

THE PHOTOGRAPHIC PLATE. III

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THE EMULSION. PART III

The difference in sensitiveness between collodion and gelatine plates shows that there is an effect due to the nature of the medium in which the silver salt is suspended. It is not a simple matter to decide to what the effect is due, and it will be well first to see what is known in regard to the matter.

Lüppo-Cramer¹ believes that the sensitizing action of gelatine is negligible and he is therefore forced to find another explanation².

"If we exclude the possibility of the medium playing any part during the exposure, the only alternative is to attribute the effect of the colloid to an action on nascent silver bromide or to an action on silver bromide during the process of ripening. If we compare gelatine with collodion, we notice one fundamental difference, that gelatine is soluble in water and collodion in a mixture of alcohol and ether. I have previously shown that this difference is fundamental because the substances which ordinarily coarsen the grain of the emulsion lose part of their efficiency in alcoholic solution.³

"My experiments on the mercuric iodide emulsion⁴ gave me a new clue. When mercuric iodide is emulsified in gelatine, the yellowish white modification is obtained, while the much more sensitive red form is obtained when gum arabic is used as binder. It seemed probable that a careful study of the conditions would enable me to show that different modifications of the silver halides are formed during emulsification. Since the two forms of mercuric

¹ Jour. Phys. Chem., 14, 145 (1910).

² Lüppo-Cramer: Phot. Correspondenz, 40, 673 (1903).

³ Ibid., 40, 89 (1903).

⁴ Eder's Jahrbuch der Photographie, 17, 30 (1903).

iodide are very easily recognized on account of the marked difference in color, I studied this compound more carefully. It may be stated in advance that the halide emulsified in gum arabic is not to be compared with the one precipitated from aqueous solution. My mercuric iodide plates have a very fine grain. When examined under a magnification of one thousand diameters, the grain is seen to be distinctly finer than that of the ordinary dry plate; no crystalline structure can be detected. One might nevertheless assume that the formation of the yellow modification in gelatine was due to the greater viscosity of the emulsifying solution. Numerous experiments have shown that the red halide never forms even in extremely dilute gelatine solutions while the yellow form is not obtained from gum arabic solutions of any concentration.

"Caseine solution behaves exactly like a gelatine solution, the emulsion always containing the yellow modification of the iodide. For this reason I have also made comparative experiments with a mercuric iodide caseine emulsion obtained as follows: Twenty grams of purest caseine were shaken up with 400 g H_2O and were carried into solution by the addition of the least possible amount of ammonia. An ammonia solution (sp. gr. 0.91) was diluted to one-tenth and 15 cc of this taken. A few drops of ether were added to the solution to get rid of the troublesome foam. Twenty grams of potassium iodide were added to the clear caseine solution, and then 20 g $HgCl_2$ dissolved in 200 cc of hot water.

"I was not able to find another medium like gum arabic which would give the red form of the mercuric iodide emulsion. No emulsion was formed when the iodide was prepared in starch solutions of different concentrations. Instead, a coarse-grained, red product separates which is very like what one gets by precipitation from water solutions. The following experiment seemed to me of importance as showing that a relatively small amount of gelatine will cause the formation of the yellow mercuric iodide even in a solution containing gum arabic.

"A solution, containing 100 cc of a ten percent gum arabic solution, 15 cc of a ten percent solution and 5 g KI, was heated to 45°. To this was added a boiling solution of 5 g HgCl₂ in fifty of water. The yellowish white form of the iodide was obtained. We get the same result if we substitute 25 cc of an ammoniacal caseine solution of the gelatine solution. If 10 cc of the gelatine solution are added instead of fifteen, the pure yellow form is not obtained but rather an intermediate product having a pinkish orange color. From these experiments one is tempted to conclude that gelatine and caseine have a specific emulsifying effect, exceeding that of gum arabic; and that in the gum arabic emulsion we have a product which resembles more closely the product obtained by precipitation under ordinary conditions.

"Further experiments seem to indicate, however, that gum arabic has a positive effect. If mercuric iodide is formed in a one percent gum arabic solution, it is pinkish orange, while in a corresponding gelatine solution it is a pure yellow. These experiments prove conclusively that the medium has a tremendous effect on the form in which a precipitate occurs. At present we are quite unable to say anything definite in regard to the nature of this effect."

