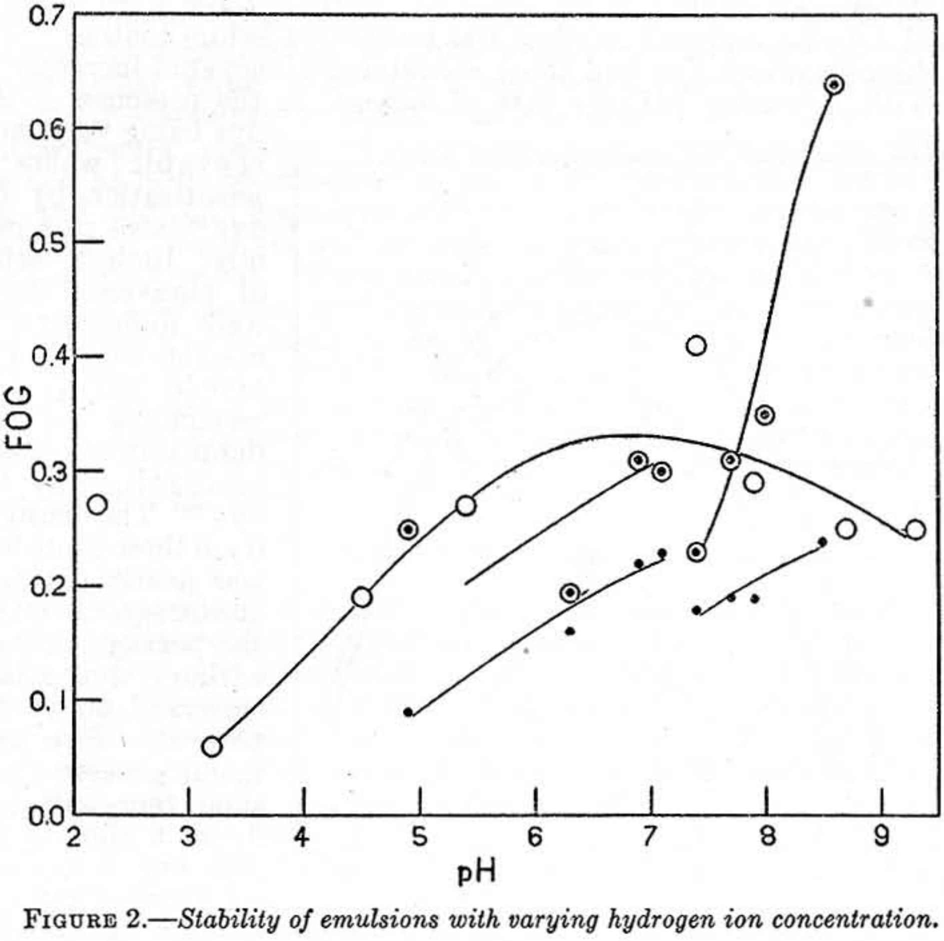

Figure 2.—*Stability of emulsions with varying hydrogen ion concentration.*

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.

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[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.

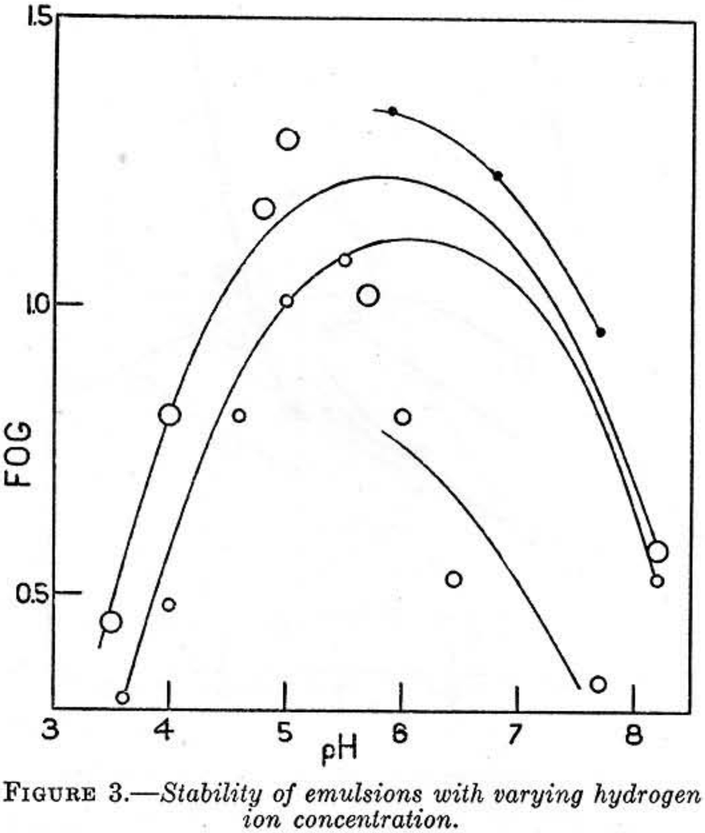

FIGURE 3.—*Stability of emulsions with varying hydrogen ion concentration.*

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

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[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

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[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.

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RP 173

SPECTRAL SENSITIZATION OF PHOTOGRAPHIC EMULSIONS

NOTES ON BATHING WITH PINACYANOL-PINAFLAVOL MIXTURES

By Burt H. Carroll and Donald Hubbard

ABSTRACT

Data are given for sensitization of three emulsions with pinacyanol-pinaflavol mixtures, with varying concentrations of dyes, and with the addition of pyridine or borax. Pyridine is found to be useful, since it both increases the effectiveness of sensitization and reduces the tendency to flocculation, which may be a serious difficulty when pinaflavol is mixed with other sensitizing dyes. Optimum conditions are bathing for one hour at not over 10° C. in a vertical position with an aquaeous bath containing per liter, 4 mg each of pinaflavol and pinacyanol and 10 g of pyridine. Good results may also be obtained with some emulsions by bathing for three minutes with agitation, with a bath containing, per liter, 10 mg each of pinaflavol and pinacyanol and 10 g of pyridine. The pyridine must be free from reducing impurities.

CONTENTS

I. INTRODUCTION

One of us [1] has already published a short communication on the photographic properties of plates sensitized by the combination of pinacyanol and pinaflavol. The dye bath has some characteristics which seemed worth further study, and as it has given trouble in other hands,[2] it was again investigated as part of a more general program.

1. DESCRIPTION OF DYES

The two dyes, pinacyanol and pinaflavol, are in different but related classes. Pinacyanol is the original trade name for the compound now given the chemical name of 1, 1′-diethylcarbocyanine chloride; the dyes marketed under the names of "sensitol red" and "erythrochrome" are iodides [3] of what is understood to be the same base; and a large part of the work here reported was done with the last named.

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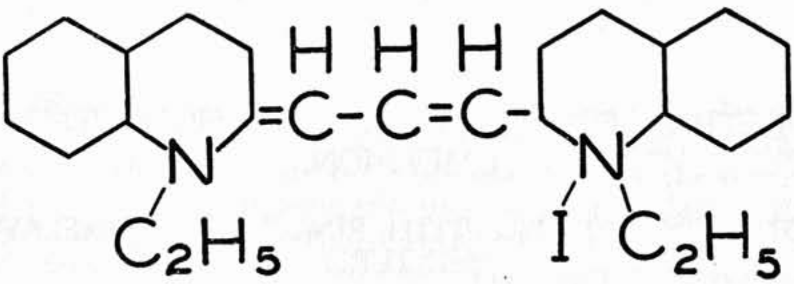
[1] Carroll, J. Opt. Soc. Am. and Rev. Sci. Inst., **13**, p. 35; 1926.

[2] Jacobsohn, Phot. Ind., **26**, p. 56; 1928.

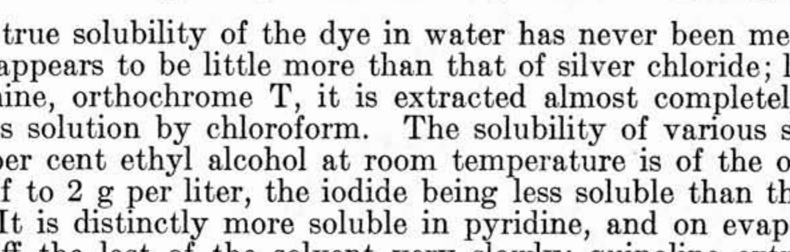
[3] We are indebted to the research laboratory of the Eastman Kodak Co. for this information, which we have checked by analysis of our samples.

All sensitize for the red with maxima at about 0.64 and 0.58 μ. The structural formula now generally accepted[4] is



The true solubility of the dye in water has never been measured, but it appears to be little more than that of silver chloride; like the isocyanine, orthochrome T, it is extracted almost completely from aqueous solution by chloroform. The solubility of various samples in 95 per cent ethyl alcohol at room temperature is of the order of one-half to 2 g per liter, the iodide being less soluble than the chloride. It is distinctly more soluble in pyridine, and on evaporation gives off the last of the solvent very slowly; quinoline extracts it almost completely from aqueous solution. The aqueous solutions are readily flocculated by halides or cyanides, although much more stable toward some other salts, such as sodium borate or carbonate. The dye is decolorized by sufficiently strong acids, but this is not complete at pH 2, in contrast to the isocyanines, some of which are decolorized by pH 5.[5]

Pinaflavol is believed to be 2-*p*-dimethylaminostyryl-pyridine methiodide,[6] or a dye of the same series. It has its maximum absorption at 0.47 μ and sensitizes to 0.6 μ, no minimum intervening between the natural sensitivity of silver bromide and that conferred by the dye. Its true solubility in water is apparently much higher than that of the isocyanines and carbocyanines. The distribution ratio between water and chloroform is of the order of 10:1, as against 1:30 or more for pinacyanol. The higher aliphatic alcohols extract a considerable amount from water, and quinoline removes nearly all the dye from the water layer. These solvents are too miscible with water to make quantitative determinations of the ratio valuable. Aqueous solutions of the concentrations used in bathing are not easily flocculated by salts. The dye is decolorized completely only at hydrogen ion concentrations greater than pH 2.



Both dyes are apparently to be classed as colloidal electrolytes, analogous to the soaps, dissociating in solution into negative halide

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[4] Bloch and Hamer, Phot. J., **68**, p. 21; 1928.
[5] Kolthoff, J. Am. Chem. Soc., **50**, p. 1604; 1928.
[6] Mills and Pope, J. Chem. Soc., **121**, p. 946; 1922.

ions and positive dye ions or polyionic micelles. Single dye ions would be so large and so lyophobic in character that they might be expected to be distinctly colloidal; the formation of micelles would increase with increasing concentration. Both pinacyanol and pinaflavol migrate to the negative electrode, the latter somewhat more rapidly. Both dye ions diffuse very slowly through collodion, if at all, while halide ions can be detected on the other side of the membrane in a few hours.

II. PINACYANOL-PINAFLAVOL MIXTURES

1. FLOCCULATION OF THE BATHS

From consideration of the sensitization produced by pinacyanol and pinaflavol separately, it is evident that the combination may be expected to produce unusually uniform spectral sensitivity. In the manufacturer's literature[7] on pinaflavol, the combination is specifically recommended, using successive aqueous baths of the two dyes for this purpose. No reason is given for this procedure, although it is mentioned that the effectiveness of pinaflavol is reduced by alcohol in the dye bath. The actual difficulty with a mixed bath became obvious in our earliest experiments. Pinacyanol, from the same makers as the pinaflavol, rapidly flocculated when a mixture of the dyes was made up in aqueous solution, the pinaflavol being relatively little affected. The plate is liable, even when the flocculation is not pronounced, to be ruined by specks of dye, visible as such on the undeveloped emulsion and as fog after development.

We later found that this immediate flocculation occurred only with two of the makes of dye, and were able to carry on the experiments with mixtures in plain aqueous solution by the use of one of the others. Since then fresh samples of the two makes of pinacyanol which previously flocculated have proved to be stable in mixtures with pinaflavol. The flocculation is liable to appear on bathing, even though the plates are previously washed and the dye bath is stable when not in use. This may be explained as a case of sensitization by the trace of protein known to be extracted from the plate. It appears to become worse with old samples of dye and old stock solutions. We have observed similar effects with kryptocyanine, dicyanine, and pinachrome when mixed with pinaflavol; orthochrome T and pinaverdol were stable.

The flocculation appears on inspection to be a mutual precipitation of colloids; but both dyes carry the same electrical charge, and it is improbable that they were stabilized by materials capable of reacting, so that no reason can be assigned for predicting such a precipitation. It is probably significant that the tendency to flocculate increases with the age of the pinacyanol, but this is a point to be taken up by the maker rather than the user of the dyes. The iodide ion introduced by dissociation of the relatively soluble pinaflavol may also increase the tendency, since iodide is the most effective of the halides in causing flocculation of pinacyanol; but it can not account for the entire effect.

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[7] "Pina" Handbuch, 10th ed.

Several of the methods of bathing recommended in the literature suggest themselves as expedients for avoiding the flocculation, but are unsatisfactory for other reasons. The addition of sufficient alcohol to stabilize the pinacyanol almost destroys the effectiveness of the pinaflavol. The dye mixture is stable when acidified to approximately pH 2, and plates may be bathed in this and subsequently hypersensitized in ammonia. An acid dye bath followed by alkali is recommended for certain other dyes which decolorize in very faintly acid solutions,[8] but in this case there is a serious tendency to irregularities, and the spectral sensitization is no better than is obtained from successive baths of the dyes. The method recommended by König,[9] which consists in bathing with solutions of dyes in 95 per cent alcohol, drying, and washing in water, gave weak sensitization by both dyes, but especially by pinaflavol. Jacobsohn [10] reports similar results.

As already reported [11] quinoline or pyridine greatly reduces the flocculation of isocyanine and carbocyanine dyes. This is probably because the dyes, at the concentrations recommended in these papers, go largely into true solution in the diluted pyridine or quinoline. Flocculation may not be prevented entirely. Jacobsohn [12] reports that the formula recommended by Carroll [13] caused specks on motion-picture film, although he followed directions scrupulously, and obtained good spectral sensitization. Since publication of the note by Carroll, we have had difficulty with specks on a film sensitized in this manner, and it seemed possible that something extracted from the film base had caused the difficulty. It was in this case, however, readily traced to the mechanical arrangements used for bathing. The plates used in the earlier experiments had been supported vertically in a tank, while the film which had given the trouble had been laid emulsion up on the bottom of a tray. On repeated tests, both with plates and with cut and roll films, no specks appeared on materials supported vertically or emulsion down, while those supported horizontally, emulsion up, in the same bath, were ruined. This precaution seems desirable in any case where a dye bath is used without continuous agitation.

2. CHOICE OF SOLVENT AND CONCENTRATION

We compared sensitization by the mixed dyes in plain aqueous solution, and in 1 per cent solutions of pyridine or borax. The tables give the data on sensitization of three different emulsions; the values in Table 1 are the average of two to four separate experiments, while those in Tables 2, 3, and 5 represent tests on two plates treated in the same bath. In all the experiments listed in Tables 1, 2, 3, and in the "dilute" baths of Table 5, both dyes were at a concentration of 4 mg per liter ("1 : 250,000"). The plates or films were rinsed for five minutes in one or two changes of cold distilled water (running tap water may be used in most places), then bathed for two hours at 5° to 10° C. An alcohol rinse assists in drying and in removing dye from the surface of the emulsion; but as it could not be used on the films, it was also omitted after bathing the plates.

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[8] Von Hübl, Koll. Zeit., **27**, p. 263; 1920. Dundon, Am. Phot., **20**, p. 670; 1926.

[9] König, Phot. Korr., **54**, p. 126; 1918; also Pina Handbuch.

[11] Renwick and Bloch, Phot. J., **60**, p. 145; 1920; also see footnote 1, p. 693.

On comparing the plain aqueous baths with those containing borax or pyridine, there appears to be no advantage in the use of borax. Pyridine caused a slight increase in sensitization of the Eastman 36 and Portrait film (Table 1) and a marked one with the Seeds 23 (Table 2). The improvement in green sensitivity was very noticeable in actual spectrographic use (with Eastman 33 plates). It is demonstrated by the microphotometer records of spectrographic exposures illustrated in Figure 1. These were made with a small concave grating, 0.5 m radius, 15,000 lines per inch, mounted in parallel light. The dispersion in the first order is 50 ÅU per mm. A Tungsarc lamp, which has a color temperature somewhat higher than that of the normal gas-filled tungsten lamp, was used for the light source, a simple lens throwing an image of the tungsten ball, enlarged 2½ diameters, on the slit of the spectrograph. The intensity was so high that a satisfactory range of exposures on fast emulsions was obtained with a camera shutter working at one-fiftieth to one-half second; this eliminates one of the objections to spectrographic tests of spectral sensitivity. The mercury arc spectrum was superimposed on that of the continuous source to give the wave-length scale. Plates were developed by the brush method. Densities were measured with a Moll microphotometer, a series of known densities being recorded with each spectrograph exposure for calibration. As with other physical photometers, the scale is linear as to transmission and logarithmic as to density, so that it is necessary to work at low densities. This is, however, desirable in determining the variation of sensitivity with wave length, since variations tend to disappear in case of overexposure. The curves in Figure 1 were made from Eastman 33 plates, bathed for two hours at 10° to 13° C. in solutions containing 4 mg per liter each of pinacyanol and pinaflavol. The solvent was in the first case water; in the second, 1 per cent pyridine. The plates were washed, bathed, and dried under otherwise identical conditions. The exposures recorded were selected to give approximately the same average density; the time for the second curve was the shorter. The magnitudes in Table 4, read from these curves, emphasize the change in relative spectral sensitivity produced by the pyridine in this case. Values of D (relative energy) are based on an assumed energy distribution in the spectrograph corresponding to a color temperature of 3,000° K. taking the value at the maximum in the blue as 1.0.

TABLE 1.—*Comparison of dye baths; average values*

EASTMAN 36 (EMULSION 2250)

	White light exposure				"Minus Blue" filter exposure				Fog 12
	Speed	γ			Speed	γ			
		3	6	12		3	6	12	
Untreated controls	420	0.67	0.95	1.23	4.7	0.74	1.03	1.17	0.22
Plain aqueous bath	260	.62	.86	1.43	31	.81	1.04	1.62	.27
Bath containing 1 per cent borax	235	.64	.94	1.28	21.8	.81	1.23	1.77	.27
Bath containing 1 per cent pyridine	281	.80	1.04	1.39	32	1.02	1.36	1.65	.29

PAR SPEED PORTRAIT FILM (EMULSION 8112)

Untreated controls	235	0.86	1.24	1.73	8.9	1.02	1.48	2.30	0.27
Plain aqueous bath	170	.73	1.01	1.55	26	.93	1.21	1.97	.27
Bath containing 1 per cent borax	150	.87	1.08	1.98	21.5	.87	1.23	2.26	.30
Bath containing 1 per cent pyridine	155	.96	1.20	1.79	26	1.02	1.57	2.38	.39

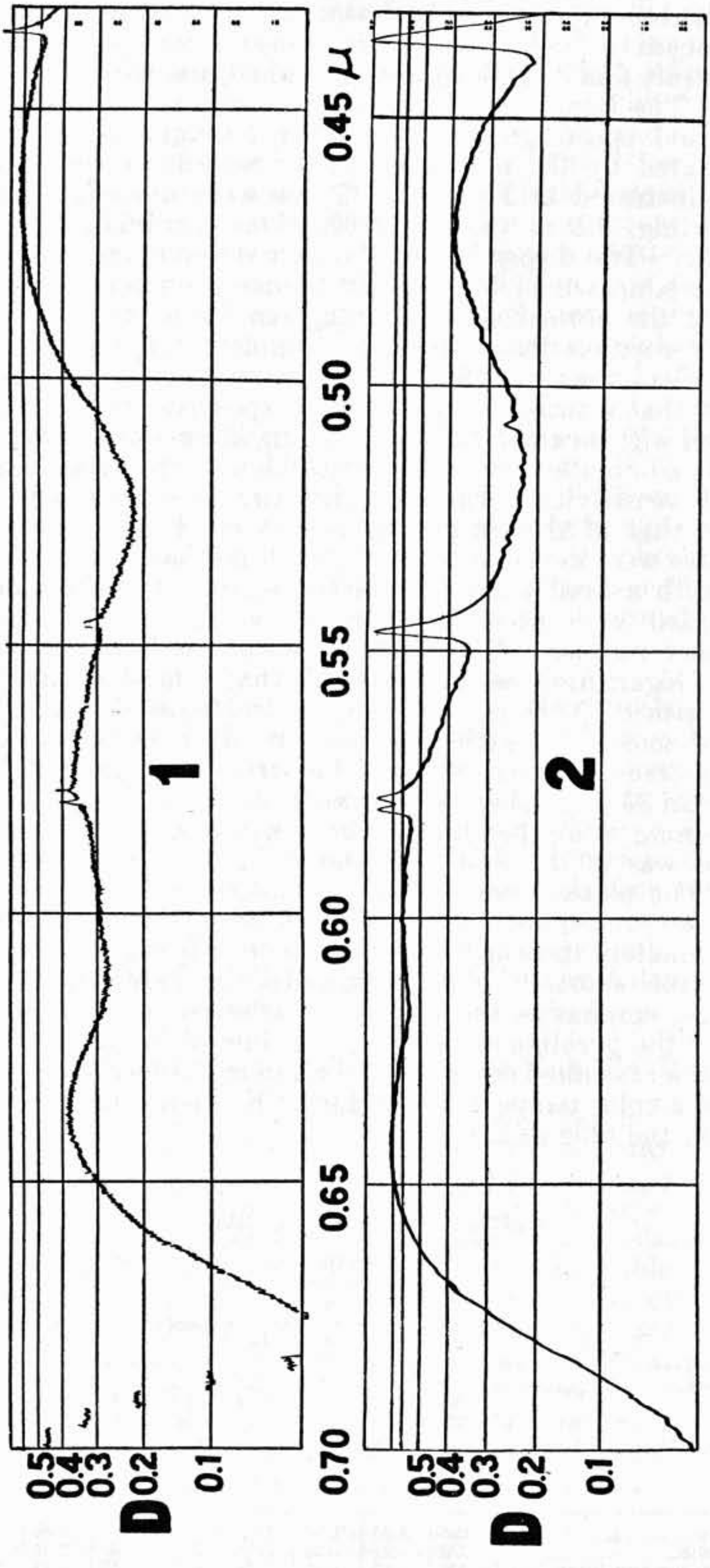

FIGURE 1.—*Microphotometer records of spectrograph exposures on plates bathed with dilute pinacyanol pinaflavol mixtures (1) in water, (2) in 1 per cent pyridine*

TABLE 2.—*Comparison of dye baths; Seeds 23 (emulsion 7743)*

	White light				"A" filter				"B" filter				Fog 12
	Speed	γ			Speed	γ			Speed	γ			
		3	6	12		3	6	12		3	6	12	
Plain aqueous bath	165	0.71	1.15	1.70	7.3	0.92	1.34	2.00	12.8	0.59	1.07	1.94	0.33
Bath containing 1 per cent pyridine	190	.86	1.37	1.90	12.4	.84	1.28	1.63	16.0	.86	1.32	1.90	.33

TABLE 3.—*Keeping qualities of bathed materials*

EASTMAN 36 (EMULSION 2250)

		White light exposure				"Minus Blue" filter exposure				Fog 12
		Speed	γ			Speed	γ			
			3	6	12		3	6	12	
Plain aqueous bath	After 1 day	260	0.62	0.86	1.43	34	0.77	0.96	1.60	0.23
	After 1 month	170	.57	.71	1.00	19	.64	1.00	1.40	.58
Bath with borax	After 1 day	287	.62	.96	1.25	28	.72	1.16	1.64	.28
	After 1 month	203	.69	.85	1.40	24	.67	1.00	1.65	.34
Bath with pyridine	After 1 day	350	.70	1.00	1.37	28	.98	1.30	1.67	.27
	After 1 month	27	.53	.71	------	6.4	.75	1.16	1.38	1.76

PAR SPEED PORTRAIT FILM (EMULSION 8112)

		Speed	γ 3	γ 6	γ 12	Speed	γ 3	γ 6	γ 12	Fog 12
Plain aqueous bath	After 1 day	190	0.75	1.02	1.50	23	0.98	1.32	2.17	0.25
	After 1 month	130	.63	.97	1.55	18	.82	1.20	2.00	.30
Bath with borax	After 1 day	150	.83	1.03	1.88	23	.88	1.20	2.15	.31
	After 1 month	148	.70	1.09	1.66	17	.98	1.31	1.85	.37
Bath with pyridine	After 1 day	143	.99	1.34	1.85	21	.99	1.63	2.35	.32
	After 1 month	50	.66	.88	1.15	5	1.00	1.23	------	1.85

TABLE 4.—*Comparison of spectral sensitivity of Eastman 33 plates bathed with pinacyanol-pinaflavol mixtures (1) in pure water, (2) in 1 per cent pyridine*

(1) Pure water			(2) 1 per cent pyridine		
λ	D	D/relative energy	λ	D	D/relative energy
μ			μ		
0.46	0.62	1.0	0.47	0.39	1.0
.52	.22	.2	.51	.22	.4
.64	.38	.2	.64	.72	.6

The pyridine ruined the keeping qualities of the plates recorded under Tables 1 and 3, although in previous experiments [14] and in practical use, plates sensitized in this way have remained in good condition for a month. The pyridine which had been used was found [15] to contain substances reducing permanganate, and on re-

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[15] Reducing materials can be simply detected by adding two drops of tenth normal potassium permanganate solution to 5 ml of pyridine; the red color should be practically unchanged for at least an hour.

peating the tests with material which had been boiled with neutral permanganate solution and distilled off, the keeping qualities of the plates were much improved. (Table 5.)

The condition of the dye is also important from this standpoint. Our stock of dyes is protected from light and moisture and kept in a refrigerator, but deterioration is usually noticeable after one or two years, and both dyes were two years old when these experiments were completed.

The principal objection to the dilute baths is the long time of bathing, especially as it is desirable to keep all sensitizing baths cold. It was found possible to make up more concentrated baths, even in pure water. These sensitized in three minutes, with rocking. Comparative data are given in Table 6. The "concentrated" bath contained 30 mg of pinaflavol and 15 mg of pinacyanol per liter, the "intermediate" 10 mg per liter of each dye. It is evident from the data that the results, especially with the films, were better with the dilute bath and long time. The difference was much smaller with the Seeds 23; the "intermediate" bath produced good sensitization, and can be recommended for use with this emulsion. The sensitization produced by prolonged bathing in dilute dye solutions is more evenly distributed over the plate than when more concentrated solutions are used for a short time.

Exhaustion tests were made on the "concentrated" baths by bathing successively six 5 by 7 Seeds 23 plates, prewashed in tap water, for three minutes each in 100 ml of bath containing 3 mg of pinaflavol and 1.5 mg of pinacyanol. They were tested with an Eder-Hecht wedge, judging spectral sensitivity from the filter strips. With 1 per cent pyridine in the bath, the sixth plate had almost the same green sensitivity as the first, and about three-fourths the red sensitivity, although the bath was flocculated and noticeably weaker. Without the pyridine the bath flocculated seriously, and the last plate had less than one-third the red sensitivity of the first. In spite of the flocculation, agitation of the bath and an alcohol rinse almost entirely prevented spots on the plates. Repeated use of these mixed baths seems undesirable; if the concentration of 10 mg of each dye per liter is used, the cost of fresh dye bath for each 5 by 7 plate is approximately 1 cent.