Later experiments by Lüppo-Cramer¹ with silver bromide emulsified in gelatine, caseine and gum arabic showed that the emulsions obtained with caseine and gum arabic are much less sensitive than the one obtained with gelatine. "After the emulsification the caseine emulsion and the gum arabic emulsion were made to solidify by addition of gelatine and the soluble binder was then washed out whereby the 'sensitizing' action of the gelatine was the same for the three emulsions. The difference in the sensitiveness could not be due either to the size of the grain of the emulsion or to the reducing action of the binder."

When silver iodide is emulsified² in gum arabic the sen-

¹ Eder's *Jahrbuch der Photographie*, 18, 436 (1904).

² Lüppo-Cramer: *Ibid.*, 20, 385 (1906).

sitiveness is ten to a hundred times as great as when the salt is emulsified in gelatine.

Schloemann¹ has made experiments on the sensitiveness of silver bromide when suspended in a silicic acid gel. I quote from this paper.

“Experiments with an emulsion of silver bromide in silicic acid are of importance for our knowledge of the photochemical reaction when silver bromide is exposed to light, because in this case the formation of the latent or of the visible image cannot depend in any way on the action of an organic binder, as may be the case with gelatine, collodion, agar-agar, starch, gum arabic, etc. It is well known that the presence of such binders during the exposure has been supposed by some to be an important factor in the photochemistry of silver bromide. As instances of this I may cite the tanning theory of solarization and the often disputed belief that the latent image consists entirely or in part of an organic silver salt. These are questions which cannot be decided off-hand by experiments with silver bromide containing no binder. It seemed desirable therefore to prepare a silver bromide emulsion in an indifferent, inorganic medium and to study the behavior of the latent image both as regards physical development after fixing and as regards the action of concentrated nitric acid. The sensitometry of such an emulsion is also a matter of interest.

“At the suggestion of and together with Professor Karl Schaum, the author undertook to work out the preparation of an emulsion of silver bromide in silicic acid and to make experiments of the kind indicated. The most important results of the investigation shall now be given.

Preparation of a Colloidal Silicic Acid Solution

“Lobry de Bruyn² describes the following method of preparing an emulsion of silver bromide in silicic acid. Into each of two flasks he places 10 cc sodium silicate (sp. gr.

¹ Phot. Correspondenz, 43, 466 (1906).

² Recueil Trav. Pays-Bas, 19, 236 (1900).

1.09) + 5 cc nitric acid (sp. gr. 1.08) and then adds 5 cc of a tenth-normal silver nitrate solution to one flask and 5 cc of a tenth-normal potassium bromide solution to the other. When the solutions in the two flasks were mixed, a white milky emulsion was obtained which was said to gelatinize in two or three minutes. According to a further statement of Lobry de Bruyn the sensitiveness of such an emulsion exceeds that of a ripened silver bromide gelatine.

"When these experiments were repeated carefully, it was found that in consequence of the high concentration of the silicic acid solution gelatinization took place too soon, so that it was scarcely possible to mix the silver and the bromide solutions satisfactorily even when working rapidly. It was seldom possible to pour several plates, one after another, from the same emulsion. A still more disturbing factor for our experiments was the formation of large amounts of potassium nitrate during the precipitation of the silver bromide.

"In order to work under the most simple conditions, we prepared a supply of colloidal silicic acid by means of dialysis. We diluted 30 cc of a water glass solution (sp. gr. 1.30) and 30 cc pure concentrated hydrochloric acid¹ each with 120 cc distilled water and then poured the acid into the silicate solution, stirring all the while. The mixture was dialyzed in two portions. By using running water, this process could usually be finished in about three days. We made a satisfactory dialyzer out of a beaker, 15 cm in diameter, by removing the bottom and covering the opening with pig's bladder which had been purified by treatment with alcohol. Since the stock solution gelatinizes very readily when apparently pure, it is not safe to carry on the dialysis until all of the hydrochloric acid and sodium chloride has been removed. The dialysis should be stopped at the point where an addition of silver nitrate still causes a

¹ Commercial water glass must always be tested as to its specific gravity and diluted if necessary. Pure concentrated hydrochloric acid can be used without test.

slight opalescence. Immediately before using, such a solution should be dialyzed again until no opalescence can be detected. It is then ready for use. The gelatinization of the sol takes place readily on heating or on addition of electrolytes, especially ammonium carbonate.

"E. Jordis¹ has discussed the question whether we should consider a solution of silicic acid as pure when it does not opalesce with silver nitrate. He found that it was scarcely possible to free a silicic acid sol or gel completely from the electrolytes used in preparing it. Owing to the amphoteric character of the silicic acid, small amounts of hydrochloric acid or caustic soda are held back because the silicic acid can react with the hydrogen ions of the one or the hydroxyl ions of the other. This explanation assumes a chemical reaction between the sol and gel and the substances which give rise to the sol. We may instead be dealing with a case of absorption or adsorption. It is still an open question which hypothesis is the more satisfactory.

"Graham² considered the colloids as entirely pure after dialysis and he was familiar with the fact that the sol is more stable in presence of a trace of acid or base. According to his view this is a case of protective action.

Preparation of Silver Bromide Silicic Acid Plates

"For the experiments to be described the silver bromide silicic acid emulsion was made up as follows:

I	II
35 cc silicic acid sol 5 cc KBr 1 : 10	35 cc silicic acid sol 2.5 cc AgNO ₃ 1 : 10

"In the dark-room solution II was allowed to drop from a separatory funnel into solution I. When this was done carefully, an extremely fine-grained emulsion was obtained which was allowed to stand for half an hour in the dark.

¹ Zeit. Elektrochemie, 11, 288, 835 (1905).

² Liebig's Ann., 121, 1 (1862).

This was filtered through flannel and poured upon glass plates which had been cleaned with pumice. About 10 cc of the emulsion was used for a plate 9 cm x 12 cm.

"The filtration of the emulsion was necessary to remove coarse-grained, precipitated silver bromide which is not embedded in the gel and which is very apt to fog because the developer comes in contact with it on all sides. The plates were placed in light-tight pasteboard boxes so that the slowly solidifying emulsion might gelatinize without being removed. When silicic acid solutions have stood for a while, they gelatinize rapidly. When freshly-prepared they sometimes need to be inoculated with ammonium carbonate, especially if the temperature of the room is low. As a rule the film is completely solidified at the end of four to six hours, so that the plates can then be washed in order to remove the excess of potassium bromide. The washing is continued until the wash water does not cloud on addition of silver nitrate.

"Among the more noticeable properties of the silicic acid plate is the one that its opacity is low, like that of a wet gelatine plate having a low sensitiveness. When examined in transmitted daylight the general color of the film is bluish white. After prolonged exposure to direct sunlight the film becomes gradually grayish black.

"If the silver bromide silicic acid emulsion is ripened in a way analogous to the ammoniacal silver oxide method, the plate then becomes blackish violet very quickly when exposed to daylight. Unfortunately, this rapid increase in the sensitiveness to light could not be taken advantage of in this investigation because the presence of ammonia was to be avoided and also because ammonia affected the rate of solidification of the sol in a way which could not be allowed for.

"When the emulsion dries it becomes somewhat brittle and tears loose from the glass. This was not prevented by superposing a film of gelatine containing chrome alum, and we therefore made our experiments with plates which were still moist.

Determination of Sensitiveness

"To determine the relative sensitiveness to light of our moist silver bromide silicic acid films we made use of a tube sensitometer, arranged in a form more suited to our purpose than the one which R. Luther¹ recommended for obtaining graded intensities of light. In order to obtain a greater exactness, we replaced the cardboard disk by one of zinc and bored round holes with a drill instead of making them rectangular. Each hole stood to the one following it in the ratio of 2 : 1. The surfaces of the sixteen holes were as follows, the values being in square millimeters:

TABLE I

181	128	90.5	64.0
45.3	32.0	22.6	16.0
11.3	8.0	5.7	4.0
2.8	2.0	1.4	1.0

"The centres of the holes were arranged at equal distances, four to a row, on a zinc disc, 9 cm x 12 cm. Over each opening there was placed a tube, ten centimeters in length, made out of a dead-black paper. The ends of all the tubes were held in a cap provided with sixteen, equally large, circular holes. A second sensitometer, just like the first one, was fastened to it so as to make a double-barrelled sensitometer. With this it was possible to compare our silicic acid films with gelatine plates, the two being exposed under identical conditions. The whole was placed in a tin box, the inside of which was painted a dead black, and the bottom of which was arranged to accommodate two plates lying side by side.