TABLE 5.—*Stability of Seeds 23 plates bathed with pinacyanol-pinaflavol mixtures in solutions made from pyridine refluxed with $KMnO_4$ solution*

Time after bathing	White light exposure				"Minus Blue" filter exposure				Fog 12
	Speed	γ			Speed	γ			
		3	6	12		3	6	12	
1 day	295	1.10	1.30	1.78	60	1.08	1.18	1.88	0.45
1 month	306	.68	.97	1.83	38	.87	1.37	2.00	.79

TABLE 6.—*Comparison of "dilute" and "concentrated" baths*

PAR SPEED PORTRAIT FILM (EMULSION 8112)

	White light exposure				"Minus Blue" filter exposure				Fog 12
	Speed	γ			Speed	γ			
		3	6	12		3	6	12	
"Dilute" bath in pure water (2 hours)	170	0.73	1.01	1.55	26	0.93	1.21	1.97	0.27
"Concentrated" bath in pure water (3 minutes)	79	.81	.96	1.60	16	.87	1.11	1.66	.25
"Dilute" bath with 1 per cent pyridine (2 hours)	155	.96	1.20	1.79	26	1.02	1.57	2.38	.39
"Concentrated" bath with 1 per cent pyridine (3 minutes)	99	.76	1.10	1.55	16	.94	1.25	1.71	.30
SEEDS 23 (EMULSION 7743)									
"Dilute" bath in pure water (2 hours)	182	0.86	1.21	1.76	32	0.98	1.26	1.98	0.35
"Intermediate" bath with 1 per cent pyridine (3 minutes)	207	.91	1.35	1.88	36.5	.99	1.47	1.97	.41
"Concentrated" bath in pure water (3 minutes)	159	.76	1.17	1.66	28	.80	1.16	2.09	.33
"Concentrated" bath with 1 per cent pyridine (3 minutes)	------	------	------	------	35	.97	1.40	1.96	.34

III. SUMMARY

The use of pinacyanol and pinaflavol for spectral sensitization is complicated by the tendency to flocculation of the mixed dye baths. Pyridine is found to be useful both as stabilizer and hypersensitizer; borax has little or no value for the latter purpose. Conditions for sensitizing by bathing are specified.

WASHINGTON, November 30, 1929.

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RP488

THE PHOTOGRAPHIC EMULSION; VARIABLES IN SENSITIZATION BY DYES

By B. H. Carroll and Donald Hubbard

ABSTRACT

These experiments were designed to test the effect of independent variables in the emulsion on the relative spectral sensitization by a given dye in a given emulsion. Four typical dyes representing four series were used in combination with emulsions of different types. Relative spectral sensitivity increased slowly with the concentration of dye. In agreement with Sheppard, it was found that the relative spectral sensitivity was little affected by the formation of sensitivity nuclei (from allyl thiocarbamide, for example) which greatly increased the absolute sensitivity to any wave length. Increased alkalinity increased relative spectral sensitivity by an extent which depended on the dye. Increased silver ion concentration generally increases sensitization by any dye, but there are differences between individual dyes which may be explained on the hypothesis that spectral sensitization depends on adsorption of the ion of the dye by the oppositely charged ion of the silver halide lattice; changes in adsorption of basic dyes may be sufficient to counteract the general trend at sufficient excess of silver.

CONTENTS

I. INTRODUCTION

The spectral sensitivity of a given photographic material in either absolute or relative terms is generally recognized to depend both on the dye or dyes, and on the emulsion. The many variables in the emulsion which influence the sensitization by the dye may be divided into those which are characteristic of the particular emulsion, such as the grain size and proportion of iodide, and those which may readily be varied in a given dye-emulsion combination, such as the silver and hydrogen ion concentrations. This paper will be primarily concerned with the latter group of variables. While it is not possible to draw a sharp distinction between these variables and those characteristic of the emulsion and dye, a study of the more general variables of sensitization will make it easier to distinguish characteristics of individual emulsions by comparing them under constant conditions. The process of hypersensitization (1) (2) [1] must obviously be connected with variation of conditions in a given dye-emulsion combination. This will be treated in full in a separate communication; a preliminary report (3) has already been made, using some of the data in this paper.

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[1] Numbers in parentheses here and throughout the text refer to the list of references at the end of the paper.

The experimental methods used in this investigation, including emulsion making, sensitometry, and determination of bromide ion concentration, have been described for the most part in previous communications (4) (5). Emulsion formulas followed the types described in one of these references (4) and will be designated by the same letters; full details are available to any interested parties. A measure of the added spectral sensitivity conferred by the dyes was obtained with the sector wheel sensitometer, inserting an appropriate filter between the light source and plate in addition to the Davis-Gibson filter used for correction of the incandescent source to sunlight quality. A Wratten "Minus Blue" (No. 12) filter was most commonly used, as it gives approximately the total sensitivity to all wave lengths longer than those absorbed by the silver bromide; absorption by the filter is not over 15 per cent in the region of sensitization by any of the dyes except pinaflavol. This general method does not determine the relative spectral sensitivity, but it is the most accurate means available for comparison of the sensitization produced by a given dye under varying conditions.

Four dyes were used in the investigation, each representing a different type. Erythrosin, which is the only acid dye in common use as a sensitizer, was included because it was important to have an acid dye for comparison with the basic sensitizers. It is soluble in water in concentrations much higher than those used in emulsions and ionizes into the colorless positively charged sodium ion, and the negatively charged ion of the acid tetraiodofluorescein. The other three dyes are basic, and ionize into colorless iodide or chloride ions, and positively charged ions of the corresponding complex nitrogen bases. They represent three distinct types—pinacyanol is a carbocyanine (6); pinaverdol an isocyanine (6); and pinaflavol, a newer type which has not been assigned a general name (7). The first two are very insoluble in water, being completely extracted from it by solvents such as chloroform, and their suspensions are readily flocculated by electrolytes, especially halides, while pinaflavol does not show these colloidal characteristics and apparently forms true solutions in water at low concentrations. However, even the insoluble dyes may be considered as colloidal electrolytes, as they appear to be highly dissociated; the iodide ion in any of these dyes may be titrated electrometrically with silver nitrate giving values corresponding closely to the calculated molecular weight.

The basic dyes were commercial products, used without further purification; the pinacyanol was the chloride of its base, the others iodides. The erythrosin used in these experiments had been prepared from an old sample of a Kahlbaum product by precipitation of the acid and recrystallization of the sodium salt made from it. It was recently found to be low in iodine, the acid containing 26.5 per cent instead of 60.75 per cent theoretical (8); apparently considerable loss had occurred on storage, with resulting formation of fluorescein. Photographic comparison with a known sample of pure erythrosin received from the color laboratory, Bureau of Chemistry and Soils, showed that it produced its maximum sensitization in exactly the same spectral region as the pure dye, but in about half the proper intensity, and that there was faint sensitization at shorter wave lengths corresponding to that produced by fluorescein. Fortunately this contamination by the parent acid dye does not affect our conclusions.

The dyes were normally added to the emulsions just before coating, in the form of dilute solutions; the alcoholic stock solutions of the basic dyes were diluted further with water to avoid coagulation of gelatin on contact with the alcohol. In all cases, the dye was added to the liquid emulsion before coating; none of the following experiments deal with sensitization by bathing finished plates.

II. CONCENTRATION OF DYES

The concentration of a given dye in an emulsion is reported to have an optimum value (9), but no quantitative data are available. Eder believed that the sensitivity fell off after passing through the maximum because of filter action by the dye. With any of the basic sensitizers used in these experiments the upper limit seems to be set rather by the tendency of the dye to cause fog.

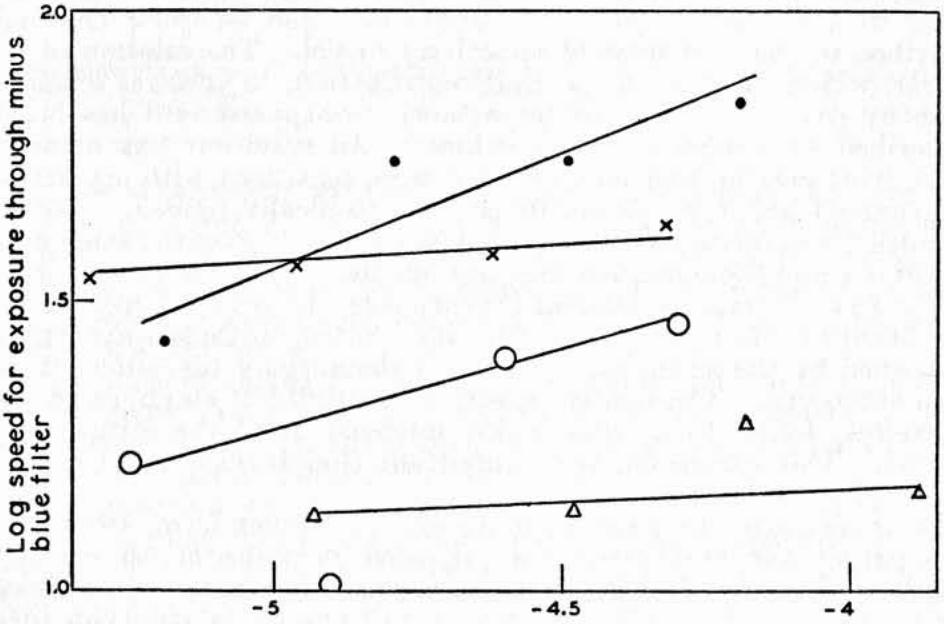

FIGURE 1.—*Effect of concentration of dye on spectral sensitization*

O, Pinacyanol.
X, Pinaverdol.
. Pinaflavol.
Δ Erythrosin.

The data illustrated in Figure 1 indicate that within the range of concentrations tested, which covers the normal values for these dyes, the sensitization by the dye increases slowly with its concentration. The emulsions used in these experiments were of the neutral (type C, reference (4)) type with 4.0 mol per cent AgI, and were coated at a bromide ion concentration 0.9 to 1.1×10^{-4} and pH 7.1 to 7.3. Speeds were in all cases measured by exposure through the Minus Blue filter.[2] Speed numbers were somewhat dependent on development time, and were, therefore, compared by interpolating the value cor-

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[2] Absorption by this filter was not taken into account in calculating the speed numbers, since relative values only were involved.

responding to $\gamma = 1.0$ from plots of speed against γ for each case. The contrast of the emulsions was not appreciably affected by the concentration of dye. The data are plotted on a logarithmic scale for compactness; concentrations have been reduced to the common basis of the molar ratio of dye to silver bromide.[3]

The slopes of the curves for pinaflavol and pinacyanol sensitization are larger than those for the other two dyes. This does not correspond to any classification of dyes; correlation with the adsorption of the dyes on silver bromide may be possible when data are available.

III. AFTER-RIPENING

After-ripening an emulsion, either with the sensitizers naturally occurring in gelatin or with known materials, such as allyl thiocarbamide, can produce a large increase in sensitivity, which is not associated with change in grain size, and which can be quite definitely ascribed to the formation of sensitivity nuclei. The relation of this effect, which we may call nuclear sensitization, to spectral sensitization by dyes, is of obvious importance. Sheppard (10) has briefly described experiments on this subject. An emulsion was made up with inert gelatin, and portions of it were sensitized with erythrosin, pinacyanol and a green sensitizer not specifically named. Another emulsion was made up with active gelatin so as to give the same mean grain size and the same size-distribution, and portions sensitized in the same way. It was found that for each dye, the ratios of red or green sensitivity to the blue-violet sensitivity (that is, for those wave lengths absorbed by the silver halide) were "substantially the same" in the two emulsions. The relative spectral sensitivity of an emulsion was, therefore, found to be practically independent of the formation of nuclei. This conclusion is so important that it was tested under a variety of conditions.

It is necessary to present the results in tabular form, because on comparing the undigested and digested portions of an emulsion made with active gelatin there are found differences both in speed and contrast. The same applies to portions of an emulsion made with inert gelatin and digested with and without a nuclear sensitizer.

Table 1 presents the data for an emulsion made with relatively inert gelatin (prepared by digesting an active gelatin with ammonia and then washing very thoroughly). After washing, the emulsion was divided in halves, to one of which was added a trace of sodium thiosulphate. After digestion, each half was divided into four portions; one was left unsensitized and the other three sensitized with three different dyes. It is impossible to express the resulting differences by single numbers. The contrast was changed both by the thiosulphate and the dyes; of the three dyes, pinacyanol produced much the strongest effect. Furthermore, the relation between speed number and time of development was changed by both types of sensitization. However, we may state with confidence that the increase in sensitivity to the longer wave lengths was less than the increase in total sensitivity (to white light). In this emulsion, the sensitivity to wave lengths transmitted by the Minus Blue filter was a

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[3] The molecular weights used for this purpose were: Pinacyanol, 412; pinaverdol, 501; pinaflavol, 366; erythrosin, 898. The concentrations are of the order of a few milligrams of dye per liter of emulsion containing 40 to 45 g of silver bromide.

small fraction of the total, so that white light and blue light sensitivities were equivalent within the necessary limits of accuracy.

TABLE 1.—*Effect of nuclear sensitization, by $Na_2S_2O_3$, on sensitization by dyes*

[Neutral type emulsion, 4 per cent AgI (4–103) coated at pH 6.4, $[Br^-]$ 9×10^{-5}; half of emulsion sensitized with $Na_2S_2O_3$ sufficient to convert 2 parts AgBr per 100,000 to Ag_2S]

	Dye	Molar ratio dye to AgBr	White light exposure						Minus blue filter exposure						Fog_{12}
			Speed			γ			Speed			γ			
			3	6	12	3	6	12	3	6	12	3	6	12	
Control	None	O	35	59	----	0.26	0.33	----	----	----	----	----	----	----	0.02
	Pinaflavol	6.7×10^{-5}	40	53	65	.34	.35	0.43	4.0	3.5	3.5	0.26	0.57	0.70	.04
	Erythrosin	1.1×10^{-4}	21.5	46	85	.26	.36	.39	3.5	3.1	3.1	.16	.30	.40	.03
	Pinacyanol	5.9×10^{-5}	31.5	30	25	.55	.77	.95	8.0	7.4	6.3	.76	1.14	1.57	.20
Sensitized with $Na_2S_2O_3$	None	O	430	255	230	.51	.94	1.41	----	----	----	----	----	----	.08
	Pinaflavol	6.7×10^{-5}	315	365	325	.64	.92	1.29	12.3	13.8	13.5	.88	1.07	1.86	.20
	Erythrosin	1.1×10^{-4}	225	235	235	.63	.95	1.40	9.6	9.2	7.6	.57	1.03	1.63	.08
	Pinacyanol	5.9×10^{-5}	120	105	96	.73	1.10	1.66	9.6	9.6	9.1	1.05	1.70	2.42	.41

Similar experiments with other emulsions and two of the dyes are recorded in Table 2. These emulsions had finer grain and lower iodide content, which probably accounts for the much better ratio of red or green sensitivity to blue sensitivity. This ratio was unchanged or somewhat decreased on increasing the total sensitivity by thiocarbamide sensitization.

The emulsions listed in Table 3 were made with active gelatin, and compared with and without digestion after washing. The variation in sensitivity nuclei in this case was obtained by varying the completeness of the reaction with the available sensitizing compounds, instead of by varying the quantity of the latter. The results are very similar to those obtained with the pure sensitizing compounds. The relative sensitivity to longer wave lengths was appreciably decreased by the after-ripening, although the absolute value of sensitivity to red or green increased two or more times.

These last experiments also included the behavior of the dye when present during digestion. Two portions of emulsion were digested under conditions identical except that the dye was added before digestion to one, and after digestion (the usual procedure) to the other. The sensitization by erythrosin was less when it was present during digestion than when it was added afterward (just before coating); pinacyanol was more effective under the former conditions, while pinaflavol was about the same.

TABLE 2.—*Effect of nuclear sensitization, by allyl thiocarbamide, on sensitization by dyes*

[Neutral emulsion (4-48), 1 per cent AgI, coated at pH 7.5, $Br^{-}1.3\times10^{-5}$; ammonia process emulsion (1-153), 1 per cent AgI, coated at pH 8.3, $Br^{-}1.3\times10^{-5}$. Half of each emulsion sensitized with allyl thiocarbamide sufficient to convert 8 parts AgBr per million to Ag_2S. "A" red filter used for exposure of pinacyanol sensitized batches; minus blue (yellow) filter for others]

Emulsion	Dye	Allyl thiocarbamide	Blue light exposure ("C" filter)						Yellow or red light exposure						Fog 12
			Speed			γ			Speed			γ			
			3	6	12	3	6	12	3	6	12	3	6	12	
4-48	Erythrosin	Without	14.0	9.5	10.0	0.37	0.61	0.84	7.9	7.9	7.9	0.52	0.74	0.97	0.24
		With	25	25	23	.54	.76	1.12	11.5	11.0	15.2	.60	.86	1.37	.28
	Pinacyanol	Without	11.5	10.0	8.3	.42	.61	.91	15.9	17.4	13.8	.55	.78	1.06	.27
		With	17	12.5	14	.57	.92	1.18	26.3	26.3	25.1	.63	1.07	1.50	.34
1-153	Erythrosin	Without [1]	24.5	24.5	24.5	1.24	1.86	2.21	2.6	2.7	2.8	1.52	2.16	2.36	.23
		With [1]	166	210	235	1.27	1.75	2.12	20.9	20.9	21.9	1.05	1.60	1.90	.29
	Pinacyanol	Without	2.6	2.4	2.6	2.00	2.40	2.75	5.3	5.3	6.4	1.82	2.49	2.73	.28
		With	9.1	9.0	10.5	1.24	1.86	2.23	17.5	17.5	20.0	1.38	2.12	2.58	.63

[1] White light exposures substituted for blue because of low speeds.

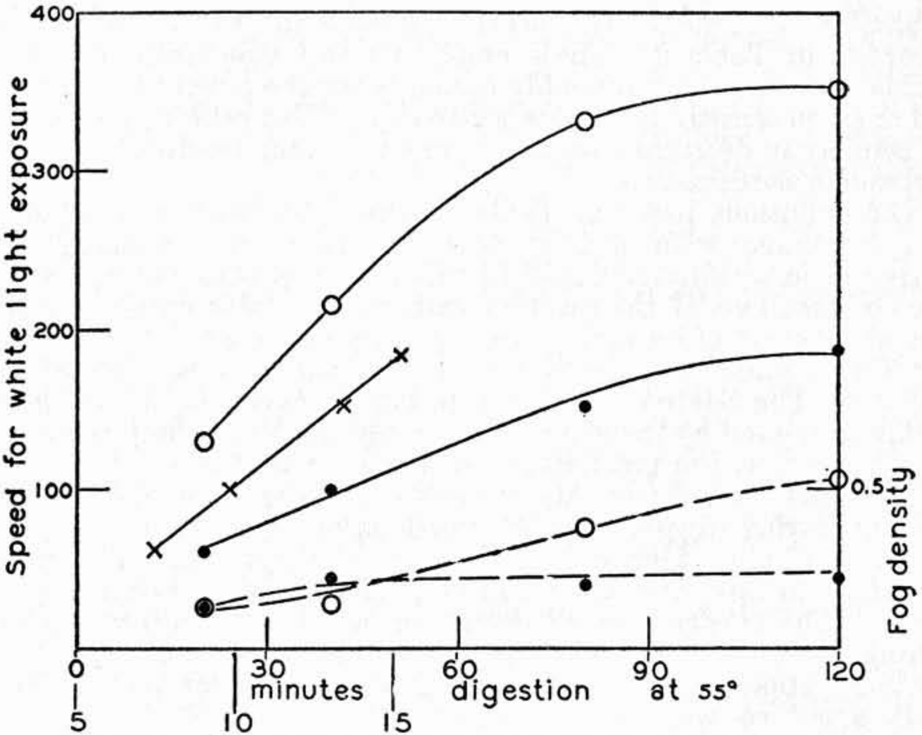

FIGURE 2.—*After-ripening with and without erythrosin in the emulsion*

. With dye. O Without dye.
———— Speed. — — — — Fog.
X Comparison of speed for exposures to white light and through Minus Blue filter at varying stages of digestion.

The data in Table 3 on sensitivities to white light show that the after-ripening was materially retarded by the presence of erythrosin during digestion, while the other two dyes had less effect. Eder (11) observed that some dyes prevented fog when present during ripening.

Lüppo-Cramer (12) has found that in Lippman emulsions erythrosin and other sensitizing dyes can produce a striking retardation of the whole ripening process, and that in normal emulsions erythrosin present during digestion retards after-ripening (13). After-ripening being essentially a surface change in the grains, it is not surprising that it is influenced by the adsorption of a foreign material. Further data were obtained by a slightly different procedure. Emulsions were divided into halves, which were digested at the same temperature and silver ion concentration, one with and one without a sensitizing dye. The results are plotted in Figures 2 and 3 as speeds (at $\gamma = 1.5$) for white light exposures against time of digestion. On the same sheet the speeds (at $\gamma = 1.5$) for exposures through the Minus Blue filter are plotted against the white light speeds. The latter curve would be a straight line if the relative spectral sensitivity were unchanged by the after-ripening.[4] The curvature indicates that it is slightly increased. The other curves show that the rate of after-

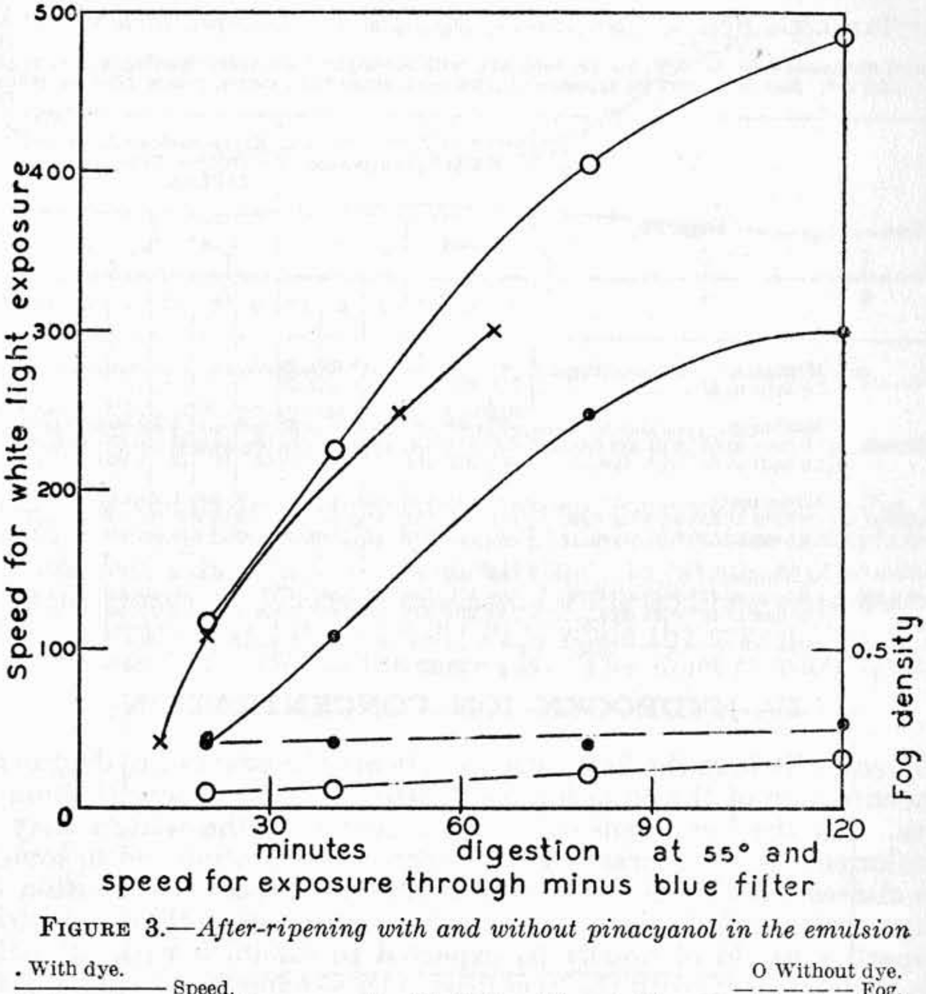

FIGURE 3.—*After-ripening with and without pinacyanol in the emulsion*

. With dye. O Without dye.
——— Speed. — — — — Fog.
X Comparison of speed for exposures to white light and through Minus Blue filter at varying stages of digestion.

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[4] In both figures, this curve intercepts the horizontal axis at a small positive value of "speed for exposure through Minus Blue filter," as the speed of the unsensitized emulsion did not fall quite to zero on exposure through the Minus Blue filter.

ripening was divided by about four when erythrosin was present. Pinacyanol approximately halved the rate. Both dyes also retarded the growth of fog. In both figures, the slope of the curve of fog against digestion time is less for the portion digested with dye than for the one digested without it. The effect is less noticeable in Figure 3 because the fog density at any time was increased by the addition of pinacyanol, although the rate of increase with time was less. The data in Table 3 also show that the fog for the portion digested with pinacyanol was less than for the one to which the same amount of dye was added after digestion.

TABLE 3.—*Effect of after-ripening (by digestion) on sensitization by dyes*

[Neutral emulsions 4–50 and 4–51; 2¼ per cent AgI, with subsequent ammonia ripening; coated at pH 8 $Br^- 1.2 \times 10^{-5}$. Red filter used for exposure of pinacyanol sensitized batches; yellow filter for others]

Dye	Digestion	White light exposure						Exposure through yellow (Minus Blue) or red (A) filter						Fog_{12}
		Speed			γ			Speed			γ			
		3	6	12	3	6	12	3	6	12	3	6	12	
None	Minimum	50	43	52	0.66	0.94	1.23	----	----	----	----	----	----	0.18
	1.0 hour at 55°	220	302	270	1.01	1.45	2.20	----	----	----	----	----	----	.21
Erythrosin	Minimum	50	40	38	.70	1.02	1.28	3.8	4.0	4.3	0.84	1.17	1.40	.19
	1.0 hour at 55° without dye	265	380	315	.92	1.30	1.85	18	19	22	1.13	1.67	2.28	.30
	1.0 hour at 55° with dye	263	263	240	.78	1.27	1.74	13	13	12	1.20	1.82	2.55	.23
Pinaflavol	Minimum	100	120	115	.67	.85	1.11	6.9	6.6	7.2	1.00	1.40	1.70	.17
	1.0 hour at 55° without dye	138	220	330	.94	1.14	1.71	15.9	15.9	20.0	1.10	1.52	1.97	.79
	1.0 hour at 55° with dye	190	210	288	.86	1.16	1.65	11.5	15.0	16.0	1.17	1.57	2.25	.58
Pinacyanol	Minimum	50	50	57	.65	.88	1.11	6.6	6.6	6.6	.99	1.40	1.69	.33
	1.0 hour at 55° without dye	150	178	175	1.07	1.54	2.37	10.5	9.6	10.5	1.41	2.35	2.91	.58
	1.0 hour at 55° with dye	200	209	220	.97	1.47	2.20	19.0	19.0	15.9	1.00	1.77	2.71	.40

IV. HYDROGEN ION CONCENTRATION

There is little in the literature to indicate the effect of hydrogen ion concentration of the emulsion on the effectiveness of sensitization by dyes. All the basic sensitizing dyes known to the writers may be decolorized by a moderate hydrogen ion concentration and in some of the classes, notably the isocyanines (14) (15), this occurs within the range which might be encountered in emulsions. The sensitizing properties would obviously be expected to diminish with the color. Approximate tests with the dyes used in these experiments showed that pinaverdol is appreciably decolorized by pH less than 7, and is almost completely decolorized by pH 5. Pinacyanol and pinaflavol did not fade appreciably at pH 5.4; the decolorization was barely perceptible at 4.2, and not complete at 2. Erythrosin has an appreciable shift in hue to the yellow, beginning about pH 5.4; the acid is mostly precipitated at pH 3.