"Luther puts the error at 10-15 percent when square holes are cut in cardboard. A greater accuracy can be obtained with circular holes bored in sheet zinc. The linear diameters of the single holes could be determined to ± 0.05 mm and those of the same size to within ± 0.025 m. The

¹ Zeit. phys. Chem., 30, 635 (1899).

larger holes were checked by means of expanding callipers and the smaller ones in an indirect way by means of callipered brass rods for each hole.

"In this double-barrelled sensitometer a silicic acid plate was placed alongside of a Hauff transparency plate which had been allowed to stand in water for half an hour. In order to get a diffused light we placed the apparatus at a distance of one meter from a window covered with several layers of silk paper. We developed with the standard ferrous oxalate developer, recommended by J. M. Eder,¹ and fixed our plates in a twenty percent thiosulphate solution.

"With an exposure of three seconds, with eight minutes development, and with the temperature of the developer 18° C, the liminal value (*Schwellenwerth*) was reached by the gelatine plate in the fourteenth field and by the silicic acid plate in the third field, the moist plates being examined, after development and fixing, with white paper pressed against the backs.

"From Table I it appears that the hole in the third field is forty-five times as large as that in the fourteenth field. With the same time of exposure this is also the ratio of the amounts of light. Since it takes forty-five times the amount of light to produce the same photochemical effect on the silicic acid plate as on the gelatine plate, we may say that a Hauff transparency plate is forty-five times as sensitive as our silicic acid plate—always assuming the general validity of Bunsen and Roscoe's intensity law.

"When left a long time in the developer, the silver bromide silicic acid plate shows a strong tendency to fog. The dried edge, where the silver bromide is not surrounded by a swelled jelly, blackens in a short time when in contact with the developer. This was perhaps what caused Lobry de Bruyn to say that silicic acid films are more sensitive than ripened gelatine films.

"A microscopic investigation showed that the silver

¹ Eder's *Handbuch der Photographie*, 5th Ed., 3, I, 213 (1902).

bromide grain, and also that of the reduced silver in the silicic acid gel was extremely fine."

It seems rather a pity that Schloemann should not have made some experiments as to the degree of sensitiveness which could be obtained by ripening his silicic acid plates. Now we know only that such plates can be made considerably more sensitive and nothing more. The reason for the omission seems to be that Schloemann was interested chiefly in the problems of the latent image and of solarization instead of the theory of ripening. Only two years ago Cooper and Nuttall¹ published a paper on the use of agar-agar as a medium for carrying the silver salts. I quote rather extensively from this paper.

"Last year, I was approached by Mr. P. Gillard, and asked to take up a new paper which he claimed to be his own invention. Demanding that he should demonstrate his process to me, I gave him facilities to do so in my laboratory. The paper was to be a self-toning paper in agar, containing gold and platinum, and having certain properties. Some of these papers were undoubtedly good, but one could not be certain of the result of any particular coating. Mr. Gillard failed very materially, in that he could not turn out consistent results. These failures are of great interest, however, and I suppose that the difficulties, which prevented him from turning out consistent results, are the same as would be encountered by others trying to use agar. Therefore they will be of interest, and we think we can point out the reasons and how to overcome them. We may mention here that Messrs. Morgan and Kidd are turning out agar P.O.P., and therefore it is possible for others to do so; moreover there are agar papers on the market in Germany. It is quite obvious to us that agar can be used as a medium for plates and bromide paper.

"Mr. Gillard's failures were chiefly:

"(1) The agar solution was not clear, containing small granules.

¹ Phot. Jour., 32, 11 (1908).

“(2) In making the emulsions one found that it would become thin and limpid, and would not set.

“(This was termed peptonizing; but the term is quite wrong, as peptones are nitrogen compounds, whereas agar contains no nitrogen, and therefore cannot be peptonized. We use the term de-gelatinize therefore.) This second fault would occur, sometimes in making the emulsion, sometimes when made and while coating; sometimes it went limpid as a whole, while at other times it occurred in parts, causing a peculiar granular appearance.

“(3) Agar does not dissolve in water, unless heated to 100° C, *i. e.*, the temperature of boiling water.

“(4) If cooled to 32°–35° C it sets very quickly and then will not dissolve again unless boiled once more; if this be done with an emulsion it is often quite spoilt.

“(5) When he added his gold chloride to the emulsion, it was necessary to get it on to the machine without a moment's delay, otherwise the gold was reduced to the metallic state before the emulsion was on the paper. The causes of these difficulties, and methods to overcome them, will be explained later.

“When I inquired of Mr. Gillard what knowledge he had of agar, I found that practically nothing was known; I could get no books on the subject, so that it was necessary to set to work to look up references to it, and to ascertain its properties. This is the work which Mr. Nuttall and myself have undertaken.

“The first question is: ‘What is agar?’ ‘To what class of substance does it belong?’ It has been shown by Payen and Porumbaru that it does not contain nitrogen, therefore it is not a proteid, peptone or albumen; nor yet is it a proteid or an albuminoid, *i. e.*, it is not a gelatine, nor a glue; it differs very materially from all these in its properties. It seems that it must be placed amongst the more complex carbohydrates, celluloses, starches and gums. On oxidation with nitric acid the two former yield oxalic acid, whereas the gums and agar-agar yield mucic acid.

For this reason Allen classifies it as a gum. Senier also classifies it as a gum. It has been shown by Payen¹ to be similar to, or to yield, pararabin, or beet-sugar gum. From its properties it appears that this is the correct group in which to put it, therefore, though in many of its properties it is anomalous.

"As bought, it is in the form of long translucent, stringy pieces, tough, dry and hard. Soaked in water, it swells up as do gelatine and the gums. The soaked substance dissolves in water when boiled, and then only slowly. Our method of dissolving it is to cut up the agar into small pieces; soak them in running water for some hours; then place in distilled water; heat the water until it boils, and continue the boiling for a quarter of an hour, stirring vigorously the whole time. If the boiling is not continued long enough two things will be noted; firstly, that the solution is lumpy, *i. e.*, that the agar has not dissolved completely; and, secondly, that it is more difficult to strain.

"For bacteriological purposes the treatment at the Cambridge laboratory is to soak the agar in a 1 percent solution of acetic acid for twenty-four hours, wash out the acid in running water, and dissolve up by boiling. We may mention in passing that the acid has no ill effect; we have treated several lots in a similar manner with good results, but the treatment seems to be unnecessary.

"Having dissolved the agar, we proceed to strain it, in order to retain solid impurities. This we do in practice through nainsook. The solution is then fairly clear, but contains a large quantity of peculiar, slightly opaque specks, and is not quite transparent as gelatine is. This renders it useless for use in emulsions for plates, but the solution can be made perfectly clear by filtering. At Cambridge it is filtered through a special paper in a large funnel, the whole being enclosed in a steam-jacketed chamber which keeps the agar hot. (The paper can be bought from any dealers

¹ Jahresbericht, 1859, 562.

in chemical apparatus.) We dissolve each gram of air-dried agar in 50 cc of water, which makes a 2 percent solution. This is then filtered at as high a temperature as possible through a hot Buchner funnel, using a pump, the flask being placed in hot water. Such a solution is quite clear and transparent.

"This forms the solution of gelose. Such a solution has the following properties, though in giving these we must note that the age of the sea-weed seems to have some effect on the properties; our results do not quite agree with those of earlier workers.

"A solution of agar in water, sets when cooled, the temperature at which it sets being about 33° – 35° . It sets very rapidly when cooled to the setting temperature, more rapidly than gelatine. The gelatinizing property is very great; it is said to be ten times as great as gelatine. Stanford puts it down as eight times as great; Allen states that gelose will form a jelly with 500 times its own weight of water.

"Peculiarly enough, and entirely different from gelatine, a solution of gelose can be boiled for a long time without becoming much less viscous. Indeed, we frequently evaporate a solution which is too weak by boiling until it is quite thick. We may boil some solutions for an hour or more. Any agar which remains over from an experiment is allowed to set, and is kept for some days; when making an emulsion, we boil it up with more water and evaporate off the excess. We found that after boiling for a quarter of an hour, the agar solution was slightly less viscous, but that continued boiling, within reason, does not make much difference for practical work. The boiling solution must be vigorously stirred in order to prevent it from being burnt; if burnt, it is quite useless for emulsions, as it produces a very dirty color. This peculiarity is of importance. Gelatine is a nitrogen compound, and when hydrolyzed by boiling or by heating with acids or alkalis, it forms various compounds, amongst which are leucine and glycocoll and ammonia. Leucine is ammonia in which one hydrogen atom is replaced

by the caproic acid group; it is an amide. Glycocoll is ammonia in which one hydrogen atom is replaced by the acetic acid group; it also is an amide. These two compounds are such as one would expect to cause fog in an emulsion, just as ammonia does, and we think that the spoiling of emulsions in gelatine may be put down to this cause in part. Now agar cannot form such compounds though it may form aldose compounds which would reduce the silver; certainly if heated with water under pressure, gelose is hydrolyzed and yields a sugar. This may account for some of the difference between working in agar and gelatine.