The experimental results are presented in Figures 4 and 5, the logarithm of the speed through the Minus Blue filter (at $\gamma = 1.5$) being plotted against pH. For comparison, the logarithm of the speed (to white light) of unsensitized portions of the emulsions sensitized with pinacyanol is also plotted in Figure 4. The emulsions were all digested after washing and before adding the dyes, under the same conditions of temperature, silver ion concentration and pH, and the pH was adjusted just before coating so that it did not affect the after-ripening. With the exception of pinaverdol, the data for each dye (and also for the unsensitized portions) represent two emulsions, one for the range below pH 7 and one for the range above. These fit sufficiently well to draw single curves, except for erythrosin. (Fig. 5.) The discrepancy between the two emulsions in this case is explained by a difference in silver ion concentration, to which erythrosin is especially sensitive. The emulsion used for the acid range had a silver ion concentration at pH 7 of 1.3×10^{-8}, while the concentration for the other was 0.66×10^{-8} at the same pH. The effect of differences in silver ion concentration in other cases was negligible. These emulsions were made with a gelatin giving very little change in sensitivity of the unsensitized emulsions with pH (upper curve in fig. 4), so so that this complication was reduced to a minimum.

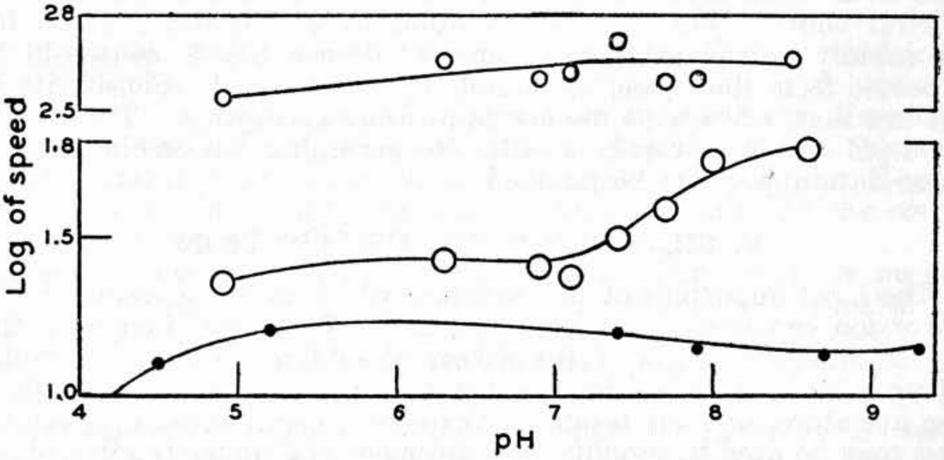

FIGURE 4.—*Variation in sensitivity with hydrogen ion concentration*

o Speed for white light exposure, unsensitized emulsions.
O Speed for exposure through Minus Blue filter, pinacyanol-sensitized emulsions.
. Speed for exposure through Minus Blue filter, pinaverdol-sensitized emulsion.

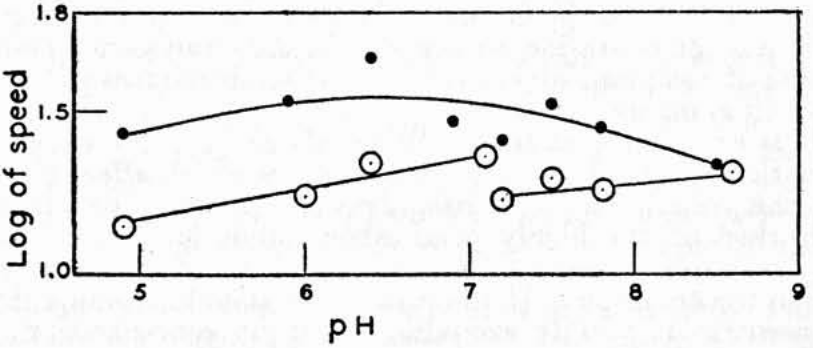

FIGURE 5.—*Variation in sensitivity with hydrogen ion concentration*

All exposures through Minus Blue filter.
. Pinaflavol-sensitized emulsions.
o Erythrosin-sensitized emulsions.

The effect of hydrogen ion concentration on sensitization by the dyes was apparently characteristic of the individual dye. At the most, it was less than the effect of silver ion concentration, as may be seen by comparison with the curves of Figures 6, 7, 8, and 9, which are on the same scale. Pinacyanol in the alkaline range (fig. 4) showed the largest effect, with little change between pH 7 and 5. Erythrosin consistently increased in effectiveness with increasing pH; this may possibly be explained by increasing dissociation, as it is the salt of a weak acid. Pinaflavol showed a maximum around the neutral point. (Fig. 5.) Sensitization by pinaverdol (fig. 4), fell off rapidly as the acidity was increased past pH 5, as would be expected from the decolorization of this dye by acid. Sensitivity at pH less than 4.5 became too low to measure accurately. The change from pH 5 to 9 was quite small. No generalization on the basis of these data appears to be justified.

V. SILVER ION CONCENTRATION

The most important of the variables which we have studied is the silver ion concentration of the emulsion. This condition may also be expressed in terms of the excess of soluble bromide or soluble silver salts in the emulsion, as has been the commonest practice in the literature, but our results indicate that the silver ion concentration may be used to simplify the statement and understanding of the condition in a manner quite analogous to the use of hydrogen ion concentration for acidity and alkalinity. As explained in previous communications (4) (5), the emulsion may be considered as saturated with silver bromide, so that the product of silver and bromide ion concentrations is a constant at a given temperature (9×10^{-13} at 30°) and either concentration may be computed from the potential of a silver electrode in the emulsion and used to express its condition. The addition of soluble bromide to an emulsion thus decreases its silver ion concentration; the addition of a soluble silver salt increases the silver ion concentration. In both cases the rate of change is less in the emulsion than it would be in plain aqueous solution. Adsorption of soluble bromide on silver bromide retards the increase in bromide ion concentration on one side of the equivalence point, and formation of unionized silver-gelatin compounds reduces the silver ion concentration on the other side.

As it is essential that the sensitizer should dye the silver halide, sensitization will be dependent on conditions which affect its adsorption to the grain. The sensitizing dyes are known to be ionized, and are adsorbed on the highly polar silver halide lattice, so that it is relatively simple to predict some of the effects of silver ion concentration in the emulsion. In the presence of soluble bromide (bromide ion concentration greatly exceeding silver ion concentration), silver bromide will strongly adsorb bromide ions at the silver ions of the crystal lattice, and will acquire a negative charge. The adsorption of the negatively charged ion of an acid dye, such as erythrosin, will thus be reduced, since it must compete with the bromide ions for the silver ions of the lattice. The presence of an excess of silver will, conversely, increase the adsorption of the color ion of an acid dye on silver bromide, because the silver ions of the lattice will be free of adsorbed bromide and thus more available to the ions of the dye.[5]

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[5] It should be remembered that in a gelatin emulsion, the adsorption of the gelatin to the silver bromide interferes very materially with the adsorption of either type of dye. This is almost certainly one of the reasons why gelatin emulsions are not sensitized as readily as collodion emulsions.

By the same type of reasoning we may predict that the adsorption of basic dyes should be greater in the presence of an excess of bromide ions, and should be reduced by an excess of silver ions.

The shift in adsorption of dyes with silver ion concentration is used in the titration of silver against halogen with adsorption indicators (16). It is of interest that the best results are obtained with acid dyes (fluorescein and the eosins, including erythrosin) and that the basic dyes which can be used as indicators (17), methyl violet for example, may be used as sensitizers for collodion emulsions. The first observation of the effect was apparently made by von Hübl (18) who discovered a change in color of cyanine on silver bromide with the addition of excess silver or bromide to the solution. Lüppo-Cramer (19) found that, in accordance with the theory, erythrosin was displaced from various insoluble salts by the corresponding anions, while basic dyes were not.

Observations on collodion emulsions (20) have been in accord with the simple theory. Acid sensitizers are adversely affected by the slightest traces of soluble bromide, and are preferably used with the addition of soluble silver salts, while the basic dyes are most effective in the presence of a slight excess of bromide. It should be remembered that collodion emulsions are not sensitized by the basic dyes, such as pinacyanol, until the alcohol has been largely displaced by washing with water, so that we are justified in discussing the ionization on the basis of an aqueous system.

Lüppo-Cramer (21) (22) found that in sensitizing gelatin emulsions by bathing, erythrosin was more affected by soluble bromide in the dye bath than was the basic dye pinachrome. However, the simple theory just given fails to predict that small amounts of soluble bromide will cause any decrease in sensitization by basic dyes, and something further is necessary to account for the fact that this decrease exists and is of such magnitude that most writers have failed to note the difference between the behavior of the acid and basic dyes. In the first place, the adsorption of the basic sensitizing dyes on silver bromide is not as simple as that of erythrosin. Sheppard, Lambert, and Keenan (14) found that at pH 5, pinacyanol was adsorbed much more strongly on silver bromide with excess of silver ions than on the same sample with excess of bromide ions. At pH 7.5 the order was reversed. Adsorption of dichlorofluorescein followed the simple theory. Bokinik (23) also reports stronger adsorption of pinacyanol on silver bromide with excess of silver ions than on an "equivalent" sample; the pH is not given. More data on adsorption of the basic sensitizers is evidently necessary for adequate theoretical treatment. In the second place, there is the possibility of some factor depending on silver ion concentration and affecting acid and basic dyes alike, the effects of changes in adsorption being superposed on this. In a system such as the photographic emulsion where gain or loss of bromine is probably the significant chemical change, the oxidation-reduction potential should depend on the silver (or bromide) ion concentration in a manner exactly analogous to its dependence on hydrogen ion concentration. If we adopt the working hypothesis that sensitization is the result of chemical reduction of silver bromide by the dye, a decrease in sensitization by increasing bromide ion concentration is to be expected. This hypothesis involves the simplest and most definite mechanism of sensitization, and in the absence of proof to the contrary,[6] we believe it is worthy of support (24). It is essentially the converse of the oxidation theory of desensitization. The implied continuous gradation between sensitization and desensitization has been realized by Kögel and Bene (27) and in this laboratory (28) by change in silver ion concentration. Independent evidence of photochemical reaction between silver bromide and sensitizing dyes is given by the accelerated bleaching of the dyes when adsorbed on silver bromide.

As the relative magnitude of the effects of changes in oxidation-reduction potential and in adsorption can not be predicted, the change in sensitization with silver ion concentration, which is the algebraic sum of these effects, may take a variety of forms, but we may at least expect that the basic dyes will be less sensitive to the addition of soluble bromide than the acid dye.

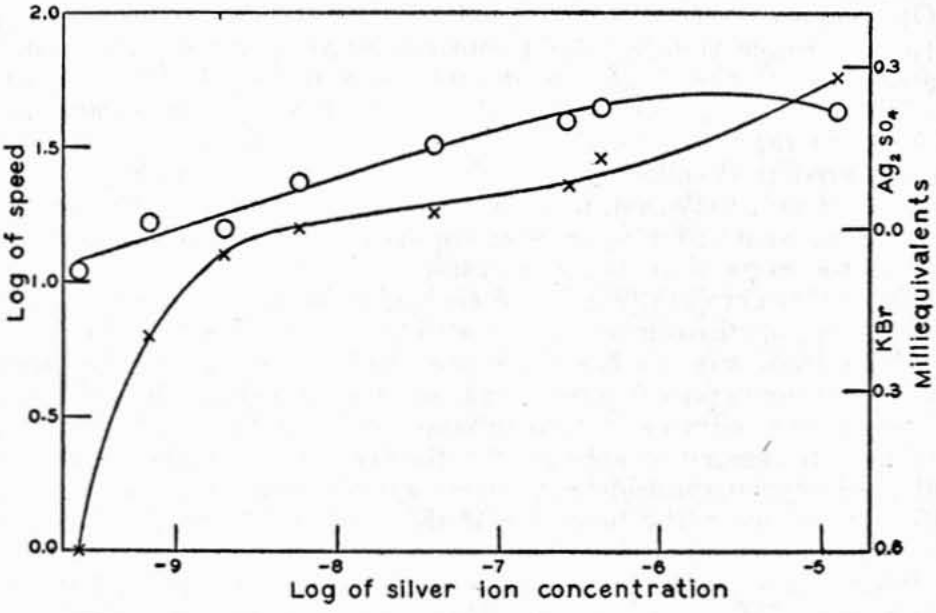

FIGURE 6.—*Variation in sensitivity with silver ion concentration*

O Speed of pinaverdol-sensitized emulsion for exposures through Minus Blue filter.
X Quantities of silver sulphate or potassium bromide added to 175 ml of emulsion, containing 0.040 equivalent of silver bromide, to produce indicated silver ion concentrations.

Our data are presented in Figures 6, 7, 8, and 9. The logarithm of the speed (at $\gamma = 1.0$) for exposures through the Minus Blue filter has been plotted against the logarithm of the silver ion concentration in the emulsions. The logarithmic scale for the speed numbers was adopted as the best means of comparing the data for emulsions which differed considerably in speed. The total (white light) sensitivity of

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[6] The results of Leszynski (25) have been widely quoted as proof that sensitization can not depend on photochemical reaction between the dye and the silver halide, since it is practically impossible thus to account for his reported yield of 20 atoms of photo-silver per molecule of erythrosin (without development). The writers are, however, unable to accept his data as adequate to a crucial test. The figure just quoted was obtained by ascribing to the action of the sensitizer all the silver found in an erythrosin-sensitized emulsion after exposure to green light, but Leszynski's own data show that the exposure used to secure the above yield was 10^5 times that necessary to produce a developable density of 1 in the same emulsion without the erythrosin, using exactly the same source of green light (an incandescent light with filter). Granting that green light was many times more effective in producing a developable image in the erythrosin-sensitized portion of the emulsion than in the unsensitized, the absence of control analysis on the unsensitized emulsion after the same exposure renders his conclusion very uncertain, especially as no details are given for his experiments which lead him to believe that the Becquerel effect was not involved. The results of Tollert (26) are open to the same criticism for lack of control experiments.

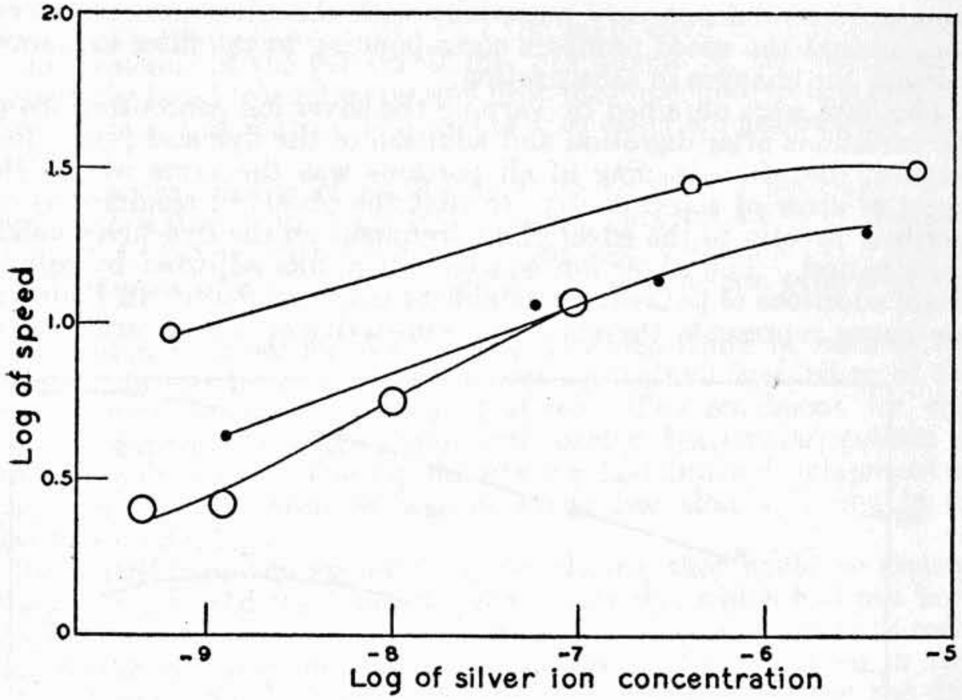

FIGURE 7.—*Variation in sensitivity with silver ion concentration, for erythrosin-sensitized emulsions*

. , o Neutral emulsions.
O Ammonia-process emulsion.
All speeds for exposures through Minus Blue filter.

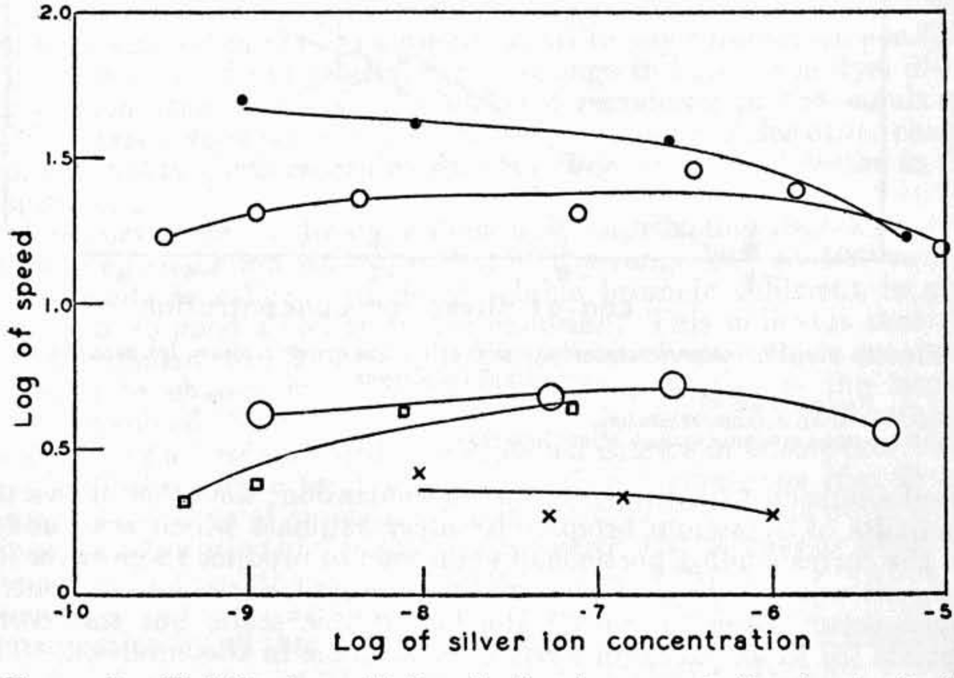

FIGURE 8.—*Variation in sensitivity with silver ion concentration, for pinaflavol sensitized emulsions*

, o Neutral emulsions.
X , □ Ammonia-process emulsions.
All speeds for exposures through Minus Blue filter.

the emulsions did not vary materially with the silver ion concentration, so that the speed numbers corresponding to the filter exposures indicate the changes in sensitization.

The data were obtained by varying the silver ion concentrations of the emulsions after digestion and addition of the dye and just before coating; the after-ripening of all portions was the same within the limits of error of sensitometry, so that the observed results may be ascribed directly to the effect of environment on the dye-silver halide combination. The silver ion concentration was adjusted by appropriate additions of potassium bromide or silver sulphate. In Figure 6, one curve represents the change in sensitivity of a pinaverdol-sensitized emulsion with the silver ion concentration; the other shows the amounts of potassium bromide or silver sulphate which were added to the corresponding portions of emulsions to produce these silver ion concentrations. Equivalence of bromide and silver ion concentrations occurs close to −6 on the logarithmic scale, but this corresponds (5) to an excess of silver over bromine in the emulsion. The emulsion after washing (with no addition of bromide or silver) contained only a very slight amount of soluble bromide, but the silver ion concentration was repressed by the gelatin, and, therefore, was much smaller than the bromide ion concentration. The curve obviously corresponds to the change in potential of a silver electrode on passing

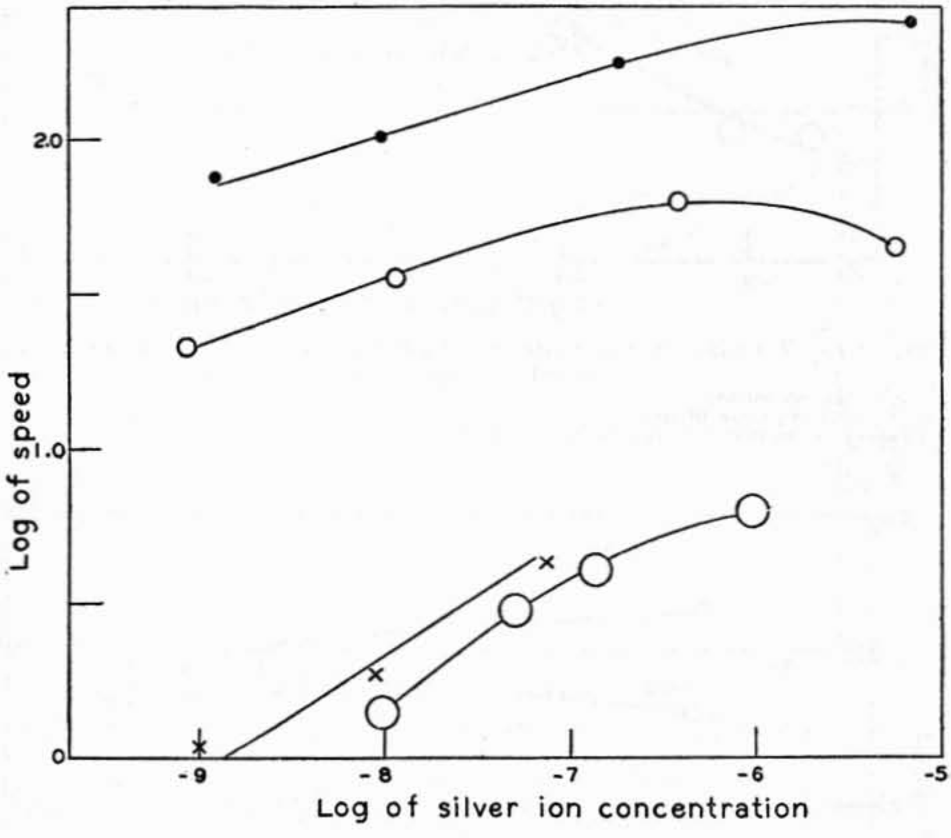

FIGURE 9.—*Variation in sensitivity with silver ion concentration, for pinacyanol-sensitized emulsions*

., o, Neutral emulsions.
X, O Ammonia-process emulsions.
All speeds for exposures through Minus Blue filter.

through the equivalence point of a titration of silver against bromide; in the presence of the gelatin at this pH (about 7), the equivalence point is displaced toward increasing bromide ion concentration and the "break" is not as sharp. The results with other emulsions were very similar.

Two general classes of emulsions were used—the neutral ("C") type, with 4.0 mol per cent AgI, coated at pH 7 ± 0.5, and the ammonia ("A") type, with 1.0 mol per cent AgI, coated at pH 8 to 8.5. No differences which could be ascribed to the emulsion type were detected.

The range of silver ion concentrations which could be used in the experiments was limited by the increasing fog and instability of the batches with increasing excess of silver. The emulsions for this series of experiments were made with partly deactivated gelatin in order to reduce fog. The fog density for 12-minute development in pyro-soda without bromide was normally less than 0.5, and in no case exceeded 0.75.

By centrifuging the experimental emulsions, they could be cleared of silver halide and the concentration of any dye which had not been adsorbed could be observed. The change in adsorption of erythrosin with changing silver ion concentration was readily detected in this way. It could not be measured with any accuracy because the dye changed in hue as well as in concentration, but by comparison with known solutions of the dye made up in a gelatin solution corresponding to the emulsion, it was estimated that in one emulsion, half the dye was adsorbed at a silver ion concentration of 1.2×10^{-9}, while five-sixths was adsorbed at a silver ion concentration of 3×10^{-6}. Pinacyanol and pinaverdol in photographically practicable concentrations were adsorbed too strongly to make any comparison possible, while the color of the gelatin, plus a change in hue of the dye, interfered with measurements of pinaflavol remaining in the emulsion. Quantitative work will obviously have to be done under other conditions, but it is worth recording that the effect could be detected in the emulsion.

The curves for all the dyes show that sensitization decreases with decreasing silver ion concentration in the range 10^{-7} to 10^{-10} which corresponds to concentrations of soluble bromide sufficient to give moderate to good stability to the emulsion. This indicates that the effect common to all dye-emulsion combinations, which we have ascribed to change in oxidation-reduction potential, is the largest factor involved. The differences between the dyes are significant and generally in accordance with the expected change in adsorption. The slopes of the curves for erythrosin-sensitized emulsions (fig. 7) are larger than those of emulsions sensitized with any of the other dyes, since the adsorption of this acid dye increases with increasing silver ion concentration and the sign of the resulting change in sensitization is, therefore, the same as that of the common factor. The curves for sensitization by all three of the basic dyes appear to reach a maximum value, the decrease in sensitization with increasing silver ion concentration being most certainly established for pinaflavol (fig. 8) and least certainly for pinacyanol. (Fig. 9.) The slopes of the curves on the bromide side of the maximum are least for pinaflavol and greatest for pinacyanol, pinaverdol being intermediate. Pinaflavol is by far the most soluble of the three basic dyes, and observations under comparable conditions both in the emulsion and with pure silver bromide indicate that it is less completely adsorbed than the other two. Changes in adsorption caused by change in silver ion concentration should, therefore, have more effect on the sensitization by pinaflavol than on that by the other basic dyes, and it is to be expected that the general trend should be more completely counteracted by the predicted decrease in adsorption with increasing silver ion concentration. The net result is that the change in sensitization by pinaflavol is close to the experimental error over a considerable range of silver ion concentration, although there is an unmistakable decrease at a sufficient excess of silver.

Increase in relative spectral sensitivity by increasing the silver ion concentration in the emulsion is very seriously limited in practice by the instability of the resulting product. If the emulsion must be kept for 6 to 12 months under ordinary conditions without serious deterioration (which might be regarded as the minimum commercial requirement) it is necessary in emulsions of the type used in these experiments to have the silver ion concentration approximately 2×10^{-9} N or less. (This corresponds to 2 to 3 molecules of soluble bromide per 1,000 of silver bromide). Silver ion concentrations up to 10^{-5} N are produced in hypersensitized materials (3), but these correspond to a useful life of a few weeks or even days. Deterioration of the emulsions in which the silver ion concentration was adjusted before coating went on at a rate increasing with this factor; the batches with the highest concentrations indicated behaved like hypersensitized materials.

A number of patents (29) have recently been secured on organic materials which are described as preservatives for emulsions. One of these, nitrobenzimidazol, has also been studied (30) as a substitute for soluble bromide in development. Since its use is patented, any practical investigation by this laboratory is unjustified, but the mechanism of its action is of considerable scientific interest. Nitrobenzimidazol was synthesized in this laboratory and purified by recrystallization from hot water and from alcohol. Its crystals formed the characteristic groups of flesh-colored needles, and melted at 209° C. The silver compound was prepared by precipitation from dilute aqueous solutions of nitrobenzimidazol and silver nitrate. After thorough washing, the silver ion concentration in saturated solutions of the compound was determined by the silver electrode at 30° C. At pH 7.1 (in 0.010 N sodium acetate solution) it was found to be 2.3×10^{-7} N, indicating that the compound is more insoluble than silver bromide. The silver is, however, readily displaced by hydrogen, since at pH 3.5 (0.010 N acetic acid) the silver ion concentration in a saturated solution was 6.4×10^{-5} N. In emulsions at approximate neutrality it produces some decrease in silver ion concentration, but experiments on afterripening with the addition of nitrobenzimidazol indicated that mol for mol, it produces about ten times the effect of soluble bromide in delaying afterripening. Something more than the decrease in silver ion concentration must be involved, and another method of attack would be necessary to decide what this might be.

Experimental emulsions were divided after digestion into portions which were, respectively, coated unsensitized and sensitized with erythrosin, pinaflavol, and pinacyanol, each of these being subdivided into halves with and without the addition of nitrobenzimidazol. It was found that the preservative selectively depressed the sensitivity conferred by the dyes, the effect being greater for the exposures through the filter than for the white-light exposures of the unsensitized portions. The effect was of the same order of magnitude as would be produced by soluble bromide with the same preservative action, although our data do not exclude the possibility that under other conditions this stabilizer might be superior to soluble bromide in this respect. The effect of the nitrobenzimidazol on the individual dyes was appreciably different from that of soluble bromide. The depression of sensitization increased in the order erythrosin < pinaflavol < pinacyanol. A possible explanation may again be found in terms of adsorption. The insolubility of the silver compound of nitrobenzimidazol indicates that this material should be strongly adsorbed by the silver bromide, most probably by the silver ions. This would bring it into competition with the basic, rather than the acid dyes, so that erythrosin should be the least affected of the three.

VI. Acknowledgment

C. M. Kretchman has rendered valuable assistance in coating and testing the experimental emulsions.

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THE PHOTOGRAPHIC EMULSION: THE MECHANISM OF HYPERSENSITIZATION

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ABSTRACT

Confirming earlier work at the Bureau of Standards, hypersensitization by bathing with ammonia is shown to consist of a selective increase in sensitivity for the spectral region of sensitization by the dye. Hypersensitization by a given solution is highly dependent on the dye and to a less extent on the emulsion; for many commercial panchromatic emulsions, water is preferable to ammonia solutions for practical use. On bathing a photographic emulsion in a solution there is set up a membrane equilibrium which is shown by electrode measurements to obey the Donnan equation. As a result of an almost unique combination of properties, bathing with ammonia and drying leaves an emulsion with an excess of silver over halogen; this is confirmed by chemical analysis of plates and baths used for hypersensitization. Comparison of data on the effect of ammonia on sensitization by known dyes with those of Research Paper 488 on the effect of silver ion concentration in the emulsion on the same dyes shows very close correspondence. There is satisfactory correlation between the photographic effects of ammonia treatment and those of excess silver in the emulsion; other theories of hypersensitization, which are discussed briefly are shown to be inadequate. Reports of hypersensitization by hydrogen peroxide are shown to be the result of inadequate control experiments, but appreciable hypersensitization by reducing agents was confirmed.

CONTENTS

I. THE PHENOMENA OF HYPERSENSITIZATION

Silver halides emulsified in gelatin selectively absorb radiation of the shorter wave lengths; for bromiodide, the absorption is very small for wave lengths greater than 500 mμ, and for other halides the limit is shorter. Photographic sensitivity necessarily corresponds to the absorption. As discovered by Vogel in 1876, certain dyes which absorb the longer wave lengths may sensitize silver halide emulsions for these regions. This increase in sensitivity for the region absorbed by the dye is, however, almost invariably accompanied by a decrease in the short wave length sensitivity of the emulsion. The magnitudes of both these changes are involved in a determination of the effectiveness of sensitization in a given case. In the comparison of the sensitization of a given emulsion by a given dye under varying conditions, which was the principal determination made in the experiments described in this paper and in our preceding communication (Research Paper No. 488) we found two of the three possible general types of change. Long and short wave length sensitivity may increse or decrease together, the change in the ratio of sensitivity to the two regions being less than the changes in absolute values. The long wave length sensitivity may increase or decrease with relatively constant short wave length sensitivity, and correspondingly large changes in relative spectral sensitivity. The third case of constant long wave length sensitivity and varying short wave length sensitivity has not been encountered. Change in the absolute values of sensitivity for both long and short wave lengths with constant relative spectral sensitivity was first reported by Sheppard (1)[1] as a result of sensitization by allyl thiocarbamide, or desensitization by chromic acid, these procedures involving, respectively, the formation and destruction of sensitivity nuclei. The writers have found similar effects (2), although the fractional change in long wave length sensitivity was generally the smaller. Changes in hydrogen ion, or even more in silver ion concentration in the emulsion (2) tend to increase the long wave length sensitivity with little change in the short wave length sensitivity. In contrast to the first case, the relative spectral sensitivity is greatly changed.

The discovery that sensitization by a dye could be improved by changing conditions in the emulsion was first made by Schumann (3), who found that a preliminary bath of ammonia improved sensitization by cyanine; in spite of numerous other suggestions, ammonia is still the most important hypersensitizing agent. We shall use the term "hypersensitization" to cover any case in which increase in sensitization by a dye is produced by treatment with a material itself colorless or absorbing a spectral region different from that of the dye. The term has been most commonly applied to after treatment of plates or films sensitized in the emulsion, but the mechanism appears to be the same whether the hypersensitizing agent is applied before, with or after the dye, and there is generally little difference in the magnitude of the effect.

Hypersensitization of course implies an increase in sensitivity to the longer wave lengths. In spite of the numerous investigations of the subject, there is still some dispute as to whether the sensitivity for the shorter wave lengths is normally increased. In the latest edition of Eder's Ausführliches Handbuch der Photographie, Dieterle (4) states that the change in this region is relatively small. Experiments at this bureau (5) (6) have been in entire agreement that hypersensitization normally involves a great increase in relative sensitivity to the longer wave-lengths; the data of Walters and Davis (6) are particularly clear on this point. However, Wall (7) reported that in a "long series of experiments where there was so-called increased color sensitiveness, there was also increased general sensitivity, and if the ratio of the blue to the color sensitiveness was taken into account, there was practically no increase in the same." We are, therefore, including in this paper data which demonstrate that in our experiments hypersensitization always involved an increase in relative sensitivity to the longer wave lengths.

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[1] **Numbers in parentheses here and throughout the text refer to the list of references at the end of the article.**

These data also show a fact which has been imperfectly understood: That a given treatment may produce marked hypersensitization in one plate or film, and none in another. These differences are to be attributed primarily to the dye and secondarily to the emulsion. The data of Walters and Davis (6) for example, show clearly that the isocyanine dyes, pinaverdol, and orthochrome *T*, were hypersensitized very little by ammonia, while it produced a large effect on sensitization by pinacyanol, and a still larger one on sensitization by dicyanine. Jacobsohn (8) has reported that a neutral emulsion could be readily hypersensitized by ammonia, while a comparable emulsion made by the ammonia process could not. Other illustrations could be given, but these will serve to make the point that it is impossible to say that a given bath will or will not cause hypersensitization without specifying the dye and emulsion. Some of the confusion on this point has probably risen from the varying requirements of users; in certain types of spectrography, for example, all other properties may be sacrificed to sensitivity, and it is possible to work with plates having fog which would be intolerable for pictorial use. The use of various methods of testing, some of them quite imperfect, have added to the misunderstandings.

The most serious error in some studies of hypersensitization has been the lack of adequate controls. The great majority of panchromatic emulsions are considerably improved in sensitivity to the longer wave lengths simply by washing with water ((6) and Table 1). It is therefore essential that the hypersensitizing action of any solution should be compared with that of water, under the same conditions of bathing and drying. If the emulsion is compared only without treatment, and after treatment with a given solution, effects which are actually caused only by the water of the solution may be ascribed to the dissolved substance.

In these experiments, sensitivity was determined by nonintermittent exposure in the sector-wheel sensitometer through appropriate filters to isolate spectral regions absorbed by the dye and by the silver halide. In a few cases, the sensitivity conferred by the dye was such a small fraction of the total that exposure to white light could be substituted for exposure to blue light without serious error. Sensitivity has been reported in terms of speed numbers $(10/i)$[2] corresponding to development to a constant γ. This was 1.0, unless the emulsion was of high contrast, when a value in the working range was chosen.

The plates or films were bathed for about three minutes at a temperature of 10° to 15° C. with constant rocking, and dried in a rapid current of air. The drying should be rapid. Unless the air temperature is less than 25° C. and the humidity at a low relative value—such as exists in heated rooms in cold weather, it is desirable to accelerate the drying by soaking the plate in alcohol for a few minutes after bathing. This treatment unfortunately can not be applied to most films. The entire emulsion surface was exposed to the air current in our drying apparatus; it is important that no part of it

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[2] In the values of inertia (i) no correction was made for the absorption by the filter, so that the speed numbers are comparative only. This results, for example, in low values of speed numbers for blue light, since the transmission of the "C" filter is not over 27 per cent for any wave length.

should be shielded by the plate rack or other obstruction if the dried plate is to be uniform in sensitivity.

Table 1 gives data on the hypersensitization of six fast commercial panchromatic emulsions. Similar data for another emulsion may be found in the control experiments recorded in the first three lines of Table 7. Exposures to "blue" light were made through the Wratten C filter, those to "red" light through the Wratten A, in both cases in addition to the Davis-Gibson correction filter. In three cases, plate B and films B and C, two emulsion numbers are represented in the comparisons of the washed emulsion with the untreated and ammonia-treated emulsion, respectively.

TABLE 1.—*Hypersensitization of commercial panchromatic plates and films*

Emulsion	Bath	Halide extracted by bath, molar ratio to AgBr $\times$ 1,000		Speed at $\gamma=1.0$		Fog for 6-minute development
		Br−	Cl−	Red light	Blue light	
Plate A	None	--	--	82	74	0.39
	Water	5.2	10.5	173	57	.41
	0.05 *N* NH_3	7.5	11.6	195	58	.44
Plate B:						
Emulsion 2	None	--	--	43	35	.28
	Water	--	--	85	31	.33
Emulsion 1	do	1.6	64	42	13	.27
	0.25 *N* NH_3	8.4	63	59	19	.42
Plate C	None	--	--	15.5	20.5	.21
	Water	.7	0	17	22	.23
	0.5 *N* NH_3	5.2	0	51.5	39	.42
Film A	None	--	--	17	34	.23
	Water	5.8	38	51	--	.23
	0.25 *N* NH_3	15.4	38	50	50	.29
Film B:						
Emulsion 1	None	--	--	23	37	.23
	Water	9.9	35	102	69	.24
Emulsion 2	do	8.8	38	60	43	.21
	0.25 *N* NH_3	17.6	35	100	60	.21
Film C:						
Emulsion 2	None	--	--	40	38	.19
	Water	4.5	13	70	56	.20
Emulsion 1	do	3.7	0	57	40	.21
	0.25 *N* NH_3	17.3	0	100	30	.72

Several observations may be made on these data. In the first place, the increase in red-light speed was invariably greater than the increase in blue-light speed, so that the relative sensitivity to the longer wave lengths increased. This is in agreement with previous experiments at this bureau, and in contradiction to Wall's statement. The sensitivity to blue light normally was increased,[3] but the increase was comparable with that in red-light speed in only two cases (ammonia treatment of pl. B and film B).

The second point of interest is that treatment with water alone was almost as effective as the use of ammonia solutions, with the one ex-

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[3] Pl. A shows the unusual and unexplained effect of a decrease in sensitivity to blue light on washing; the change is small, but apparently real. The decrease in film C on ammonia treatment is obviously the result of the heavy fog which was produced.

ception of plate C.[4] The difference between water and ammonia was much more marked for the panchromatic emulsions tested by Walters and Davis (6) and for some of our experimental emulsions sensitized with known dyes, recorded in Tables 2, 3, and 5. Spectrograms indicate that the dyes now used for sensitization are different from those in use only a few years ago. As the use of water involves less risk of causing fog than the use of ammonia, especially if the plates are to be kept any time after bathing, it is preferable for most cases. The increase in speed which is obtainable even from the fastest panchromatic emulsions by simple bathing with cold water is evident from the data.

TABLE 2.—*Hypersensitization of experimental emulsion 4–143*

[Speed numbers are relative only, the correction filter having been omitted in these tests; all values are for development to $\gamma=1.0$]

Bath	Speed numbers		
	Unsensitized emulsion	Pinacyanol-sensitized emulsion	
	Blue-light exposure	Blue-light exposure	Red-light exposure
None	18.5	12.5	70
Water	22	17	165
0.001 *M* N_2H_4	27	17.5	250
0.25 *M* NH_3	63	39	800

TABLE 3.—*Hypersensitization of experimental emulsion 4–145*

[Speed numbers are relative only, the correction filter having been omitted in these tests; all values are for development to $\gamma=1.0$]

Bath	Speed numbers		
	Unsensitized emulsion	Pinacyanol-sensitized emulsion	
	Blue-light exposure	Blue-light exposure	Red-light exposure
None	45	23.5	55
0.001 *M* N_2H_4	47	45	365
0.25 *M* NH_3	89	110	635

The magnitude of the change in sensitivity to blue light is of considerable importance in deciding on the mechanism of hypersensitization. In panchromatic emulsions, it is generally larger than would be expected from the fact that many unsensitized emulsions are practically unaffected by washing or ammonia treatment. Moderate speed commercial emulsions (Seeds 23, Eastman 33 and 36), and comparable experimental emulsions showed no increase in speed on bathing in ammonia, although other unsensitized experimental emul-

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[4] Reference to column 3 shows that pl. C contained an unusually small amount of soluble bromide. This accounts for the constant sensitivity on washing. The data on bromide extracted by the ammonia solutions will be discussed later in the paper. The increase in red-light speed of film C on ammonia treatment was accompanied by an increase in fog which made the film practically useless.

sions have given positive results. The experiments recorded in Tables 2 and 3 demonstrate that the sensitizing dye changes sensitivity to blue light, although it does not sensitize for this region. The emulsions used for these experiments were made by the neutral process, differing only in that the silver iodide was 1 per cent of the total silver in 4–143 and 4 per cent in 4–145. After washing, potassium bromide in the molecular ratio of 5 KBr per 1,000 AgBr was added to each emulsion, and they were digested to rather less than maximum sensitivity. Each emulsion was coated in two portions, one unsensitized and the other with the addition of pinacyanol. After drying, plates were treated as indicated in the tables and tested. The tables show that the pinacyanol, plus the soluble bromide, reduced the sensitivity of the emulsions to blue light. On washing with water which removed the soluble bromide, the blue-light sensitivity of the pinacyanol-sensitized portions was restored to the original value; that of the unsensitized portion was only slightly increased, as would be anticipated from the relatively small effect of silver ion concentration on sensitivity in the absence of dyes (9). The increase in blue-light sensitivity on washing the commercial emulsions recorded in Table 1 may therefore be interpreted as the removal of a desensitizing effect, since all dyes in the presence of bromide cause some desensitization to the blue. Emulsions 4–143 and 4–145 (Tables 2 and 3), probably because of incomplete digestion, increased in speed on ammonia treatment of the unsensitized portions; the blue-light speed of the sensitized portions increased in about the same ratio. In all cases, the increase in red-light speed was much greater than the increase in blue-light speed.

In order to understand the photographic effects produced by bathing with ammonia, it will be necessary first to consider the chemical equilibrium set up by this process.

II. THE EQUILIBRIUM BETWEEN PHOTOGRAPHIC EMULSIONS AND AMMONIA SOLUTIONS

If two solutions are separated by a membrane which is permeable to the solutes, diffusion through the membrane will ultimately bring the concentrations on both sides to the same values. If, however, there is present in one of the solutions an ion which can not diffuse through the membrane, this will result in an uneven distribution of all the ions between the two sides of the membrane when the system has reached equilibrium. Donnan (10) has demonstrated that the equilibrium is governed by the relation that the ratios of concentrations of all diffusible univalent ions of the same sign, on the two sides of the membrane shall be the same, and that the product of the concentrations of any pair of (univalent) positive and negative ions on one side of the membrane shall be the same as the product of the concentrations on the other side.

When a jelly, such as a photographic emulsion, is immersed in a solution, the Donnan equation may be applied to the concentrations of the solution inside and outside the jelly. Let us consider first the case of an emulsion of pure $AgBr$ in gelatin bathed in a solution of an alkali, such as $NaOH$. The gelatin is permeable to all the ions of $NaOH$ and $AgBr$, so that all four of these will be found both inside and outside the emulsion at equilibrium. However, the gelatin combines with OH^- to form a negatively charged complex which acts as a nondiffusible ion present only inside the gelatin and thus causes an uneven distribution.

According to Donnan's equation

$$\frac{[OH^-]_o}{[OH^-]_i}=\frac{[Br^-]_o}{[Br^-]_i}=\frac{[Na^+]_i}{[Na^+]_o}=\frac{[Ag^+]_i}{[Ag^+]_o}$$ (where the subscripts i and o indicate the inside and outside solutions, respectively)

$[OH^-]_o > [OH^-]_i$ because of the combination of OH^- and gelatin, so that

$$[Ag^+]_i > [Ag^+]_o \text{ and } [Br^-]_i < [Br^-]_o$$

The excess of positively charged diffusible ions in the gelatin is electrically balanced by the negative (gelatin $OH)^-$ complex, and $[Ag^+]_i > [Br^-]_i$. If the emulsion is removed from the solution and dried, it will be left with an excess of Ag^+ over Br^-, the excess Ag^+ being in combination with the gelatin (11); the solution will contain an excess of bromine over silver, since these were originally in equivalence in the emulsion.

Silver bromide being very difficultly soluble, the quantities involved are very small, and it is only by repeated extraction that any considerable excess of silver can be left in the emulsion. If, however, ammonia is substituted for the simple alkali, the solubility of silver bromide is so increased that much larger effects may be produced. The equilibrium is essentially the same although complicated by the second equilibrium

$$\frac{[Ag^+]\times[NH_3]^2}{[Ag(NH_3)_2{}^+]}=K$$

which results in a decrease in $[Ag^+]$ to a very small value, with corresponding increase in $[Br^-]$ to maintain the condition that $[Ag^+]\times[Br^-]=S$ (solubility product of AgBr). The principal ions in the outside solution are therefore $Ag(NH_3)_2{}^+$, $NH_4{}^+$, Br^-, and OH^-. The same ions, plus the nondiffusible (gelatin-OH)$^-$, are present inside.

$$\frac{[Ag(NH_3)_2{}^+]_i}{[Ag(NH_3)_2{}^+]_o}=\frac{[NH_4{}^+]_i}{[NH_4{}^+]_o}=\frac{[Br^-]_o}{[Br^-]_i}=\frac{[OH^-]_o}{[OH^-]_i}$$

Ammonia being alkaline, we have, as before, that $[OH^-]_o > [OH^-]_i$ and consequently that $[Ag(NH_3)_2{}^+]_i > [Ag(NH_3)_2{}^+]_o$ and $[Ag(NH_3)_2{}^+]_i > [Br^-]_i$. The concentrations of $Ag(NH_3)_2{}^+$ and Br^- being much greater than those of Ag^+ and Br^- in simple alkali solutions, an emulsion bathed in an ammonia solution is left with an appreciable excess of $Ag(NH_3)_2{}^+$ over Br^-. On drying the film the complex ion must decompose, since all known compounds of silver salts and ammonia are in equilibrium at room temperature only with ammonia pressures of the order of 100 mm of mercury. Before drying, the $Ag(NH_3)_2{}^+$ ions had been electrically balanced by the negative gelatin ion, formed by combination of the gelatin and OH^- ions. As the ammonia is removed, the remaining Ag^+ ions tend to combine with the gelatin ion. In the quantities formed by hypersensitization, the silver gelatin complex is in equilibrium (11) with a silver ion concentration enormously greater than that of the emulsion before treatment. A normal emulsion contains about 3×10^{-3} g equivalent of AgBr per gram of gelatin; if 1 per cent of this is decomposed by the ammonia treatment, 3×10^{-5} g equivalent of Ag^+ will be combined with 1 g of gelatin; this corresponds at pH 9 with a silver ion concentration of 10^{-6} N as against 10^{-10} N in an average emulsion as coated. In an emulsion bathed with water alone, the final silver ion concentration will probably be less than one-tenth that produced by ammonia.

It will be noted that this final result is dependent on several conditions, which are fulfilled almost uniquely by ammonia and some of the amines. Ammonia gives an alkaline solution which dissolves silver salts by formation of a positively charged complex ion of silver, which breaks down on drying. If the complex ion containing the silver is negatively charged, as in cyanide, thiosulphate, sulphite or thiocyanate solutions, its distribution will follow the same ratio as the bromide ion and there will be no excess of silver left in the emulsion and no hypersensitization.[5] A nonvolatile complex would also prevent the final rise in $[Ag^+]_i$ on drying. The magnitude of the final effect will increase with increasing solubility of silver bromide, and consequently with increasing concentration of ammonia. The presence of soluble bromide reduces the effect of the ammonia, since $[Br^-]_i$ may be greater than $[Ag(NH_3)_2^+]_i$ if there is enough soluble bromide present, even though the ratios of inside and outside concentrations are the same as in the absence of soluble bromide. Conversely, the effect is increased by the addition of silver salts, such as the chloride or oxide, to the ammonia bath. An acid solution dissolving silver salts by formation of a volatile negative complex would produce the same effect as ammonia, but as far as we know, no such solution exists.

The applicability of the Donnan equation to equilibrium between silver bromide-gelatin emulsions and ammonia solutions was demonstrated experimentally. For quantitative results it was necessary to use liquid emulsion, separated from the ammonia solution by a membrane. Ion concentrations can not be measured in the set emulsion on a plate; and because of the volatility of the ammonia and the necessary change in temperature, it was also impracticable to bring the emulsion on a plate to equilibrium, then strip and melt it for measurements. Accordingly, 50 ml samples of emulsions were placed in small sacks of goldbeater's skin or collodion which were surrounded with ammonia solution, the system being maintained at 30.0° C. by an air thermostat. Stoppers into the sack and the outside vessel made it possible to insert into either one a silver-silver bromide electrode and salt bridge to determine the bromide ion concentration, or to remove samples of either solution. The readings taken with the electrode near the membrane were found to be somewhat uncertain, so that the final readings were all taken on samples which had been pipetted into a closed cell. The bromide ion concentration never became entirely constant, even after agitation for 24 hours or more, but the slow drift after this time was apparently caused by hydrolysis of the gelatin in the emulsion by the ammonia, with conse-

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[5] One hypothesis as to the mechanism of hypersensitization was that it is caused by intragranular etching of the silver halide grains by the ammonia, with consequent exposure of fresh surface for the dye. Lüppo-Cramer (12) tested this by adding one-half per cent Na_2SO_3 or KSCN to dye baths; we used 0.0034 N KCN, which is equivalent to 0.5 N NH_3, in solvent action for silver bromide. The negative results which were obtained could have been predicted from the failure of these baths to leave the emulsion with excess silver, and the strong adsorption of the anions of these solutions, which would tend to replace the basic dyes.

quent formation of diffusible amino acids whose buffer action in the outside solution reduced the pH difference between the inside and outside; after the first day, the drift in electrode potential became less than 1 mv per day. Readings were then taken on samples from the emulsion and the outside solution both with the silver-silver bromide electrode and the glass electrode (each being compared with a standard calomel electrode). We are indebted to M. R. Thompson, of the chemistry division of this bureau, for making the difficult measurements of hydroxyl ion concentration in these systems with the glass electrode.

If the equilibrium obeys the Donnan equation, then

$$\frac{[\mathrm{Br}^-]_o}{[\mathrm{Br}^-]_i}=\frac{[\mathrm{OH}^-]_o}{[\mathrm{OH}^-]_i}$$

Since the potential of either electrode is proportional to the logarithm of the corresponding ion concentration, if these two ratios are equal, the differences in potential of the two electrodes in the emulsion and the outside solution will be the same. The data in Table 4 show that this condition was fulfilled for both membrane materials and over a moderate range of conditions. The variations in the absolute values were caused by the concentration and volume of the emulsion samples and possibly by greater permeability of the collodion. Ammonia concentration was limited to about 0.05 N by the decreasing accuracy of the glass electrode at higher alkalinities.