"On soaking agar and squeezing to extract the surplus water, we noticed that some matter appeared to be washed out. We took some agar and soaked in distilled water, poured off the water through a filter paper, and added a further quantity of distilled water. We repeatedly poured off the water in which the agar was soaked, at intervals of about an hour. The washings were then evaporated to dryness, and it was found that 18 percent had been washed out of the agar by the water, for the filter paper would have retained any solid matter.

"Air-dried agar usually contains about 21 percent moisture driven off at 100° C.

"The percentage of ash in our sample was 0.487 percent.

"The density of a solution of agar at 50° C is less than that of water at 50° C. We attempted to determine if the density could be used to ascertain the amount of agar in solution, but this has not been done up to the present.

"The viscosity of a solution of agar is much greater than that of gelatine with the same percentage of solid. We have estimated that a solution of gelatine of definite strength is about as 'thick' as a solution of agar containing 1/8 of the amount percent, this agreeing with the figures given by Stanford.

"Barker's P.O.P. formula contains 8 percent of gelatine; Valenta's contains 9.6 percent; Beadle's contains 11

percent; so that a solution of agar 1-1 1/4 percent, or 2 ozs. to the gallon, should be sufficient. We recommend that those trying agar for the first time should start with a 1 1/2 percent solution.

"A solution of 3 percent is difficult to use, as it is too thick. We find a 1 percent solution is most convenient, though a 2 percent solution is quite easily worked. A 1 percent solution is about as thick as an 8 percent solution of gelatine. If two emulsions containing the same amounts of chemicals, except that the medium in the one is gelatine, and in the other is agar, and if the solutions are of the same 'thickness,' then the amount of agar will be one-eighth the amount of gelatine; in coating a plate or paper with these solutions and drying, one will get the same amount of silver per square foot, but only one-eighth of the amount of medium when using agar. In the case of paper this would not matter so much perhaps, but with plates it means that the pellicle will be extremely thin. It will be of great interest to ascertain what influence this has, on the sensitiveness of the emulsion and on the development. If the pellicle is so much thinner, the light will be able to act more rapidly on the sensitive salt and should give increased rapidity. One would expect that in development, the developer would penetrate more rapidly and therefore develop more energetically; on that account also less exposure should suffice. In that case, one should be able to obtain plates of extreme rapidity, great latitude, and with a fine grain. Would the gradation be as delicate, however? The plates which we made worked like wet plates; they were developed and washed as quickly. One of them will be shown to-night which was intensified with mercuric chloride and potassio-silver cyanide three times, and completely washed, all within 5 minutes; it will be seen that (though the plate is badly coated) there is a total absence of the stain which would have existed had the intermediate washings been incomplete. This emulsion was matured by being plunged in boiling water for 5 minutes. The speed was about 65 H and D.

"The following do not form a precipitate with the solution of gelose:

- | | |
|------------------------------|----------------------|
| 1. Copper sulphate | 9. Platinum chloride |
| 2. Lead acetate (normal) | 10. Gold chloride |
| 3. Nickel sulphate | 11. Chlorine |
| 4. Mercuric chloride | 12. Bromine water |
| 5. Iron chloride | 13. Iodine |
| 6. Iron sulphate | 14. Chromic acid |
| 7. Potassium bichromate | 15. Picric acid |
| 8. Potassium chloroplatinite | 16. Formalin. |

"The following give a precipitate with the solution of gelose:

- | | |
|--------------------|-----------------------|
| Basic lead acetate | Phospho-tungstic acid |
| Mercuric nitrate | Alcohol." |
| Tannin | |