TABLE 4.—*Equilibrium between AgBr-gelatin emulsions and ammonia solutions (originally 0.050 N) at 30.0° C.*

[Emulsions inside membrane, ammonia solution outside]

Membrane	[OH⁻]		[Br⁻]		Potential difference of electrodes outside and inside (in millivolts)	
	Outside	Inside	Outside	Inside	Glass electrode	Ag-AgBr electrode
Gold beater's skin	3.3×10^{-4}	1.12×10^{-4}	6.1×10^{-4}	2.0×10^{-4}	28	29
	4.2×10^{-4}	1.20×10^{-4}	3.9×10^{-4}	8.6×10^{-5}	31	38
	4.8×10^{-4}	1.31×10^{-4}	3.6×10^{-4}	7.2×10^{-5}	33	41
Collodion	3.5×10^{-4}	2.6×10^{-4}	2.3×10^{-4}	1.6×10^{-4}	7.6	9.1
	2.4×10^{-4}	1.7×10^{-4}	2.7×10^{-4}	2.1×10^{-4}	8.1	6.1
	4.0×10^{-4}	2.5×10^{-4}	2.4×10^{-4}	1.54×10^{-4}	11.6	11.5

The equilibrium was also studied under conditions comparable to photographic practice. Plates were bathed with constant rocking in ammonia solutions for three to five minutes, thereby approaching equilibrium within the limits of error of analysis, and the bath analyzed by electrometric titration. In order to eliminate the dissolved silver bromide from the solutions, the ammonia was either neutralized with acid or removed by evaporation; the two methods were found to agree within the limit of reproducibility of either one. The solution was then acidified to pH2–3 to prevent the trace of extracted protein from interfering with the end point, and titrated with 0.001 N $AgNO_3$ in the apparatus described in a previous communication (11). Electrometric titration is desirable, as many commercial emulsions contain soluble chloride in amounts as large as 10 molecules to 1 of soluble bromide; we have found the electrometric determination both simpler and more accurate than the possible purely chemical separations, such as the Lang method (13) (14). Figure 1 gives the results for extraction of Seed's 23 plates (emulsion 7,855) with varying concentrations of ammonia. These and subsequent data have been reduced to ratios of soluble bromide to silver bromide in the emulsion; the latter was determined by titration with cyanide according to the methods of Eggert (15) or Marasco (16). The data in the figure show that approximately 1 per cent of the silver bromide in the emulsion is decomposed by bathing in 0.25 N ammonia solution, the quantity increasing with ammonia concentration as would be expected. The existence of the excess silver in bathed plates is readily detected analytically. For example, Seed's 23 plates were given three successive extractions with 0.75 N NH_3, the sum of the soluble bromide in the extracts being 2.97 and 3.17 per cent of the total bromide in the emulsion. Nonhalide silver in the emulsion was then determined by cyanide extraction (14) to be 2.30 and 2.38 per

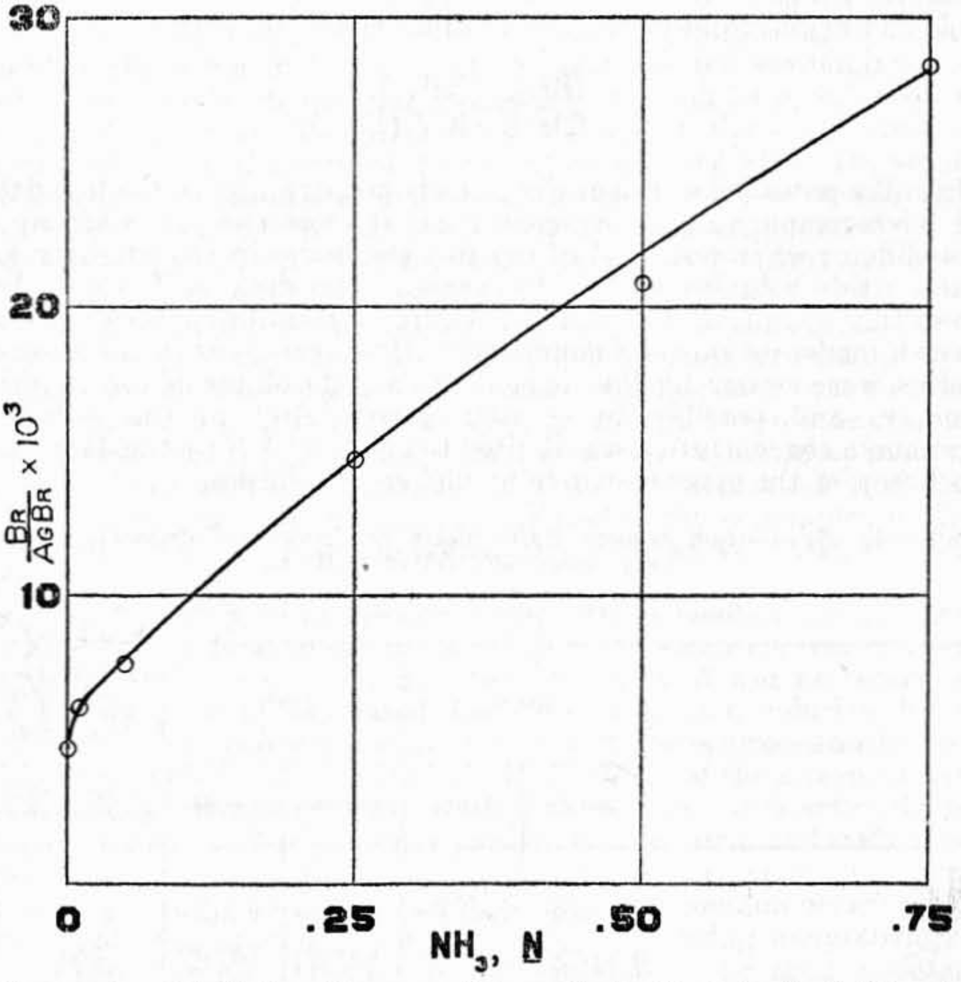

FIGURE 1.—*Soluble bromide removed from Seed's 23 plates by bathing in solutions of ammonia*

Ordinates, ratio of soluble bromide to silver bromide; abscissæ, concentration of ammonia.

cent of the total silver. The differences, 0.67 and 0.79 per cent are slightly larger than the soluble bromide originally present in the emulsion, 0.47 per cent by water extraction. Similar results were obtained with other emlusions demonstrating that the emulsion is left with an excess of silver over halogen corresponding to the excess of soluble bromide found in the ammonia extract over the soluble bromide originally present in the plate. Analysis of the complete emulsion for total silver and halogen by Clark's method (25) also proved that the soluble bromide found in the ammonia extracts of the Seed's 23 must have come from decomposition of the silver bromide, since no such amounts of soluble bromide were originally present in the emulsion.

The data of Table 1, columns 3 and 4, show that the commercial panchromatic emulsions were left with an excess of 0.2 to 1.0 per cent of silver over halogen after the ammonia treatment which produced the indicated photographic effects. The single extraction with water left the emulsions with a chemically negligible excess of either bromide or silver. As the increase in bromide extracted by the ammonia solution is the result of decomposition of silver bromide in consequence of the membrane equilibrium, the emulsion must have been left with an excess of silver equivalent to the difference between the ammonia and water extracts. It should be noted that the chloride extracted was the same whether water or ammonia was used, indicating that the emulsion closely approached equilibrium with the bath.

Having predicted and established that the result of bathing photographic plates or films with ammonia is to leave them with an excess of silver over halogen, proof of the mechanism of hypersensitization may be completed by comparison of the effects on sensitization produced by ammonia treatment and by addition of soluble silver salts to the emulsion.

III. CORRELATION OF THE CHEMICAL AND SENSITOMETRIC DATA ON HYPERSENSITIZATION

In previous communications (2) (17) we have reported the effects of increasing the silver ion concentrations of emulsions by addition of soluble silver salts before coating. In the absence of sensitizing dyes, there was a slight increase in sensitivity at normal values of pH. Sensitization by dyes was found to be selectively increased by large amounts, so that the most characteristic change was an increase in relative sensitivity for the longer wave lengths. Sufficient increase in silver ion concentration, however, caused a decrease in sensitization by some of the basic dyes, which had been predicted by theoretical consideration of adsorption relations.

Data on the effect of ammonia treatment of emulsions sensitized with known dyes are presented in Table 5. These are representative of a considerable number of experiments; they were selected as far as possible to compare the behavior of different dyes in the same emulsion. It will be observed that in all cases sensitization by pinacyanol was increased by ammonia; this is also true for erythrosin, although the increase in one case was quite small. Sensitization by pinaflavol was decreased by ammonia in every case where the dye was applied by bathing. In one emulsion, 4–103, the sensitivity passed through a maximum with increasing concentration of ammonia, corresponding to sensitization by pinaflavol with increasing silver ion concentration in the emulsion (2) which also passes through a maximum. This indicates that the failure of many commercial panchromatic emulsions to hypersensitize may be attributed to the characteristics of the dyes which are used. (Table 1.) Results with emulsion 4–128 are an exception; in the other experiments not recorded, hypersensitization of pinaflavol-sensitized emulsions occurred about one time in three. The sensitization by pinaverdol appeared to approach a maximum with increasing ammonia concentration, as would be expected from its behavior with increasing silver ion concentration.

TABLE 5.—*Hypersensitization with known dyes*

[Letters represent commercial emulsions which were bathed in the dye solutions, the ammonia being added to the dye bath. Figures represent experimental emulsions which were sensitized before coating and subsequently bathed with water or ammonia solutions]

Dye	Emulsion	Ammonia concentration N	Speed number for exposure through minus blue filter (compared at constant γ)	Fog for 6 minute development
Pinacyanol	A	0	25	0.40
		.05	59	.63
	4–103	0	13	.09
		.05	20.5	.05
		.25	50	.19
	4–128	0	36	.13
		.25	76	.24
Pinaflavol	A	0	28	.49
		.05	21	.50
	4–103	0	10	.18
		.05	17	.28
		.25	12.5	.39
	4–128	0	10	.65
		.25	23	.72
Erythrosin	B	0	21	.13
		.50	44	.28
	4–103	0	8	.02
		.05	19.5	.02
		.25	24	.04
	4–128	0	27	.15
		.25	29	.24
Pinaverdol	A	0	26	.09
		.05	53	.29
		.25	60	.72

Other amines are capable of producing effects similar to ammonia, by the same mechanism. We have already reported the mild hypersensitizing action of pyridine (18). Extraction of Seed's 23 plates with $N/2$ pyridine solution was found to remove soluble bromide equivalent to 0.66 per cent of the total bromide, indicating that the plate was left with 0.2 to 0.3 per cent excess silver. Triethanolamine has recently (19) been recommended for hypersensitizing. We have tested its action with pinacyanol and pinaverdol, and found that it is photographically equivalent to ammonia of lower concentration. Correspondingly, 0.25 N triethanolamine left a given emulsion with 0.3 per cent excess silver, and 0.25 N ammonia with 0.9 per cent excess. The lower alkalinity of triethanolamine is probably an advantage in cases where there is serious tendency to fog.

Bokinik (20) has recently observed, by comparing plates bathed with water and with dilute silver nitrate solution, that increased silver ion concentration has little effect on sensitivity in the absence of dyes, but produced typical hypersensitization of panchromatic emulsions. He further demonstrated that it was not a development effect. We have also experimented with hypersensitization by bathing in dilute silver nitrate solutions; pinacyanol-sensitized emulsions were hypersensitized, and pinaflavol-sensitized emulsions were slightly decreased in speed, but the results were more difficult to reproduce than when the silver salts were added to the emulsion before coating.

As predicted theoretically, dissolved silver salts in an ammonia bath increase its effect without change in the mechanism; typical examples are given as part of the data in Tables 6 and 7. In general, we have found little advantage in their use, as few emulsions are improved by silver ion concentrations higher than those produced by bathing in 0.5 *N* ammonia. As the membrane equilibrium just discussed would not apply to a collodion emulsion, it would be necessary to add silver salts to the hypersensitizing bath to leave such an emulsion with excess silver.

The increased silver ion concentration produced by ammonia treatment is the principal factor in hypersensitization. However, others have been suggested, and some of these must be considered seriously.

Alkalinity tends to increase sensitization by some of the dyes, notably pinacyanol and erythrosin (2). The effect is not large. One per cent borax solutions (pH 9.2) were carefully compared with pure water as solvent for dyes and for after treatment of emulsions sensitized before coating; the difference was negligible. Of course, if the dye has been applied from an acid bath, as is recommended for kryptocyanine (21) and isocyanines (22), it is desirable to neutralize the remaining acid with some alkaline buffer, such as borax.

Jacobsohn (8) has suggested that treatment with ammonia may break down silver bromide-allyl thiocarbamide complex, thus forming new sensitivity nuclei of silver sulphide. He had originally observed in his extensive experiments on hypersensitization that some emulsions were much more affected by given treatment than others; comparison of otherwise similar emulsions made by the neutral ("boiled") and ammonia processes showed that the former was much better adapted to hypersensitization than the latter. As the neutral type of emulsion might be expected to contain more unchanged complex, he explained the difference between the emulsions on this basis. It is impossible to say that this does not occur, even with the short time and low temperatures of hypersensitization, especially as the reaction is accelerated not only by the ammonia, but by the increased silver ion concentration. The emulsions used for the experiments recorded in Tables 2 and 3 were such that appreciable quantities of unchanged complex might have been present, and the increase in sensitivity of the unsensitized portions on treatment with ammonia indicates that new nuclei may have been formed. However, Jacobsohn's hypothesis is inadequate as a complete explanation of hypersensitization. The experiments by Sheppard (1) on the effect of silver sulphide nuclei on sensitization by dyes, which were quoted by Jacobsohn in support of his hypothesis, show that the relative sensitivity to the longer wave lengths remains practically constant on the formation of nuclei. Experiments in this laboratory (2) have also indicated that the relative sensitivity is constant, or decreases, whereas an increase in this ratio is characteristic of hypersensitization. The large effects of bathing with pure water are certainly to be explained by extraction of soluble bromide rather than by formation of new nuclei, since no commercially stable emulsion could be appreciably ripened in the short time and low temperature of bathing and drying. The effects of ammonia appear to differ only quantitatively from those of water. No certain explanation of Jacobsohn's observations can be given, since the actual emulsions are not available. However, factors other than unchanged silver bromide-thiocarbamide complex may make neutral emulsions better adapted to hypersensitization than those made by the ammonia process. Their pH is lower, so that more change both in hydrogen and silver ion concentrations would be produced by ammonia treatment. We have observed that under the same washing conditions ammonia process emulsions reach the lower bromide ion concentration, so that this may also reduce the change caused by the ammonia.

It has also been suggested that formation of silver nuclei by reduction of silver bromide might be a cause of hypersensitization. This explanation was used by Schmieschek (23) to account for hypersensitization by mixtures of silver salts and hydrogen peroxide. However, his conclusions are not supported by the experimental evidence. As far as can be determined by study of his publications, Schmieschek compared the plates treated with the mixed solutions only with untreated plates, and thus failed to observe that the hydrogen peroxide contributed nothing to the hypersensitization. His formulas were carefully tested on two emulsions, one of which, the Agfa Special Rapid panchromatic, had been used in his own experiments. The results are recorded in Tables 6 and 7. All the data in each table were obtained from plates which had been bathed under the same conditions of temperature, agitation, and time, dried together, and developed together after exposing. It is evident from the data that the ammonia-silver tungstate-hydrogen peroxide mixture was less satisfactory as a hypersensitizing bath than the ammonia alone, since at the best it produced no greater increase in sensitivity and the fog was higher. The same results were obtained in repeated tests. The peroxide decreased the effect of ammonia, and was of very doubtful advantage to the mixture of ammonia and silver salts, so that we are unable to agree with Schmieschek that it has any significant function. The Agfa plates were also bathed with mixtures of acetic acid, silver sulphate, and hydrogen peroxide as recommended by Schmieschek, and with the acid and silver sulphate, the plates being washed in faintly alkaline tap water after bathing. Both baths caused fog and desensitization, the decrease in sensitivity being greater from the mixture with the peroxide. Bokinik (24) also reports that he was unable to confirm Schmieschek's results, hydrogen peroxide decreasing rather than increasing the effect of silver salts.

TABLE 6.—*Hypersensitization of Agfa Special Rapid panchromatic plates (emulsion Q1666) by combinations of ammonia, silver tungstate, and hydrogen peroxide*

Composition of bath, grams per liter			Speed at γ=1.0		
Ammonia	Silver tungstate	Hydrogen peroxide	White light	Red light	Fog for 6-minute development
0	0	0	265	18	0.15
.65	0	0	360	38	.23
.65	0	.75	380	29	.28
.65	.14	0	430	31	.41
.65	.14	.75	320	39	.66

TABLE 7.—*Hypersensitization of Wratten "M" plates (emulsion 5173) by combinations of ammonia, silver tungstate, and hydrogen peroxide*

Composition of bath, grams per liter			Speed at γ=1.8		
Ammonia	Silver tungstate	Hydrogen peroxide	Blue light	Yellow light	Fog for 6-minute development
Untreated plate			10.5	59	0.13
0	0	0	11.5	86	.20
.65	0	0	15.2	180	.33
.65	0	.75	9.2	85	.22
.65	.14	0	9.7	140	.33
.65	.14	.75	13.5	145	.34

Bokinik (24) reports that both panchromatic and unsensitized plates were increased in sensitivity by bathing with 0.1 per cent (0.02 *M*) solutions of hydrazine hydrate. A reference in the summary of his paper indicates that other reducing agents were used, but no others are mentioned in the text. Bokinik's experiments with hydrazine were repeated with a number of commercial and experimental emulsions, some of the data being given in Tables 2 and 3. It was found necessary to use more dilute solutions than his; 0.001 to 0.0015 *M* gave at least as much increase in sensitivity as stronger solutions, and less fog. Commercial unsensitized emulsions such as the Eastman 33 were not increased in sensitivity by either hydrazine or ammonia. The effect of the hydrazine on the unsensitized portions of experimental emulsions 4–143 and 4–145 (Tables 2 and 3) was quite small, so that it is improbable that it produces new sensitivity nuclei of silver. The pinacyanol-sensitized portions of emulsions 4–143 and 4–145 were hypersensitized by the hydrazine, the action being similar to that of ammonia, but considerably less. Similar results were obtained with Eastman infra-red sensitive plates (emulsion 5,875).

The hypersensitizing action of the hydrazine is greater than can be explained by its alkalinity alone. Analysis of 0.0015 *M* hydrazine hydrate solutions which had been used for bathing plates showed that they had extracted practically no more bromide than water, so that the increase in silver ion concentration in the emulsions, compared to that produced by water, was negligible. Formation of new sensitivity nuclei by reduction of the silver bromide was improbable because the sensitivity to the longer wave lengths was selectively increased. It is possible that the increase in reduction potential of the emulsion can cause a moderate amount of hypersensitization. In order to test this hypothesis without the complications of membrane equilibria introduced by bathing the plates, small amounts of hydrazine and other reducing agents were added to sensitized emulsions just before coating. In this case, however, the reducing agent comes in contact with the warm liquid emulsion followed by a relatively slow drying, and a concentration of reducing agent producing a given potential may cause fog when it would not do so at the low temperature and short drying period used in bathing; for example, hydrazine at five times the maximum concentration given in Table 8 was found to cause heavy fog, although this amount made the liquid emulsion only 0.0010 *M* with respect to the hydrazine. The data are given in Table 8, omitting negative results with sodium arsenite and hydroxylamine hydrochloride. Ammonia is included in this table for comparison with the results obtained by bathing similar emulsions (as 4–145) with ammonia, not because it was considered to have appreciable reduction potential. The increase in sensitivity is about what might be expected from the increase in pH, which amounted to one unit, and is of a lower order of magnitude than the effect of bathing with ammonia solutions with the resulting membrane equilibrium.

TABLE 8.—*Effect of reducing agents on sensitization by dyes*

[Speed numbers are relative values, obtained by exposure through the Wratten filters only, without the Davis-Gibson correction filter; all values for development to $\gamma=1.0$. "B" (green) filter used for erythrosin-sensitized emulsion; "A" (red) filter for pinacyanol-sensitized]

Dye	Reducing agent	Molar ratio, reducing agent to silver halide	Speed through "C" (blue) filter	Speed through "B" or "A" filter	Ratio of speed numbers
Erythrosin	Control	0	125	54	0.44
	Ammonia	1.3×10^{-2}	130	55	.43
	Sodium sulphite	1.3×10^{-2}	155	87	.56
Pinacyanol	Control	0	64	165	2.6
	Ammonia	1.3×10^{-2}	75	215	2.9
	Sodium sulphite	1.3×10^{-2}	75	265	3.5
Pinacyanol	Control	0	37	130	3.5
	Hydrazine	2.8×10^{-4}	43	175	4.0
	Hydrazine	1.1×10^{-3}	53	180	3.4
	p-hydroxyphenylglycine	1.5×10^{-3}	60	170	2.9

The positive results with hydrazine, sodium sulphite and "Glycine" indicate that reducing agents may produce some increase in sensitization by dyes, even though they are without effect on the unsensitized emulsion. Control experiments demonstrated that neither sodium sulphite nor hydrazine added in these quantities and under these conditions increased the sensitivity of similar emulsions in the absence of dyes. This is at least consistent with the simple chemical theory of sensitization which we advocate as the best starting point for a complete theory. If the reduction potential of the emulsion is increased, activation of the dye by light might be expected to cause more reaction with the silver bromide. It should be understood, however, that in admitting the possibility of hypersensitization by reducing agents, we do not accept this as the explanation of hypersensitization by ammonia or amines, or combinations of ammonia or amines with soluble silver salts. The much greater hypersensitization produced by the latter class of materials is caused by increase in the silver ion concentration of the emulsion, as the result of membrane equilibrium followed by drying with the removal of the ammonia or amine. In this case there has been an increase in the oxidation potential of the silver bromide by adsorption on it of free silver ions, instead of increase in the reduction potential of its environment.

Knowledge of the mechanism of hypersensitization serves to point out the inherent limitations of the process rather than to suggest improvements in procedure. Increase in sensitivity is necessarily gained at the expense of stability; the optimum excess of silver, which may be controlled by the ammonia concentration, depends on the use to be made of the hypersensitized material. In general, the more rapid the drying the higher concentration of ammonia may be used. Addition of alcohol to the bath aids in drying; it decreases the effect of a given concentration of ammonia by decreasing the dissociation, so that it is generally better to use aqueous solutions, followed by soaking the plate in 95 per cent alcohol to accelerate drying. Attempts to improve the stability of bathed plates by adding bromide to the dye bath must necessarily do so at the expense of sensitivity, since the effects of the ammonia and the bromide are opposed to each other. As soluble bromide is shown to accumulate in hypersensitizing baths or dye baths, it is obvious that their effectiveness will rapidly fall off with use, even though the ammonia concentration remains practically the same. Combination of silver salts with ammonia is little different from the use of higher concentrations of ammonia, although it may be preferable if it desired to avoid high alkalinity; difficultly soluble silver salts, such as the chloride or tungstate, are preferable to silver nitrate, since the maximum silver ion concentration which they can produce is limited by their solubility and there is less danger of fog from use of an excess.

IV. ACKNOWLEDGMENTS

C. M. Kretchman has rendered valuable assistance in the sensitometric work, in coating the experimental emulsions, and in some of the bathing experiments.

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PHOTOGRAPHIC REVERSAL BY DESENSITIZING DYES

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ABSTRACT

Latent image on a photographic plate which has been exposed, then bathed in a solution of a desensitizing dye, may be destroyed by a second exposure to light of the proper wave length. Quantitative measurements of the variation of density with wave length were made on plates treated with five desensitizing dyes. In three cases it was also possible to make indirect determinations of the spectral distribution of energy absorbed by the dyed silver bromide; less complete data are available for the other two. There is good correlation between reversal and energy absorption. Where the absorption by silver bromide and by the dye are sufficiently separated in wave length, there are maxima corresponding to each. The Herschel effect in the absence of dyes was negligible, and there is no evidence that it is increased by the dyes. It was demonstrated that safranine may produce either reversal or normal sensitization depending only on the bromide ion concentration. Characteristic curves of the process were made by time scale exposures. The evidence supports the hypothesis that the process is an oxidation, and is the reverse of ordinary sensitization chemically as well as photographically.

CONTENTS

I. SPECTRAL SENSITIVITY OF THE REVERSAL PROCESS

Positive images of passable gradation may be produced by the following process, the sensitivity being about one-tenth that of a lantern-slide plate so that camera exposures are possible. The plate or film is given a moderate uniform exposure; then bathed in a solution of any one of many desensitizing dyes, preferably with the addition of soluble bromide, dried, and again exposed. The latent image formed by the first exposure is destroyed by the second, and a positive image is formed on normal development. The process is characterized by sensitivity to a wide range of wave lengths, and in many cases the relative sensitivity to the longer wave lengths may be greater than in a good panchromatic emulsion, although the absolute value is much less.

This phenomenon was first observed by Waterhouse,[1] but our knowledge [2] of it is very largely due to the extensive experiments of Lüppo-Cramer, which are now summarized in the latest edition of Eder's Handbuch der Photographie.[3] While as a pictorial process it is of very little value, its mechanism is of considerable interest because of its possible bearing on the mechanisms of sensitization and desensitization, and of other reversal phenomena.

The primary object of the experiments to be described in this communication was to determine the relation of the spectral sensitivity of the process to the spectral absorption of the dye which is used. As

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[1] Waterhouse, Proc. Roy. Soc. London, vol. 29, p. 186, 1875.

[2] No attempt will be made in this paper to give complete references to the extensive literature of dye reversal and the Herschel effect.

[3] Vol. 2, pt. 1, Grundlagen der photographische Negativverfahren; vol. 3, pt. 3, Sensibilisierung und Desensibilisierung.

already mentioned, the longer wave lengths are usually effective. Lüppo-Cramer has come to the conclusion that the process is essentially the same as the Herschel effect (reversal by red and infra-red radiation on preexposed plates, in the absence of dyes) and that the spectral absorption of the dye "plays only a secondary rôle if at all." Experiments by Mauz,[4] which were made at Lüppo-Cramer's suggestion, were considered as confirming this conclusion. On the other hand, in earlier experiments by one of the writers [5] the maximum reversal corresponded to the maximum absorption by the dye with considerable regularity after allowing for a displacement to the red of about 50 mμ, like that found in ordinary sensitization.

In this process, results depend on the experimental conditions even more than in normal photography. As it was desired to find the region or regions of maximum sensitivity, the diffraction spectrum was used for exposure because the change of energy with wave length is much less than in a prism instrument. It was essential to avoid overexposure. It is well known that by sufficient exposure it is possible to record a continuous spectrum on an unsensitized emulsion as far as 0.6 to 0.7 μ, even though the sensitivity in this region is negligible for practical purposes. Stray light in even the best instruments may also give the appearance of continuous sensitivity if the exposure is excessive.

The best apparatus available was a small spectrograph having a concave reflection grating mounted in parallel light, giving a dispersion of 5 mμ/mm. A Tungsarc lamp was used as the light source. The intensity is quite high, test exposures on fast panchromatic emulsions being made at one twenty-fifth to one-half second, and the stray light is much less than with a transmission grating. This apparatus has been previously used for experiments with methods of spectral sensitization.[6] While the use of the grating spectrograph avoids the great concentration of energy in the longer wave lengths produced by a prism instrument with an incandescent source, the energy from the Tungsarc lamp (color temperature about 3,000° K.) increases so rapidly with wave length that the exposure of the plates to the red end of the spectrum was several times as great as to the blue end.

The test plates were given the white light exposure in a special exposure box, which had been tested photographically for uniformity of illumination. They were then bathed with the mixed solution of desensitizing dye and soluble bromide, swabbed with moist cotton to remove the surplus solution, and dried in a rack designed so that there was unobstructed flow of air over the entire surface of the plate. There are liable to be local irregularities in these plates under the best conditions, and unless the drying is quite uniform, quantitative work is likely to become impossible. The spectrograph exposures were made directly after drying. After the second exposure they were brush developed for four minutes at 20° C. in metolhydroquinone, using the Eastman D–11 formula.

Most of the experiments were done with an experimental pure bromide emulsion. (No. 4–97–2), having a Bureau of Standards speed of 25 and a γ of 0.8 for the above development. This emulsion was used because it was possible to observe the Herschel effect on it under the

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[4] E. Mauz, Zeit. f. wiss. Phot., vol. 27, p. 49, 1929.
[5] B. H. Carroll, J. Phys. Chem., vol. 29, p. 693, 1925.
[6] Carroll and Hubbard, B. S. Jour. Research, vol. 4 (RP173), p. 693, 1930.

same conditions as the dye reversal; pure bromide emulsions are generally best for this purpose, as they have a minimum of normal sensitivity to the red.

Densities were measured by a physical photometer improvised from a Fabry-Buisson microphotometer. The illuminating system was used to focus a narrow line of light on the plate, and the transmission measured from the deflection of a galvanometer connected directly to a caesium photoelectric cell receiving only radiation transmitted by the plate. Within the range used, the accuracy of the assumption that the deflection was proportional to transmission was of the order of 5 per cent. The photometer obviously is accurate only for low densities, but these were the most important in the reversal work. Densities measured in this way are higher than those determined under diffuse illumination. The wave-length scale was supplied by exposures of the helium spectrum; these could not be superposed on all the reversal plates because the sensitivity was too low, but the scale could be reproduced to 0.2 mm on the plate which is quite sufficient.

The dyes used were as nearly as practicable the same as those used by Mauz.[7] Pinakryptol green and yellow were obtained from the I. G. Farbenindustrie. Fuchsin (pararosaniline) and safranine were Kahlbaum products, believed to be Nos. 646 and 841, respectively, in the Colour Index; phenosafranine was not available, but the tolusafranine is so closely related that no important difference is to be anticipated. Some experiments were also made with the parent dye of the pinakryptol series, 2-*m*-nitrostyrrylquinoline dimethyl sulphate, for comparison with those described by Lüppo-Cramer on pages 284–285 of Eder's Handbuch, vol. 3, p. 3. This material was synthesized by the research laboratory of the Eastman Kodak Co., from *m*-nitrobenzaldehyde and quinaldine dimethylsulphate at our request; we wish here to acknowledge their generous assistance.

In the previous experiments by Carroll,[8] and by Mauz,[9] the spectral sensitivities of the plates were compared simply with the absorptions of aqueous solutions of the dyes; data for the latter were obtained either from the literature or by relatively crude measurements. We are indebted to Dr. K. S. Gibson and Miss Mabel E. Brown, of the colorimetry section of this bureau, for quantitative data on the spectral absorptions of the dye solutions used in these experiments. It is more satisfactory, however, to know the absorption of the dyed silver bromide, which is the actual absorbing system in the plates. Eder [10] has proved in this way that the maxima of absorption and sensitization actually correspond for some of the sensitizing dyes. Apparatus for transmission measurements on highly diffusing materials like photographic plates was not available, but the absorption maxima were located by measuring the spectral reflection. Silver bromide was prepared by precipitation from equivalent solutions of silver nitrate and potassium bromide, washed five times by decantation, then agitated with approximately 1:5,000 solutions of each of the four dyes, plus a trace of potassium bromide. The silver bromide was considerably peptized by the dyes. The mixture was allowed to stand overnight, and the supernatant solution carefully decanted

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[10] Eder, Photographie mit Bromsilber-Gelatine (1903 edition), p. 151.

from the silver bromide, which was then suspended in distilled water. This process was repeated twice to eliminate dye not adsorbed to the silver bromide. The final suspension was coated on small pieces of glass, previously coated with a thin gelatin substratum, and dried. The reflection of these samples was measured in diffuse illumination by the colorimetry section. The blackening of the silver bromide under the intense illumination in the spectrophotometer gave considerable difficulty, but error from this source was very largely reduced by rapid readings on a number of samples, measurements being made both on increasing and decreasing wave length. It was, however, impossible to make satisfactory measurements on the sample dyed with pinakryptol green, with its relatively broad and flat absorption bands. All values are relative to the reflectance of a diffusing surface of magnesium oxide, used as a nonselective standard.

Comparison of spectral absorption and spectral sensitivity for each of the dyes may be made from the data presented in Figures 1 to 4. In each of these figures the densities of plates after spectrograph exposures are plotted (in solid lines) as ordinates, against wave lengths as abscissæ. A minimum of density obviously corresponds to a maximum of reversal, and vice versa. The data for spectral absorption are given by the broken lines. Curve 1 in each figure represents the absorbancy (minus log transmittancy) for an aqueous solution of the corresponding dye, at a concentration chosen so as to give a range of logarithms comparable to the other curves. In each case there is a maximum of reversal corresponding to the maximum of absorption by the dye, but displaced by 40 to 60 mμ toward the longer wave lengths. In Figure 2 the maximum reversal at 465 mμ obviously corresponds to the principal absorption band of the dye at 430 mμ; the change of slope from 590 to 650 mμ indicates that a faint secondary maximum corresponding to the absorption band at 580 mμ is superposed on the main curve. The reversal curve for plates bathed with fuchsin (fig. 3) and safranine (fig. 4) have minimum densities at about 420 mμ in addition to those at 610 and 580 mμ, respectively, which may be attributed to the dyes. There is no absorption by fuchsin or safranine in the region of 360 to 380 mμ to account for these minima at 420 to 430 mμ. The quantitative measurements of spectral absorption by these solutions were carried to 390 mμ without any indication of a second maximum at shorter wave lengths, and approximate photographic tests failed to show any significant absorption between 400 and 310 mμ. We are therefore forced to the conclusion that the minima around 420 mμ correspond to absorption by the silver bromide itself; this conclusion will be discussed more fully later in the paper.

Curve 2 in Figures 1, 3, and 4 represents the spectral reflection of silver bromide dyed with the corresponding dyes; the data are plotted as minus log reflectance, so that a maximum in the curve corresponds to minimum reflectance and maximum absorption. It will be noted that the maxima of these curves are displaced approximately 20 mμ toward the longer wave lengths from the maxima of absorption in solution. In the case of silver bromide dyed with pinakryptol yellow, the dye and the silver bromide absorb in the same spectral region, so that the two components of reflection can not be distinguished.

Curve 3 in Figures 1, 3, and 4 represents on a logarithmic scale the variation with wave length in the energy radiated by a black body at

3,000° K. The curves in the three figures are displaced vertically by varying amounts to fit the scales of the figures. The color temperature of a Tungsarc lamp is not over 3,000°, and possibly nearer 2,900°. The relative energy incident on the plates may, as a first approximation, be taken as equal to this, since nothing in the spectrograph or illuminating system introduces appreciable selective absorption or reflection in the visible region.

Curve 4 approximates the relative energy absorbed at each wave length from a source of 3,000° color temperature by a material of the reflectance represented by curve 2. In making this calculation, the transmission by the dyed silver bromide was taken as negligible and the absorption as (1 − reflectance); the absorption was multiplied by the relative energy for this wave length, and the logarithm of this quantity plotted. The transmission was not measureable with the available apparatus, but appeared to be not over 10 per cent for the samples actually used for measurement of reflectance. Curve 5 in each of the figures was obtained by dividing the energy absorbed at each wave length by the frequency of the radiation (the inverse of the wave length). This procedure gives the relative number of quanta of energy absorbed. The logarithm of the number was plotted. As curves 3, 4, and 5 all express only relative values, plotted on a logarithmic scale, they have been shifted vertically so as to produce

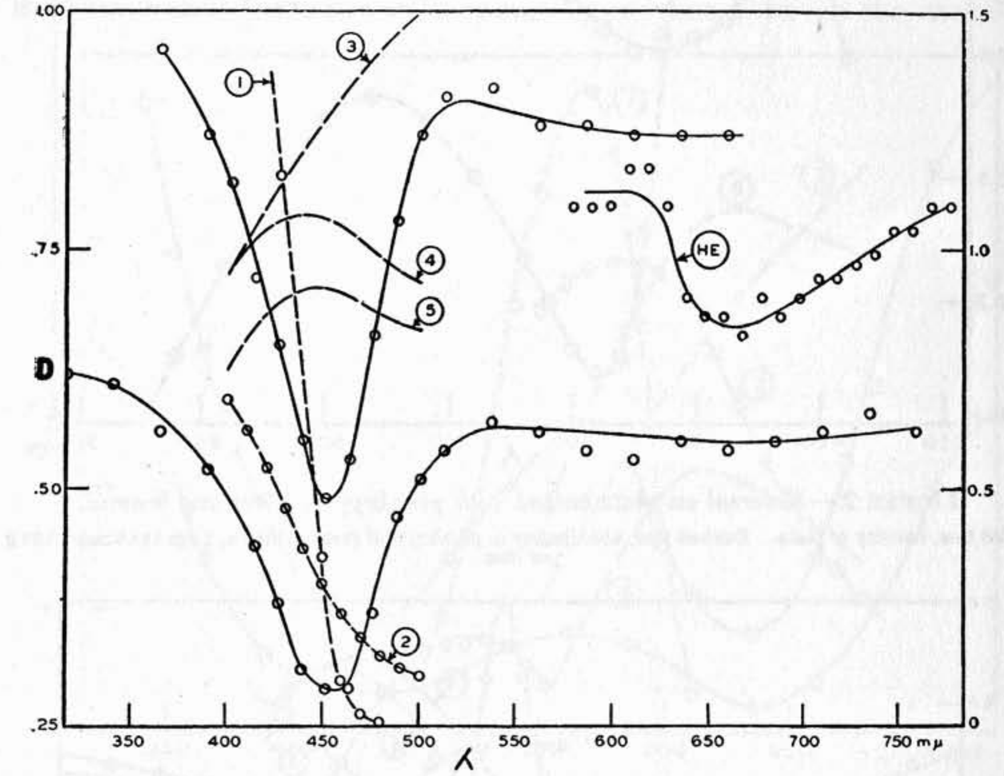

FIGURE 1.—*Reversal on plates bathed with pinakryptol yellow and bromide*

Solid lines represent densities of plates, on left-hand ordinate scale. The curve marked *H E* is for the Herschel effect on a pure bromide emulsion without dye; 1.5 has been subtracted from all densities to bring the curve on the same plot with the others. Dashed curves (right-hand ordinate scale) are: (1) Absorbancy (minus log transmittancy) of pinakryptol yellow solution, 1.0 g per liter, in 1 cm thickness; (2) minus log reflectence of silver bromide dyed with pinakryptol yellow; (3) log relative spectral energy distribution of a black body at 3,000° K.; (4) log spectral distribution of energy absorbed from a source such as (3) by silver bromide dyed with pinakryptol yellow; and (5) log quanta absorbed under these conditions

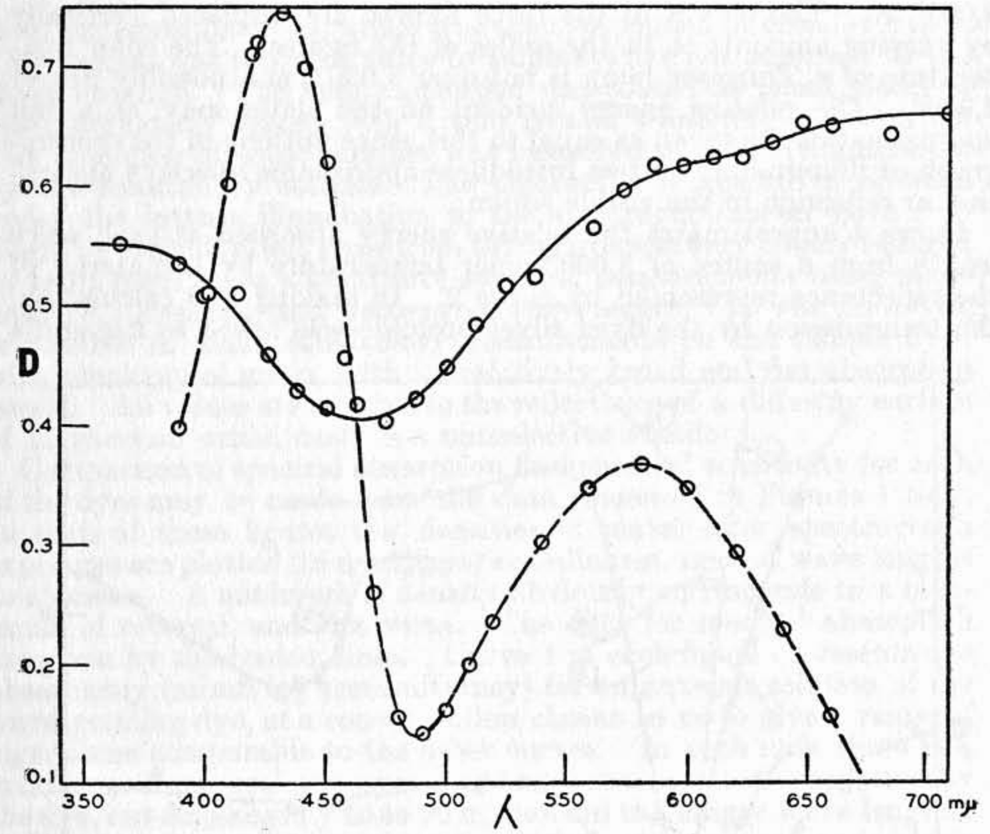

FIGURE 2.—*Reversal on plate bathed with pinakryptol green and bromide*

Solid line, density of plate. Dashed line, absorbancy of pinakryptol green solution, 1 cm thickness, 0.02 g per liter

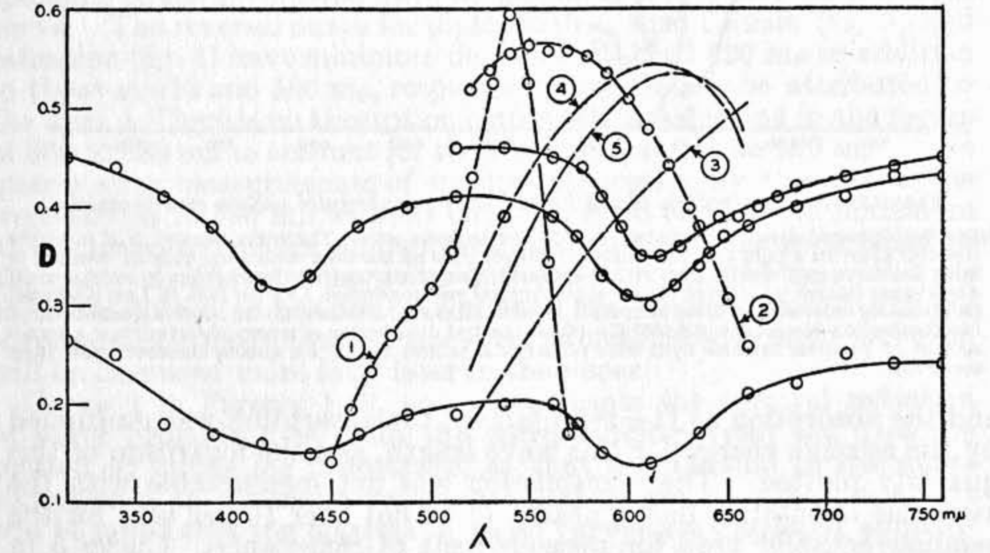

FIGURE 3.—*Reversal on plates bathed with fuchsin and bromide*

Solid lines represent densities of plates; upper curve made with red filter over slit of spectrograph. Dashed curves: (1) Absorbancy of fuchsin solution, 0.0024 g per liter, in 1 cm thickness; (2) minus log reflectance of silver bromide dyed with fuchsin; (3) log relative spectral energy distribution of a black body at 3,000° K.; (4) log spectral distribution ofenergy absorbed from a source such as (3) by silver bromide dyed with fuchsin; and (5) log quanta absorbed under these conditions the minimum confusion in the figures. As a first approximation, the extent of a given photochemical reaction produced by different frequencies not too widely separated may be expected to be proportional to the number of quanta absorbed at each frequency. There are in many cases very large deviations from this theoretical prediction, the higher frequencies (shorter wave lengths) tending to be the more effective, but in the absence of more definite knowledge the effect of varying frequency on a reaction should be compared with the number of quanta absorbed by the material which is believed to be chemically activated by the radiation.

Considering the region covered by curve 5 in Figures 1, 3, and 4, it is obvious that there is excellent correspondence between the reversal and the energy quanta absorbed by the dye on the silver bromide. The maxima fall together within the limits of error of the determinations. Figure 2 shows that the relation between reversal and the absorbancy of dye solution is the same for pinakryptol green as for the other dyes. The inevitable conclusion from these data is that the spectral sensitivity of the reversal process depends on the absorption by the dye as directly as does spectral sensitization of the ordinary type. This confirms the earlier work by one of us.[11] It is in direct contradiction to Lüppo-Cramer's conclusion, which we shall be able to show is the result of the misleading impression of spectral sensitivity which may be given by inspection of exposures through filters.

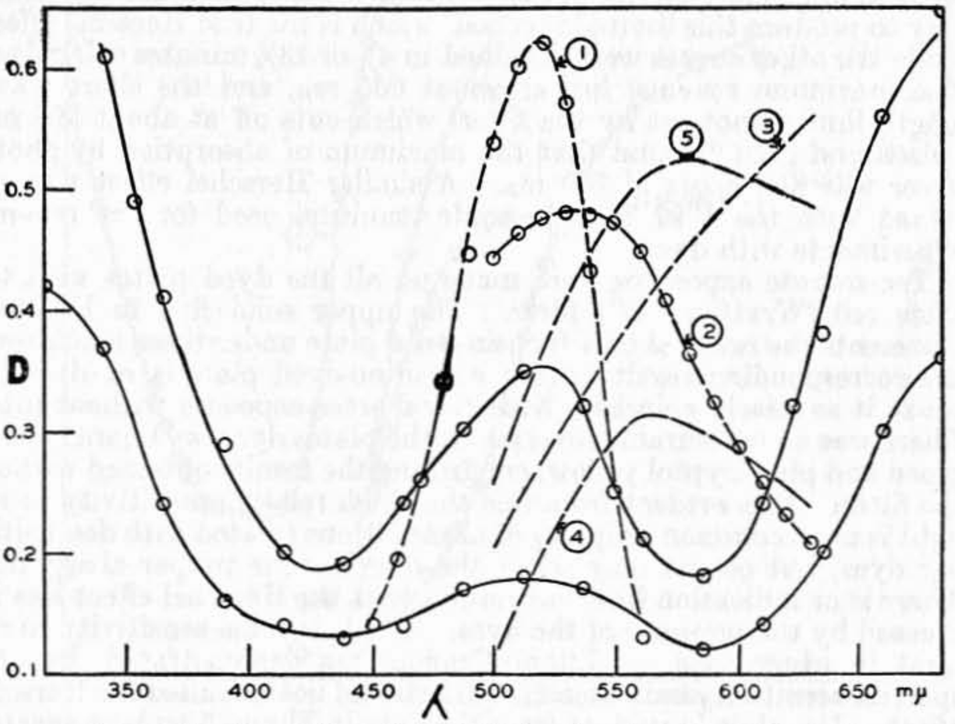

FIGURE 4.—*Reversal on plates bathed with safranine and bromide*

Solid lines represent densities of plates. Dashed curves: (1) Absorbancy of safranine solution, 1 cm thickness, 0.008 g per liter; (2) minus log reflectance of silver bromide dyed with safranine; (3) log relative spectral energy distribution of a black body at 3,000° K.; (4) log spectral distribution of energy absorbed from a source such as (3) by silver bromide dyed with safranine; and (5) log quanta absorbed under these conditions

In Figures 3 and 4, there are marked minima of density around 420 to 430 mμ, which are obviously the result of light absorbed by the silver bromide itself. The combination of absorption which increases with decreasing wave length and energy incident on the plate in amounts increasing with increasing wave length determines the location of maximum absorption and hence of maximum reversal. In Figures 1 and 2, this maximum of reversal is shifted to 450 and 465 mμ, respectively, by the absorption of the dye superposed on that of the silver bromide.

In Figure 1, the curve marked *H E* represents the density of a plate coated with pure bromide emulsion which, after the first uniform exposure, had been bathed in 1 per cent potassium bromide solution without dye, then dried and exposed in the spectrograph using a red filter over the slit to eliminate the second order spectrum and stray light of short wave lengths. An exposure of 2½ hours was necessary to produce this limited reversal, which is the true Herschel effect, while the other curves were obtained in 4½ or 13½ minutes using dyes. The maximum reversal lies at about 660 mμ, and the short wavelength limit is not set by the filter, which cuts off at about 590 mμ. Hilsch and Pohl [12] found that the maximum of absorption by photosilver was just short of 700 mμ. A similar Herschel effect was obtained with the 4-97 pure bromide emulsion used for the reversal experiments with dyes.

Ten-minute exposures were made on all the dyed plates with the same red (Wratten "A") filter. The upper solid line in Figure 3 represents the reversal on a fuchsin-dyed plate under these conditions; the corresponding result on the safranine-dyed plate is omitted because it so nearly coincides with the shorter exposure without filter. There was no measurable reversal on the plates dyed with pinakryptol green and pinakryptol yellow, confirming the results obtained without the filter. It is evident from this that high relative sensitivity to red light is not a common property of all emulsions treated with desensitizing dyes, but occurs only when the dye has the proper absorption. There is no indication from our results that the Herschel effect was increased by the presence of the dyes. There is some sensitivity to red light in every case, as Lüppo-Cramer has demonstrated, but the spectral sensitivity indicates that this should not be called the Herschel effect. Its origin is evident from the data in Figure 5 on long spectrograph exposures. Process plates were given the usual uniform exposure to white light, then bathed with pinakryptol green, pinakryptol yellow and 2-*m*-nitro-styrrylquinoline dimethylsulphate, each at a dilution of 1:5,000 in bromide solution, dried, and exposed in the spectrograph for five minutes without filter, and one hour with the minus blue filter (absorbing radiation of wave length less than 500 mμ) over the slit. Curves 1 and 2 show clearly that as the exposure was increased, the region of reversal on the pinakryptol yellow bathed plate extended into the red without indication of a second maximum. The behavior of the plate bathed with pinakryptol green (curve 3) was similar, but there are indications of a secondary maximum about 640 mμ corresponding to the secondary maximum of absorption of the dye.

The reversal obtained with 2-*m*-nitrostyrrylquinoline dimethylsulphate, one of the simplest dyes of the pinakryptol series, is of particular interest because Lüppo-Cramer [13] has used this as evidence that the reversal effect is independent of the spectral absorption of

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[12] Hilsch and Pohl, Proc. 8th. Int. Cong. Phot., p. 29, 1931.

[13] Lüppo-Cramer, reference 3 "Sensibilisierung und Desensibilisierung," pp. 284-285, and Figure 53.

the dye. The 5-minute exposure without filter on the plate treated with this dye produced a reversal which would be represented by a curve quite close to (1) in Figure 5. Examination of curve 4 shows that the slope on the long wave length side is steeper than that of curve 2, made with pinakryptol yellow. This is to be expected, since absorption by 2-*m*-nitrostyrrylquinoline dimethylsulphate was found to be very slight at wave lengths over 400 mμ; the spectral sensitivity was therefore determined almost entirely by the absorption of the silver bromide.

On visual inspection of the plates made with this material the reversal could be detected to over 700 mμ, but could not be measured with any accuracy on the microphotometer because it involved small changes in relatively high densities. Another piece of the same plate used for curve 4 (fig. 5) was exposed behind an Eder-Hecht wedge for two and one-half minutes at 30 cm from a 75-watt, gas-filled lamp. The result is reproduced in Figure 6; the similarity to Lüppo-Cramer's results (reproduced in his fig. 53) is obvious. The wedge and filter exposure appears to indicate a relative sensitivity to the longer wave lengths which is not confirmed by the quantitative measurements on the spectrograph exposures. The answer appears to lie in what Lüppo-Cramer has called the "time effect," the marked failure of the reciprocity law for this process in the sense that the photographic effect falls off much less rapidly than the intensity. This shows in the original of the Eder-Hecht exposure as an extraordinarily long

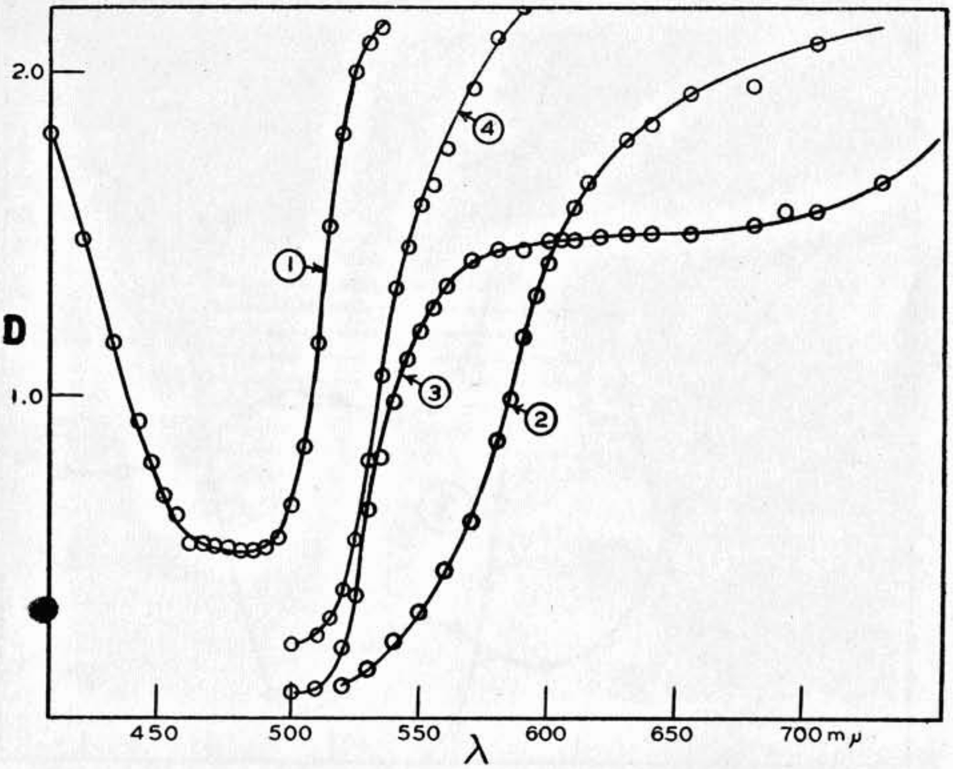

FIGURE 5.—*Reversal on plates given long spectrograph exposures*

Curve 1, 5-minute exposure; curves 2, 3, and 4, 60-minute exposures with minus blue filter in front of slit of spectrograph. Curves 1 and 2, plate bathed with pinakryptol yellow and bromide; curve 3, plate bathed with pinakryptol green and bromide; and curve 4, plate bathed with 2-*m*-nitrostyrrylquinoline dimethylsulphate and bromide.

and flat "toe" of the characteristic curve. The consequence is that intensity differences, as judged from the threshold of photographic effect, tend to be equalized and the filter strips on the Eder-Hecht wedge are printed for a distance out of proportion to the relative spectral sensitivity.

II. EFFECT OF BROMIDE AND DYE CONCENTRATIONS

The curves of Figure 7 represent the results of an experiment which we believe to have considerable theoretical significance. Process plates were given suitable preexposures. They were then cut in halves. One half of each was washed for five minutes in running water to remove all soluble bromide, then bathed in a 1: 30,000 solution of safranine in distilled water, dried, and exposed in the spectrograph. The other half was bathed in a 1: 30,000 solution of safranine in 1 per cent KBr solution, then dried and exposed in the spectrograph. All plates were given a series of spectrograph exposures. Curve 1 in Figure 7 represents a plate given 4-second preexposure, washed and bathed in safranine without bromide, and exposed 30 seconds in the spectrograph. Curve 2 is for a plate given 8-second preexposure, bathed in safranine plus bromide, and exposed 90 seconds in the spectrograph. Spectral sensitivity was not dependent on the exposure times; densities for the above values were

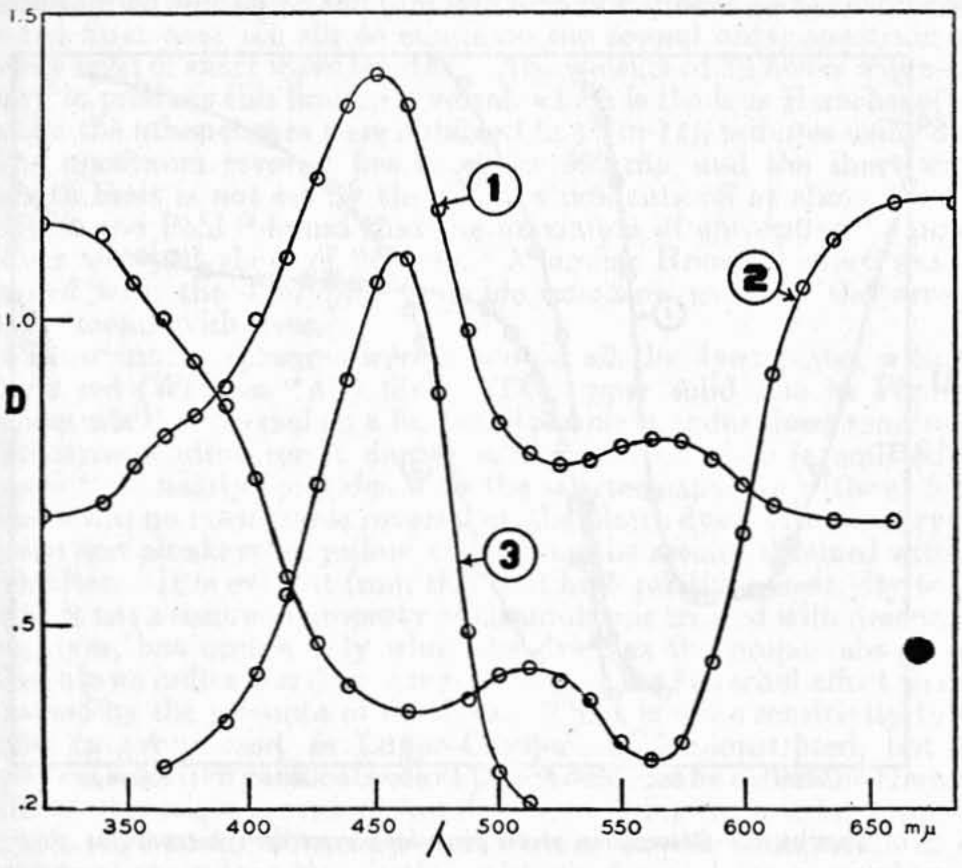

Figure 7.—*Densities of plates after spectrograph exposures*

(1) Preexposed, washed, bathed with solution of safranine in pure water, and dried before spectrograph exposure; (2) preexposed, bathed with solution of safranine and potassium bromide, and dried before spectrograph exposure; and (3) plate of same emulsion, untreated

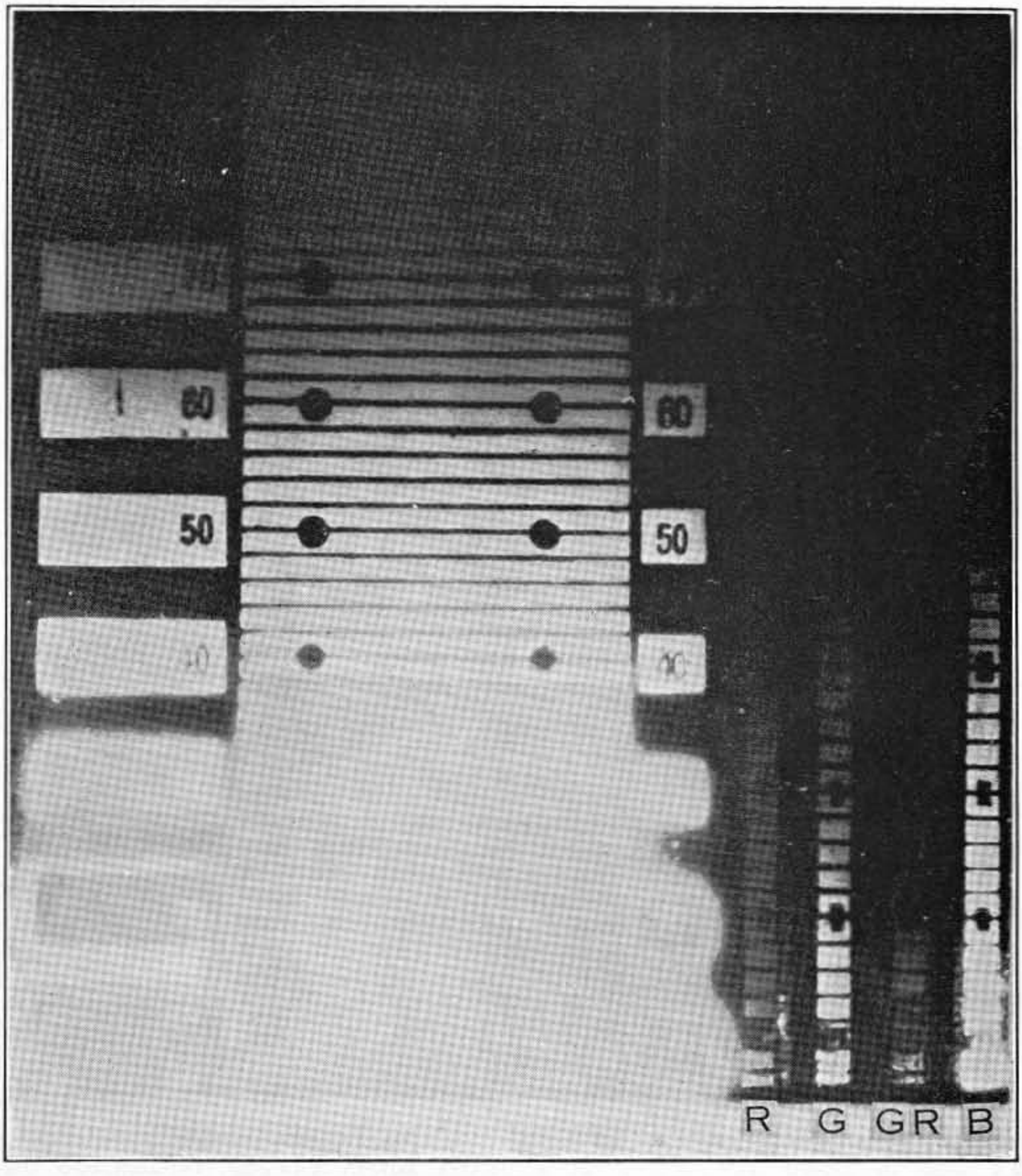

FIGURE 6.—*Process plate given uniform exposure to white light, then bathed in a mixed solution of 2-m-nitrostyrrylquinoline dimethylsulphate and potassium bromide, dried, and exposed again to incandescent light through an Eder-Hecht wedge*

Letters on the narrow strips to the right have the following significance: *R*, red filter; *G*, yellow; *GR*, green; *B*, blue.

chosen as the most suitable for plotting together. Curve 3 in Figure 7 is for an untreated plate of the same kind exposed in the spectrograph for 1 second, without preexposure.

Curve 1 has a maximum of density at 565 mμ; curve 2 has a minimum of density at the same wave length. The maximum at 565 mμ in curve 1 obviously indicates sensitization in the ordinary sense by safranine (in spite of its marked desensitizing properties, this dye is described in the 1903 edition of Eder as "a moderately good green sensitizer"). The corresponding minimum in curve 2 demonstrates beyond question that the reversal process is also brought about by light absorbed by the dye. The energy acquired in this way may either form or destroy latent image, depending on the conditions in the emulsion, the silver (or bromide) ion concentration being the variable involved in this experiment.

The maxima in curves 1 and 3, and minimum in curve 2 at 450 to 460 mμ [13] demonstrate that the same relation holds for radiation absorbed by the silver halide itself as for that absorbed by the dye. Under normal conditions, it is used to form latent image, but in the presence of both dye and soluble bromide it instead destroys image already existing. A maximum of reversal in this region can be detected in Figure 2 of Mauz's paper illustrating exposures on fuchsin bathed plates.

The dye reversal process has generally been associated in the literature, with the longer wave lengths, but there are other illustrations of reversal by radiation absorbed by the silver halide. This is the case for solarization [14] and for reversal on plates which have been converted to iodide.[15]

Further evidence on the nature of the reversal process was obtained from a different type of experiment. Lüppo-Cramer [16] has given characteristic curves of dye reversal with varying concentrations of dye. These curves were made with an intensity scale, and in view of the marked anomalies of the process with regard to intensity it seemed worth while to repeat them with the time scale, which might be simpler to interpret. The experiments were made with safranine on process plates. After constant preexposure, the plates were bathed in solutions of the dye at a dilution of one part of dye to 15, 30, 60, 120, 240, and 480 × 10^3 parts of 1 per cent KBr solution. These dilutions are indicated by the corresponding numbers on the curves of Figure 8. All plates were dried together, then given a nonintermittent sector wheel exposure (0.11 to 30 seconds) to the light from a 500 c. p. "Point-o-lite" lamp at 0.9 m, with a Wratten Minus Blue filter. A second set of plates was exposed 2 to 512 seconds. The combined curves from three test strips for each of the two exposures are plotted in Figure 8 as changes in density from the unexposed portion of the plate. The reproducibility of these curves was relatively poor, although the individual curves for each set of conditions were smooth; the probable error in location of each curve is of the order of 0.2 in density.

The curves for dilutions of 30 to 480 × 10^3 fall into a regular progression, the reversal beginning after longer and longer exposure as the

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[13] On the pure bromide emulsion used for the exposures recorded in Figure 4, the corresponding minimum lay at 420 to 430 mμ. The shift is explained by the presence of 3 per cent silver iodide in the silver halide of the process emulsion used for Figure 7.

[15] Renwick, J. Soc. Chem. Ind., vol. 39, p. 156 T, 1920.

[16] Lüppo-Cramer Phot. Ind., vol. 25, p. 1099, 1927. Zeit. f. wiss. Phot., vol. 26, p. 345, 1929

dilution increases. The most unexpected feature of the data is the formation of a negative image in the early stages of exposure at the highest dilutions, preceding the reversal. This has been observed by Lüppo-Cramer [17] in a few cases of exposures with the intensity scale. With the intensity scale, the reversal may be followed by a negative image (at the highest intensities). This has frequently been observed by Lüppo-Cramer, and confirmed in this laboratory; it is faintly visible in Figure 6. No indications of this second negative were found in these time-scale exposures; it is possible that it might have occurred if the exposure could have been sufficiently prolonged, but at the lower dilutions of dye the minimum density was maintained without change over a range of exposure of more than 10 times.

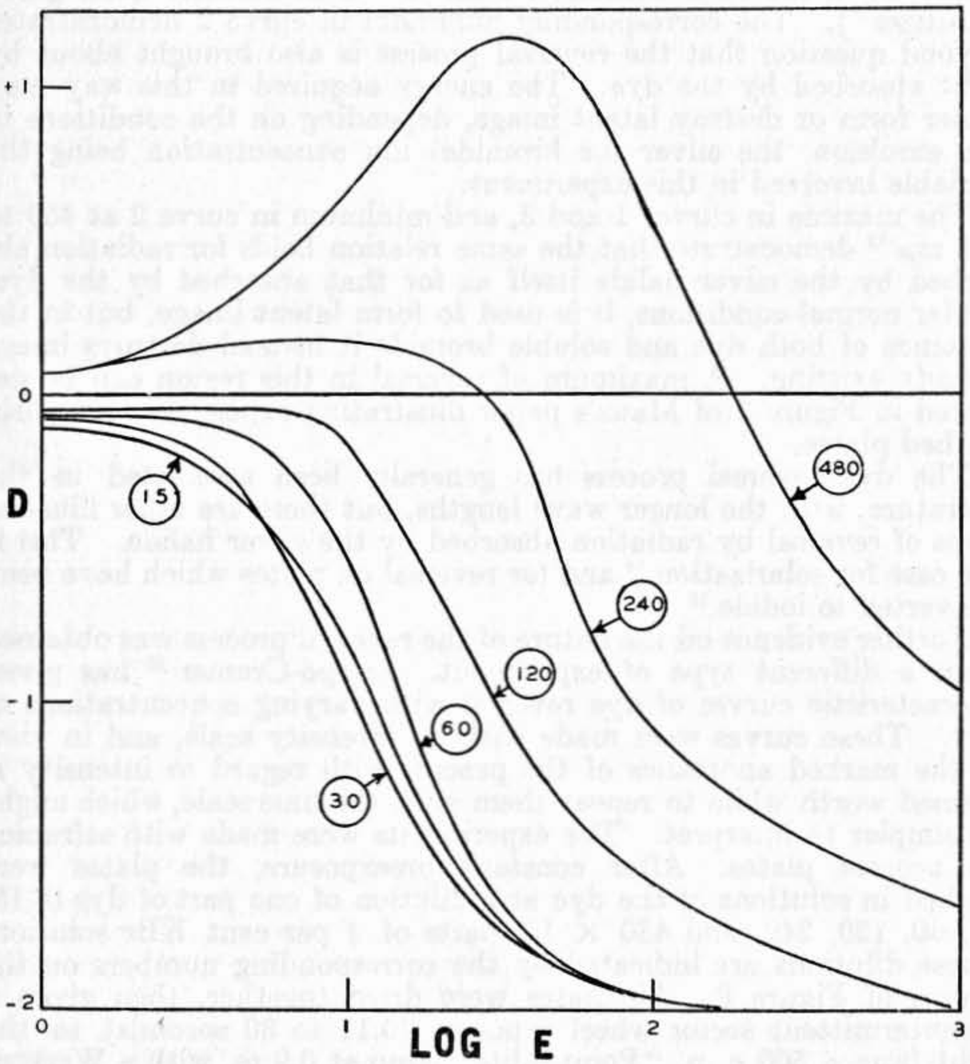

FIGURE 8.—*Characteristic curves of reversal process with safranine-dyed plates, made by time-scale exposures*

Densities on curves are changes from value produced from original uniform exposure. Numbers on curves multiplied by 10^3 indicate dilution of safranine.

The dye at a dilution of 15×10^3 produced slightly less effect than at the next higher dilution. Lüppo-Cramer [18] has frequently observed

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[17] Lüppo-Cramer, Zeit. f. wiss. Phot., vol. 26, p. 350, 1929. Camera, vol. 6, p. 182, 1928.

that the more concentrated solutions may produce less effect, and has explained this on the basis of the mutual replacement of adsorbed dye and bromide ions on the silver halide with varying concentrations. It is not excluded, however, that in the plates bathed with the stronger solutions the excess unadsorbed dye may act as a filter to reduce the light absorbed by the dyed silver halide.

III. DISCUSSION

The outstanding feature of these data is the excellent correspondence between the energy absorbed by the dyed silver bromide and the reversal.

It must be remembered that any photochemical process is necessarily the result of absorption of radiant energy by the reacting system. In the plates as exposed in the spectrograph there are three materials possessing selective absorption in the visible spectrum and near infrared. These are the silver halide, the dye, and the products of the first exposure (probably, but not positively identical with the latent image). Absorption by silver sulphide (sensitivity nuclei) may also reasonably be included with the products of exposure. Silver halides have strong selective absorption for radiation of wave lengths less than 500 mμ; the dyes have strong selective absorption for regions depending on the dye; and the products of exposure, plus silver sulphide, have selective absorption for the red and near infra-red,[19] which is extremely weak because of the minute traces present. Energy absorbed by any of these three from radiation in or near the visible region is a potential source of photochemical reaction in the plate, since the absorbing molecules must thereby become "excited" or "activated." The energy of activation may simply be transformed to heat, without reaction; an unknown proportion is so lost in the plates under discussion. A chemical reaction may follow activation either because the activated molecule itself breaks down, or because the energy of activation is transferred [20] to some other species of molecule, causing it to be chemically activated and therefore to react. This second process is commonly termed sensitization or photochemical catalysis. The spectral sensitivity of the plate will be determined by the primary process, the absorption of energy; but the photochemical yield from a given energy absorption (expressed when possible in terms of molecules reacting per quantum of energy absorbed) depends enormously on secondary chemical processes following the primary absorption; that is, on the chemistry of the system in which the absorption takes place.

Assuming anything like equal yield in terms of molecules reacting per quantum of light absorbed in different parts of the spectrum, we would therefore expect a marked reaction to be produced by the spectral regions absorbed by the silver bromide and the dye, respectively, and a very slight one in the red where the selective absorption by the latent image is strongest. The observed photographic reversal corresponds to this assumption. The plates bathed with fuchsin and safranine, on which the two main regions of absorption are far enough

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[20] This process in gases occurs largely by "collision of the second kind." This same term has been applied by Leszynski and others to hypothetical energy transfer from sensitizing dyes to silver halide; without denying the possibility of such energy transfer in photographic sensitization, it seems quite undesirable in the present state of our knowledge to apply the term of "collision" to a process occurring in the solid state.

separated so that they can be clearly distinguished, were most sensitive in the region around 420 to 430 mμ, since the reversal was as strong as in the longer wave lengths, while the energy received on unit area was much less. As the absorption could not be measured quantitatively in the plates, it is impossible to estimate the relative quantum yield in the two regions.

In the opinion of the writers, the results given by Mauz [21] are in agreement with ours, in spite of their superficial differences. His use of a prism spectrograph with an incandescent source of about 2,850° color temperature caused a great concentration of energy in the red end of the spectrum. A simple calculation from the scale of his published figures and the energy distribution of such a source shows that the plates received about 85 times as much energy per unit area in the spectral region 600 to 700 mμ as in the region 400 to 420 mμ, as against a ratio of 6 for the same regions in our instrument. His exposures were, furthermore, so long as to produce reversal over the entire visible spectrum in every case, thus tending to obscure the differences between the plates bathed in different dyes. However, the influence of the absorption by the dye is clearly evident from his figures. The plates bathed with fuchsin and phenosafranine have marked maxima in the red which are not shared by the other dyes. That bathed with pinakryptol yellow has its strongest reversal between 400 and 500 mμ. The results with pinakryptol green are more difficult to interpret, but the appearance of the plates between 400 and 500 mμ, where the central part of the spectrum is dark and the edges light, is most probably explained by a maximum sensitivity in this region, combined with overexposure sufficient to produce the second negative. The light edges are the result of reversal in the region of irradiation from the more strongly exposed central portions. A similar effect may be detected in spectrum 8 (fig. 2) of the paper by Carroll. In Figure 2 of Mauz's paper the reversal in the region of absorption by the silver halide, where it is distinct from that of the dye, was obscured by the low intensity incident on this portion of the plates, but a secondary maximum is detectable at about 460 mμ.

Conclusions based on a process as complicated as this must be accepted with considerable caution, but the field for speculation is extensive and tempting. The theory of the true Herschel effect (reversal without dyes) is apparently simple. Absorption of red and infra-red radiation by the products of the first exposure causes them to react, naturally destroying their effectiveness as latent image whether the reaction is regression to the original form or not. The photographic sensitivity is very low, corresponding to very weak absorption; emulsions containing iodide show the Herschel effect with great difficulty because the traces of absorption by brom-iodide in the longer wave lengths cause a reaction (latent image formation) which counteracts the Herschel effect at least photographically, and probably chemically. The Herschel effect may be materially increased by changes in the chemistry of the emulsion, increase in bromide ion concentration and the presence of traces of copper salts being definitely established as promoters of the effect. As alkali bromides have no absorption in the visible region their effect must be on the secondary chemical processes following absorption.

The possible views of the effect of the dyes on reversal are that: (1) Energy absorbed by the dye is used in the reversal reaction, either directly or indirectly, and (2) the dye, like soluble bromide, increases the effect of absorption of energy by other materials, via the secondary chemical processes; this is the view taken by Lüppo-Cramer.[22] These theories are not mutually exclusive, since the second may apply independent of the first. The tendency to reversal in the presence of the dye certainly exists, since the rate of fading of the latent image in the dark is quite appreciable, especially when soluble bromide as well as desensitizer is present. This is essentially the same reaction, going on slowly under thermal activation of the dye molecules, and rapidly under photochemical activation. Further evidence that the dye causes a tendency to regression independent of its absorption of light comes from the observed reversal by radiation which must be absorbed by the silver bromide itself. In this case, we must assume that the energy absorbed by the silver bromide is transferred to the latent image. This is reasonable, since the converse process—spectral sensitization of silver bromide by colloidal silver—is a well-known phenomenon. Energy absorbed by the products of exposure must be effective in producing reversal in the presence of the dye, but it is nearly negligible in comparison to that acquired by the other absorbents. Our data fail to show that the sensitivity of the dyed plates to the red and infra-red resembles what might be expected if the true Herschel effect played any appreciable part in the reversal process. We accordingly consider that it is unjustifiable to identify the Herschel effect and the dye reversal to the extent which has been common in the literature.

The analogy between sensitization in the ordinary sense and the reversal phenomena under discussion is evident from the data on spectral sensitivity. It receives considerable confirmation from the effect of variables common to the two processes. The most important of these is the silver (or bromide) ion concentration. Increase in silver ion concentration (up to the point where fog interferes) greatly improves [23] the effectiveness of ordinary sensitization; conversely, increase in bromide ion concentration by addition of soluble bromide increases reverals by desensitizing dyes,[24] and decreases sensitization. We have shown in Figure 7 that the action of safranine, as the result of activation by light which it selectively absorbs, may be either, an increase or a decrease in density, depending on the bromide ion concentration of the emulsion. We have already expressed the opinion that the bromide ion concentration alters the oxidation-reduction potential of the silver halide grain with respect to its environment through the varying adsorption of bromide or silver ions to its surface. Further evidence that the reversal is an oxidation process is given by Lüppo-Cramer's observations [25] that photo-silver may be bleached by pinakryptol yellow plus bromide in light, and that under some conditions desensitization and reversal may be appreciably decreased by the presence of reducing agents, such as nitrite. We also have the increase in sensitization (hypersensitization) by reducing

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[22] "Die an und für sich, besonders in langwelligen Gebiete vorhandene Tendenz zur Umkehrung der Bromsilberzersetzung (Herscheleffekt) durch die Farbstoffe infolge Keimisolierung unterstützt wird." (Handbuch, vol. 3, pt. 3, p. 285.)

[23] Carroll and Hubbard, B. S. Jour. Research, vol. 9 (RP488), p. 529, 1932.

[24] Lüppo-Cramer, Die Kinotechnik, vol. 11, p. 399, 1929.

[25] Lüppo-Cramer, Phot. Ind., vol. 28, p. 365, 1930.

agents,[26] and the increase in reversal by oxidizing agents.[27] These effects are somewhat erratic and difficult to reproduce, but appear to be real. The evidence establishes a strong presumption. that sensitization and reversal by dyes are not only photographically but chemically opposite directions of the same process.

The nature of the characteristic curves with varying dye concentrations, in Figure 8, may be interpreted by the hypothesis that reversal begins when a given oxidation potential is reached. Oxidation potential under constant illumination should tend to increase with increasing concentration of dye, and with increase in latent image. The required potential may then be built up either by more concentrated dye and less image, or by an increase in image with the most dilute dyes. Once the reversal process is started, it may be able to continue without a decrease in reduction potential to the original value, if the quantity of dye is assumed to be chemically equivalent to many times the silver of the latent image.

Sensitization and reversal by dyes may be both brought about by energy absorbed by the dye. The simplest and most probable theory is that the dye, chemically activated by absorption, then takes part in an oxidation or reduction reaction with silver bromide or photo-silver. The evidence from spectral sensitivity, however, does not distinguish between this case and the transfer of the activation energy from the dye to another material which then reacts.

WASHINGTON, February 13, 1933.

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[26] Bokinik, Zeit. f. wiss. Phot., vol. 30, p. 330, 1932; Carroll and Hubbard, B. S. Jour. Research, vol. 10 (RP525), p. 211, 1933.

[27] Lüppo-Cramer, Die Kinotechnik, vol. 10, p. 506, 1928.

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RP183

A COMPARISON OF RESOLVING POWER AND SENSITIVITY OF PHOTOGRAPHIC PLATES WITH VARYING DEVELOPMENT

By Burt H. Carroll and Donald Hubbard

ABSTRACT

Special developers recommended for reducing the graininess of photographic images are all based on increasing the solvent action of the solution on silver bromide, and decreasing the reduction potential. Five of these formulas were compared with ordinary pyrogallol and metol-hydroquinone by testing sensitivity and resolving power of three emulsions, each developed with each of the developers. These results were supplemented by practical spectrographic tests, and experiments with two other developers. Little useful improvement over the standard developers was obtained in any case, as increased resolution was, in general, accompanied by decreased sensitivity. These results do not apply to the pictorial use of special development to reduce graininess.

CONTENTS

I. INTRODUCTION

Both scientific and practical applications of photography tend to demand a better combination of sensitivity and resolving power than is now available. While recent investigations have shown that, other conditions being the same, sensitivity increases with the size of the silver halide grains in an emulsion so that there is a fundamental connection between the two, the resolving power of the developed image is always far less than the limit imposed by the silver halide grain size. Part of this is caused by clumps of grains in the emulsion, and part by the substitution of irregular and much larger grains of silver in the developed image for the original grains of silver halide. The latter at least is obviously susceptible to some control by the conditions of development. In the extreme case of development after fixation, where the silver halide grain has been removed and the silver of the developed image is deposited from the developing solution, Seyewetz[1] has shown that the metal may be deposited in compact hexagonal crystals quite different from the spongy grains produced by any developing agent[2] under the conditions of "chemical" development.

"Chemical" development may, however, be modified so as to produce smaller silver grains, with a probable decrease in the frequency of clumps, by decrease in the reduction potential, and increase in the solubility of the silver halide in the developing solution. The result is that a considerable proportion of the silver halide is reduced in solution, and the silver deposited on the development nucleus as in "physical" development. This type of developer was first used and explained by the Lumières and Seyewetz,[3] and the same principles are involved in the "borax" developers now in wide use by the motion-picture industry. A high concentration of sodium sulphite is used to increase the solubility of the silver halide, and carbonate is entirely omitted, so that the alkalinity is relatively low (pH approximately 9) and the reduction potential is correspondingly decreased. The alkalinity of sulphite solutions is somewhat too low and borax is generally added to raise it to the desired value; being a good buffer, it may be added in sufficient quantity to maintain the pH reasonably constant during development. The use of borax has given its name to this class of developer, although the high concentration of sulphite is really the more important feature. Practical studies of the variables in this class of developer are given by Carlton and Crabtree[4] and by Moyse and White.[5]

This comparison of a number of developer formulas by their effect on the characteristics of three emulsions was intended primarily for choice of developers for use in difficult spectography, such as stellar spectra, Zeeman patterns, or band spectra. The requirements may be summarized as (1) the minimum error in determination of the distance between closely separated lines, combined with (2) the minimum exposure for recording the lines. The first is not determined solely by the grain size of the image, since resolving power is dependent to a very large extent on fog, and contrast; the factors involved are summarized by Sandvik,[6] who emphasizes the necessity of measuring resolving power by tests related to the intended application. The second requirement makes it necessary to consider the effect of development on the effective sensitivity of the plate, since the differences in resolving power characteristic of emulsions differing by 50 per cent in speed are, in general, as great as any which can be produced by special development. There is obviously no advantage in the use of a high-speed emulsion and special developer if both sensitivity and resolving power can be equaled by a moderate speed emulsion with standard development, and we are unable to understand how the Lumières and Seyewetz[7] are able to pass so lightly over this point.

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[1] Seyewetz, Chimie et Ind., Special No.; p. 418; September, 1925.

[2] Ross, The Physics of the Developed Silver Image, chap. 1.

[3] A. and L. Lumière and A. Seyewetz, Brit. J. Phot., **51**, pp. 630, 866; 1904.

[4] Carlton and Crabtree, Trans. Soc. Motion Picture Engrs., **13**, pp. 406–444; 1929.

[5] Moyse and White, Trans. Soc. Motion Picture Engrs., **13**, pp. 445–452; 1929.

[6] Sandvik, Proc. 7th Int. Cong. Phot., p. 243; 1928.

[7] A. and L. Lumière and A. Seyewetz, Sci. et. Ind. Phot., **12**, p. 128; 1928; "On compensera facilement l'inconvénient de la legère surexposition exigée par ce révélateur en s'addressant à une émulsion trés sensible comme celle de la plaque Lumière 'Étiquette Violette'."

II. EXPERIMENTAL PROCEDURE

1. CHOICE OF PLATES

All tests were made with plates, as the precision measurements of spectrography and astronomy are still impossible on film base.

The Seed's 23 was chosen as a moderate-speed emulsion of the general type most useful in spectrography. The Speedway and Press plates are the fastest emulsions available on glass from their respective makers. The resolving power most frequently becomes a serious consideration when it is necessary to use this type of plate, and the advantages of special developers may be expected to be most evident with those emulsions.

2. SENSITOMETRY

Sensitometric measurements were made by the standard methods of this bureau. Exposure was by nonintermittent sector wheel at an intensity of 1 m candle of the quality of noon sunlight.

The Seed's 23 and Speedway plates were tested with a light source consisting of a gas filled incandescent light operated at a color temperature of 2,810° K. and a filter of Corning "Daylite" glass. The Press plates were exposed to the source adopted by the Seventh International Congress of Photography, an incandescent light operated at 2,360° and the corresponding Davis-Gibson filter. The difference in speed numbers with these sources appears to be within the limits of error of sensitometry. Development was carried out at 20° using the brush method for the developers where the maximum time did not exceed 12 minutes. The slow developers, requiring 30 to 120 minutes, were necessarily used without agitation; the plates were left emulsion up in the solution and did not develop the streaks which are liable to occur in a vertical tank. Densities were measured in diffuse light, the fog density being automatically subtracted; using backed plates, the fog strip was uniform throughout. Speed numbers are $10/i$. Where a single number is given, the curves crossed on the exposure axis within the limits of error; a noticeable shift with time of development is indicated by the use of three speed numbers. Some indication of the changes in the underexposure region is given by the density at an exposure of 0.0294 candle meter second; the exponent (as $D^{1.0}_{0.029}$) indicates the contrast to which the plate was developed.

3. MEASUREMENT OF RESOLVING POWER

Resolving power was measured with the same parallel-line test object and lens used for this purpose by Davis and Walters,[8] their procedure being in complete agreement with the later recommendations of Sandvik.[9] The test object consists of groups of six parallel lines separated by spaces of equal width, in which the density exceeds that of the lines by approximately 4. This was photographed on the backed test strips at such scale that the distances between centers of lines in the image varied from 8.3 μ to 25 μ. Each test strip was given a series of exposures increasing by a factor of about one-third. The performance of the lens at *f*/11 was found to be slightly superior to that at *f*/16 because of the distinct appearance of diffraction at the smaller stop.

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[8] Davis and Walters, B. S. Sci. Paper No. 439.

Plates were developed to a contrast within their normal working range. On completing the sensitometer tests, γ was plotted against the time of development, and also against the corresponding values of fog, and the required time read off the curve. As a check on the interpolation, sensitometer exposures were developed with each set of resolution tests strips. Except where excessive fog would be produced, the Seed's 23 plates were developed to a γ of approximately 1.5 and the Speedway to approximately 1.0. The Press plates were developed to what was judged, from inspection of the curve of γ against fog, to be the optimum contrast; we consider the results with this emulsion the most satisfactory.

The greatest uncertainty in determination of resolving power lies in assigning a number to any given test image. The strips were observed with a binocular microscope with 25 mm objectives and 10× eyepieces under lighting conditions found to impose very little eyestrain. A considerable number of readings were also made by projection at 800 diameters, the image being observed from 1 or 2 m distance; the light intensity was too low for comfort, and the results while in reasonable agreement with those by the other method, are considered less satisfactory. The criterion for resolution which was applied, was that all six lines of a group should appear suitable for definite settings of a cross hair. The resolution number assigned to a test strip was the minimum separation resolved at any one of the series of exposures. All tests were made in quadruplicate; the number given in the tables for a given emulsion, developer, and observer is the average of four strips.

Three or four observers were used in all cases. The identity of the test strips could not be entirely concealed from the observers, but there is little evidence of prejudice. The errors of observation will be discussed with the results.

4. SPECTROGRAPHIC TESTS

Some of the developers were compared under conditions of actual spectrographic work. The carbon arc band at 3,883 A was photographed with the large grating spectrograph of the spectroscopic section of this bureau, using a concave grating of 21-foot radius, 15,000 lines per inch and a 5 μ slit width. After careful focusing on backed lantern-slide plates, Speedway plates (emulsion 2469) were given a series of eight exposures each to the same source. Figure 1 is a reproduction at 163 diameters of the band head on the lantern slide focus plate and on Speedway plates developed with five formulas, the best exposure in each case being selected for enlargement.

5. DEVELOPERS

(a) MATERIAL

The developing agents were commercial materials passing the United States Government specifications with the exception of paraphenylenediamine (base). This is very unstable in air. The available material was twice sublimed under reduced pressure at the start of the investigation, the product being white and giving a nearly colorless solution, but it was distinctly darkened in a few weeks. Sodium carbonate was assayed by acid titration, and sodium sul-

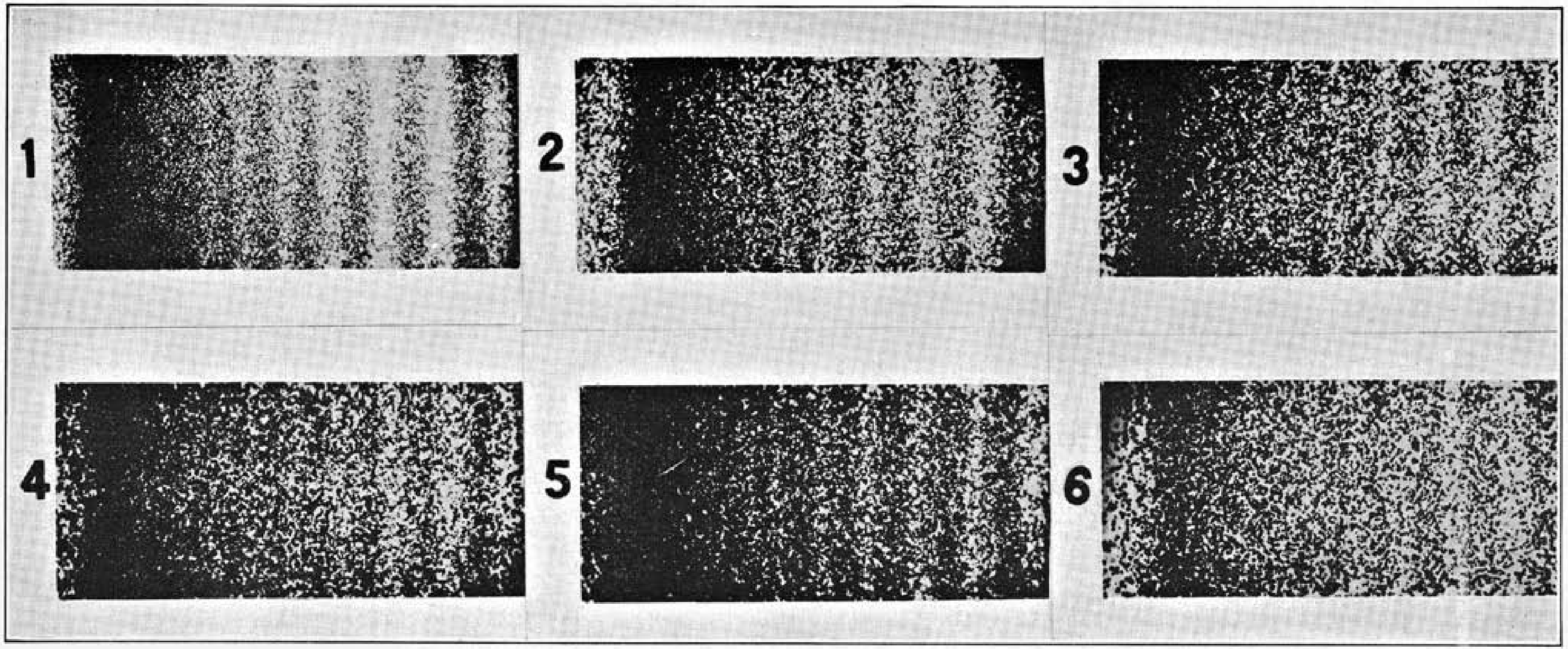

Figure 1.—*Spectrograms of carbon arc band at 3,883 A*

Taken on—
1. Lantern slide plate.
2. Speedway plate developed with *p*-phenylenediamine-borax formula.
3. Speedway plate developed with metol-hydroquinone-borax formula.
4. Speedway plate developed with metol-borax formula.
5. Speedway plate developed with metol-borax formula +0.5g *KBr*/liter.
6. Speedway plate developed with concentrated metol-hydroquinone formula.

phite by iodine titration. The amounts given represent actual Na_2CO_3 and Na_2SO_3; U. S. P. borax was twice recrystallized for use.

(b) FORMULAS

Pyrogallol.—This is the developer normally used for sensitometry at the Bureau of Standards:

Stock solutions:

A	Water	ml	1,000
	Pyrogallol	g	60.0
	Potassium metabisulphite	g	12.0
B	Water	ml	1,000
	Sodium sulphite	g	95
C	Water	ml	1,000
	Sodium carbonate	g	70

For use, 1 volume each of A, B, and C plus 7 volumes of water.

Concentrated metol-hydroquinone.—A developer of the universal type much used for practical work at this bureau:

Water	ml	1,000
Metol	g	1.6
Hydroquinone	g	5.6
Sodium sulphite	g	21.3
Sodium carbonate	g	30.0
Potassium bromide	g	.75

Dilute metol-hydroquinone.—Recommended by Lumières and Seyewetz [10] as giving a slight reduction in grain size, equivalent to the Metol-hydroquinone-borax formula:

Metol	g	0.16
Hydroquinone	g	.30
Sodium sulphite	g	3.0
Sodium carbonate	g	1.6
Potassium bromide	g	.2
Water to make	liter	1.0

Metol-hydroquinone-borax.—Recommended for reduction of graininess in motion-picture negatives: [11]

Metol	g	2.0
Sodium sulphite	g	100
Hydroquinone	g	5.0
Borax	g	2.0
Water to make	liter	1.0

Carlton and Crabtree [12] state that graininess can be further decreased by reducing the concentration of developing agents in this formula to one-half, other concentrations being unchanged.

Metol-borax.—Recommended by Moyse and White for use with motion-picture negatives.[13]

Metol	g	2.5
Sodium sulphite	g	75
Borax	g	5.0
Water to make	liter	1.0

p-Phenylenediamine-borax.—Recommended by the Lumières and Seyewetz [14] as "giving the best results."

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[10] Lumières and Seyewetz, Sci. et. Ind. Phot., **8A**, p. 126; 1928.

[11] Crabtree, Trans. Soc. Motion Picture Eng., p. 77; 1927.

[13] Moyse and White, Trans. Soc. Motion Picture Eng., **13**, p. 445; 1929.

[14] Lumières and Seyewetz, Sci. et. Ind. Phot., **7A**, p. 108; 1927.

p-Phenylenediamine (base)	g	10
Sodium sulphite	g	60
Borax	g	50
Water to make	liter	1.0

p-Phenylenediamine-carbonate.—The Lumières and Seyewetz[15] state that this formula gives more rapid development and better density than the diamine-borax, but the grain is noticeably coarser.

p-Phenylenediamine (base)	g	10
Sodium sulphite	g	60
Sodium carbonate	g	3.0
Water to make	liter	1.0

Hydroquinone-borax:

Hydroquinone	g	5.0
Sodium sulphite	g	75.0
Borax	g	5.0
Water to make	liter	1.0

Physical developer:[16]

Metol	g	25.0
Citric acid	g	50.0
20 per cent gum arabic solution	ml	50.0
Water to make	liter	1.0

For use add 2 ml of 10 per cent silver nitrate to 50 ml of the above.

Of these developers, the pyrogallol and concentrated metol-hydroquinone are common practical formulas. The metol-hydroquinone-borax and metol-borax formulas, which can now be classed as practical, are based on the use of high sulphite concentration and greatly reduced alkalinity with a developing agent of high reduction potential; the rate of development indicates that only a small proportion of the silver in the developed image can be derived from the slow process of solution of silver halide and reduction in solution. In the *p*-phenylenediamine developers the "chemical" development is greatly decreased by the use of a developing agent of low reduction potential,[17] and reduction takes place at a low rate which probably corresponds to "physical" development. The hydroquinone-borax formula is comparable to the *p*-phenylenediamine-borax, in reduction potential and solvent action; it was introduced only to see if a specific effect of the developing agent on the resolution was detectable, as we did not expect it to be of practical value. Physical development is known to have a favorable influence on resolution both by its effect on grain size and because it gives a surface image free from the effects of irradiation. It might be of value in spite of the known depression of speed in case it made possible a resolution which could not be obtained with any emulsion by normal development.

III. DISCUSSION OF RESULTS

1. SENSITIVITY

The sensitometer tests of the three emulsions listed in Tables 1, 3, and 5 show a wide variation in effective sensitivity of a given emulsion developed with the different formulas. This variation increases with

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[15] Lumières and Seyewetz, Sci. et. Ind. Phot. **8A,** p. 126; 1928.

[16] Lüppo-Cramer, Phot. Ind., **13,** p. 660; 1915.

[17] Nietz, Theory of Development, rates *p*-phenylenediamine hydrochloride at 0.4 and metol at 20, hydroquinone being taken as 1.0; *p*-phenylenediamine base probably has a slightly higher potential than its salt.

the speed of the plate, but the order in which the developers fall is practically the same for all three emulsions.

The special developers with high solvent action and low reduction potential (*p*-phenylenediamine-borax, *p*-phenylenediamine-carbonate, hydroquinone-borax) caused a very considerable depression in speed; in the extreme case of purely physical development, the loss was 80 to 90 per cent. The dilute metol-hydroquinone developer, which would be closely reproduced merely by diluting the concentrated formula to ten times its volume and doubling the bromide, gave normal speed numbers, but, by far, the worst fog for a given contrast.

The metol-hydroquinone-borax and metol-borax developers somewhat unexpectedly gave higher speeds than the standard formulas, and better densities in the underexposure region at moderate values of γ.

TABLE 1.—*Sensitometric characteristic of Seed's 23 plate (emulsion No. 7855) with the different developers*

[Figures in parentheses indicate time of development in minutes]

Developer	Speed	D $^{1.5}_{0.029}$	γ			Fog		
Standard pyrogallol	230	0.12	(3) 1.05	(6) 1.50	(12) 2.03	(3) 0.07	(6) .19	(12) 0.42
Concentrated metol-hydroquinone	200	.09	(1.5) 1.44	(3) 2.03	(6) 2.17	(1.5) .08	(3) .14	(6) .41
Dilute metol-hydroquinone	245	--------	(30) .65	(60) .96	(120) 1.30	(30) .31	(60) .65	(120) 1.12
Metol-hydroquinone-borax	320	.13	(3) .73	(6) 1.13	(12) 1.50	(3) .05	(6) .15	(12) .29
Metol-borax	330	.15	(3) .77	(6) 1.20	(12) 1.69	(3) .07	(6) .18	(12) .33
p-Phenylenediamine-borax	165	.10	(30) .84	(60) 1.17	(120) 1.60	(30) .13	(60) .19	(120) .24
p-Phenylenediamine-carbonate	165	.08	(15) .86	(30) 1.07	(60) 1.31	(15) .18	(30) .21	(60) 0.26
Physical developer 10°	(10) 19 (20) 27 (40) 37	.00	(10) .77	(20) 1.30	(40) 1.64	(10) .05	(20) .10	(40) .18

TABLE 2.—*Resolution of Seed's 23 plate (emulsion 7855)*

[The resolution is expressed in microns spacing of the closest set of lines resolved, and values are rounded to 0.5 μ]

Developer	γ	Fog	Resolution as determined by observer			
			C	D	H	S
Standard pyrogallol	1.50	0.24	15.0	15.0	15.0	15.0
Concentrated metol-hydroquinone	1.45	.06	14.0	15.0	16.0	14.5
Dilute metol-hydroquinone	.56	.17	14.5	15.0	17.5	15.0
Metol-hydroquinone-borax	1.57	.36	14.0	15.5	16.0	16.0
Metol-borax	1.33	.24	13.0	15.5	16.5	16.0
p-Phenylenediamine-borax	1.35	.19	12.0	13.5	14.5	14.0
p-Phenylenediamine-carbonate	1.37	.27	13.5	13.5	16.5	15.0
Physical	.90	.08	13.0	14.0	14.5	15.5

Table 3.—*Sensitometric characteristics of Eastman Speedway plate (emulsion Nos. 2357 and 2469) with the different developers*

[Figures in parentheses indicate time of development in minutes]

Developer	Emulsion No.	Speed	$D_{0.029}^{1.0}$	γ			Fog		
Standard pyrogallol	(2357)	400	0.15	(3) 0.70	(6) 1.10	(12) 1.30	(3) 0.10	(6) 0.18	(12) 0.35
	(2469)	490	.12	(3) .55	(6) .86	(12) 1.33	(3) .05	(6) .20	(12) .37
Concentrated metol-hydroquinone.	(2357)	300	.12	(1.5) 1.31	(3) 1.33	(6) 1.52	(1.5) .18	(3) .20	(6) .35
Dilute metol-hydroquinone	(2357)	530	.17	(30) .45	(60) .61	(120) .95	(30) .18	(60) .32	(120) .53
Metol-hydroquinone-borax	(2357)	510	.22	(3) .54	(6) .77	(12) .97	(3) .10	(6) .20	(12) .32
Metol-borax	(2469)	525	.20	(3) .45	(6) .80	(12) 1.10	(3) .05	(6) .16	(12) .27
	(2357)	430	.18	(3) .66	(6) .88	(12) 1.20	(3) .12	(6) .20	(12) .30
Metol-borax+0.5 g *KBr/liter*	(2357)	(3) 300 (6) 440 (12) 510	.25	(3) .51	(6) .77	(12) 1.00	(3) .04	(6) .09	(12) .15
p-Phenylenediamine-borax	(2357)	210	.11	(30) .72	(60) .87	(120) 1.05	(30) .15	(60) .26	(120) .39
p-Phenylenediamine-carbonate	(2357)	(30) 220 (60) 220 (120) 420	------	(30) .67	(60) .95	(120) .90	(30) .23	(60) .30	(120) .41
Physical developer 20°	(2357)	(2) 31 (4) 34 (8) 52	.00	(2) .20	(4) .60	(8) 1.06	(2) .10	(4) .13	(8) .23

Table 4.—*Resolution of Eastman Speedway plate (emulsion 2357)*

[The resolution is expressed as microns spacing of the closest set of lines resolved, and values are rounded to 0.5+ μ]

Developer	γ	Fog	Resolution as determined by observer			
			C	D	H	S
Standard pyrogallol	0.84	0.15	15.0	16.5	17.5	16.0
Concentrated metol-hydroquinone	.87	.06	15.5	17.5	17.5	17.0
Dilute metol-hydroquinone	.47	.24	16.0	19.0	19.0	16.0
Metol-hydroquinone-borax	1.09	.36	14.5	18.5	18.5	17.5
Metol-borax	.84	.20	14.0	18.5	18.5	16.5
p-Phenylenediamine-borax	.97	.36	14.0	15.0	15.5	15.0
p-Phenylenediamine-carbonate	.72	.30	15.0	17.5	16.0	15.0

TABLE 5.—*Sensitometric characteristics of Hammer Press plate (emulsion 4063) with the different developers*

[Figures in parentheses indicate time of development in minutes]

Developer	Speed	$D_{0.029}^{1.0}$	γ			Fog		
Standard pyrogallol	680	0.32	(3) 0.64	(6) 1.05	(12) 1.33	(3) 0.08	(6) 0.13	(12) 0.27
Concentrated metol-hydroquinone	495	.26	(1.5) 1.00	(3) 1.45	(6) 1.57	(1.5) .06	(3) .12	(6) .24
Dilute metol-hydroquinone	730	-------	(15) .36	(30) .61	(60) .77	(15) .09	(30) .17	(60) .33
Metol-hydroquinone-borax	715	.33	(3) .40	(6) .75	(12) 1.20	(3) .06	(6) .13	(12) .26
Metol-borax	725	.36	(3) .51	(6) .82	(12) 1.13	(3) .07	(6) .14	(12) .23
p-Phenylenediamine-borax	215	.12	(30) .68	(60) .88	(120) 1.13	(30) .14	(60) .19	(120) .27
p-Phenylenediamine-carbonate	300	.22	(15) .54	(30) .73	(60) .92	(15) .14	(30) .18	(60) .24
Hydroquinone-borax	(30) 155 (60) 290 (120) 400	.17	(30) .28	(60) .70	(120) 1.00	(30) .03	(60) .14	(120) .40

TABLE 6.—*Resolution of Hammer Press plates (emulsion 4063)*

[The resolution is expressed in microns spacing of the closest set of lines resolved, and values are rounded to 0.5 μ]

Developer	γ	Fog	Resolution as determined by observer		
			D	H	C
Standard pyrogallol	1.14	0.15	15.0	15.0	19.0
Concentrated metol-hydroquinone	1.35	.11	15.5	15.5	18.0
Dilute metol-hydroquinone	.50	.11	17.0	17.0	18.0
Metol-hydroquinone-borax	1.03	.22	16.5	15.5	18.0
Metol-borax	.92	.16	16.0	15.0	18.5
p-Phenylenediamine-borax	.75	.19	16.0	14.5	15.5
p-Phenylenediamine-carbonate	.75	.16	14.0	14.0	16.5
Hydroquinone-borax	.57	.08	16.0	14.0	16.0

TABLE 7.—*Rating of developers, on resolving power only, by the different observers*

[Two or three numbers are assigned where the resolution numbers for the corresponding developers were identical]

Developer	Numerical order of the developers on scale of decreasing resolution										
	Observer D			Observer C			Observer H			Observer S	
	Seed's 23	Speedway	Press	Seed's 23	Speedway	Press	Seed's 23	Speedway	Press	Seed's 23	Speedway
Standard pyrogallol	3-4-5	2	2	7	5	7	2	3-4	3-4	3-4-5	3-4
Concentrated metol-hydroquinone	3-4-5	3-4	3	4	6	3	3	3-4	5-6	2	6
Dilute metol-hydroquinone	3-4-5	7	7	6	7	6	7	7	7	3-4-5	3-4
Metol-hydroquinone-borax	6-7	5	6	5	3	4	4	5	5-6	6-7	7
Metol-borax	6-7	6	4-5	2	2	5	5-6	6	3-4	6-7	5
p-Phenylenediamine-borax	2	1	4-5	1	1	1	1	1	2	1	1-2
p-Phenylenediamine-carbonate	1	3-4	1	3	4	2	5-6	2	1	3-4-5	1-2

2. RESOLVING POWER

The discrepancies between the observers are of the same order as the differences produced by the developers, so that the only unqualified statement possible is that the development has little effect on resolution. This is disappointing, since both our own photomicrographs and those of the Lumières and Seyewetz [18] show distinctly smaller silver grains in the images developed by the special formulas, while the increasing use of the metol-hydroquinone-borax developer for reducing graininess in motion-picture negatives indicates that this type can decrease the number of clumps of grains. It seems necessary to conclude that resolution as measured by the standard test is not directly dependent on grain size, or on the factors controlling graininess. Preliminary experiments on the accuracy of setting a cross hair on fine lines developed by standard and special formulas gave no indication of any marked improvement; refinements on the technique employed will be necessary, but we believe that a study of the factors influencing accuracy of such distance measurements on plates might be of greater utility than the usual determination of resolving power.

Table 7 shows that the individual observers were more likely to agree on the order in which they placed the developers than on the absolute magnitude of the resolution numbers; there was, however, also a tendency to individual preferences for or against one or two developers, which were maintained on all emulsions and which can not be ascribed to previous bias. The data indicate:

1. Both *p*-phenylenediamine formulas, the hydroquinone-borax, and the physical developers, improved resolution over the standard formulas. The physical developer was no better than those first mentioned.

2. The metol-hydroquinone-borax and metol-borax developers were no better than the standard pyrogallol or metol-hydroquinone in their effect on resolution.

3. The dilute metol-hydroquinone formula gives probably the worst resolution. It is interesting to compare this with the concentrated formula, which gives a much coarser grain, but is so far superior as to contrast and fog that resolution is distinctly better; on a test object of lower contrast ratio, or in actual spectrographic work with faint lines, the superiority would be more marked.

Such improvement as was obtained was as distinct with the Seed's 23 as with the faster plates. The Lumières and Seyewetz [18] report that in the case of a process plate the grain is practically independent of the developer.

In spite of the negative results of the resolution test, there has been general agreement that the spectrum plates developed with the metol-hydroquinone-borax and metol-borax formulas show more detail than the plate developed with the concentrated metol-hydroquinone; this is unquestionably true with the *p*-phenylenediamine-borax. Viterbi [19] has already illustrated good results obtained with the metol-hydroquinone-borax formula, but unfortunately gives nothing for comparison.

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[19] Viterbi, Proc. 7th Int. Cong. Phot., pp. 365-367.

The resolution number and silver grain obtained with the hydroquinone-borax and *p*-phenylenediamine-borax developers are very similar. We doubt that the latter reducing agent has a specific influence independent of its reduction potential.

3. UTILITY OF THE DEVELOPERS

Judging the developers by their effects both on resolution and sensitivity, it appears that none of those tried offer a marked improvement over the standard formulas. The *p*-phenylenediamine developers are unfortunately eliminated by their effect on sensitivity. By way of illustration, the Press plate, developed with *p*-phenylenediamine-borax to a γ of 0.75 and fog of 0.19, has a speed of 215 and resolution number of 15; the Seed's 23, developed with concentrated metol-hydroquinone to a γ of 1.45 and fog of 0.06, has a speed of 200 and resolution number of 14. In practice, the use of the latter combination is very obviously preferable. The metol-hydroquinone-borax and metol-borax developers increase the effective sensitivity and may appreciably improve the detail of the image in some cases. They are thoroughly practical developers if it is remembered that they are quite sensitive to the soluble bromide which accumulates in use. A small amount can be compensated by increasing the development time (see Table 3) and may be an advantage; but it is well to remember that in most scientific applications of photography the overhead expense on a given exposure normally makes it very false economy to endanger results by saving developer.

IV. SUMMARY

1. Six developers characterized by increased solvent action on silver bromide and decreased reduction potential have been compared with standard pyrogallol and metol-hydroquinone formulas. The comparison is based on (*a*) sensitometric tests, using three emulsions; (*b*) tests of resolving power by the parallel-line test object, using the same emulsions; and (*c*) spectrographic exposures with one of the emulsions.

2. Only the developers with lowest reduction potential effected an appreciable improvement in resolving power. These developers are of no practical use because they greatly decrease the effective sensitivity.

3. The "borax" developers used in motion-picture laboratories are satisfactory for spectrographic work, but improvement over the standard formulas can not be expected to be large.

V. ACKNOWLEDGMENTS

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