"Alcohol will precipitate a solution of gelose, if added in sufficient quantity. A solution containing $1\frac{1}{4}$ percent of the solid dried at 100°C (about 2 percent ordinary dry agar), is precipitated by adding about 40 percent of rectified alcohol; whereas it appears that, to a solution containing $2\frac{1}{2}$ percent of the solid dried at 100°C , even more than 40 percent may be added without definite precipitation. If a solution of agar be poured into excess of 90 percent alcohol, a white precipitate is formed at once, which collects into a coagulum, which can be separated by muslin or filter paper. Payen states that precipitation of agar by alcohol is not a good method, as it increases the percentage of ash, or solid matter. In our experiment, the ash before precipitating was 0.487 percent, but after precipitation by alcohol it was 4.06 percent; though we think this is somewhat excessive. Certainly part of the agar is left in solution in the alcohol, because, on evaporating, the alcoholic filtrate to dryness, a gummy mass is obtained. Is this part of much importance to the photographer? At present, we cannot say.

"Like gelatine, when heated with acids or alkalies, the setting property is destroyed. This will be dealt with later.

"Though the presence of small quantities of mineral acids in the solution causes it to lose the gelatinizing property, yet the solid substance soaked in water can be treated in the cold with dilute acids and alkalies without doing much harm. Hydrochloric and sulphuric acids, however, dissolve the agar; Payen says that it is dissolved by the concentrated acids, to form a hard brown mass which is insoluble in almost any ordinary reagent. We have found that it forms a brown solution, but we have not obtained the hard, insoluble mass. The solid agar can be boiled with glacial acetic acid without much change; but if containing water it dissolves the agar on heating. The 1 percent solution used for soaking, will have no detrimental effect, but will keep in solution all iron salts contained in the water, and so tend to prevent discolorations. Agar soaked in 10 percent acetic acid, however, then washed, and dissolved, had lost considerably in viscosity.

"The effect of alkalies on agar is to make the solution lose its setting properties, but at the same time it makes it a little more sticky and gummy. With a fresh solution of agar, if one puts one's finger into it the adherent drop soon separates from the main part of the solution; but when heated with a small quantity of alkali, the solution becomes somewhat more sticky and the drop does not immediately separate from the main part of the solution.

"On adding borax to a solution this effect is greatly augmented and the solution becomes so sticky (tacky) that one can draw out strings of the substance some feet in length. On rubbing between the finger and thumb it will be noticed that the untreated solution has more 'body' but is much less 'tacky.' We are of the opinion that this property will be found of great use in the practical application. We have coated paper with such a solution quite readily. The solution treated with borax in this manner sets, though much more slowly than when not so treated. The resulting jelly is much less friable and seems to be more tenacious.

"The reaction with iodine is peculiar. On adding

iodine either in potassium iodide or in alcohol, to a hot solution of gelose in water, the light yellow colour, due to the iodine, remains. On cooling, however, the yellow changes to a red purple, very much like that of iodine vapor. On heating, the purple changes to a yellow once more; the purple is developed again on cooling, and one can cool and warm repeatedly, with the same effects. There is not a perfectly sharp temperature at which this takes place, but it is between 27° C and 29° C. This darkening and lightening can be detected when so dilute as 1 part in 10,000. On adding hydrogen peroxide to the mixture of gelose and iodine and warming, the red purple given when the solution is cooled changes to a blue similar to that given by iodine and starch. This disappears on warming, and reappears on cooling; but it is quite transient, and the exact conditions determining this blue color, and its cause and meaning, have not yet been ascertained.

"Agar will absorb a small quantity of iodine, and also of bromine, the amount being 1.65 percent, whereas gelatine absorbs 6.21 percent, at 15° C. This difference will be of interest in considering any theory of the latent image in agar as compared with that in gelatine. We may say that, though one would suppose, on theoretical grounds, that on this account agar would be less suitable for emulsion work than gelatine, this is not so. We find that its physical properties are not inferior to that of gelatine, and with scarcely any maturing one can prepare a comparatively fast emulsion. We shall show some lantern slides, made on plates with a speed of about 65 H and D. It has been mentioned that a pellicle of agar will be about one-eighth as thick as a similar one of gelatine; so that the comparative ability to absorb iodine will be 6.2 percent for gelatine, and $1.65/8 = 0.2$ percent for agar; that is to say that, per area, gelatine will absorb about thirty-one times as much iodine as will agar.

"Silver nitrate forms no precipitate with a solution of gelose, but on mixing a hot solution and keeping hot, dark-

ening in color takes place; this also occurs slowly at 50° C, different samples varying considerably in the time necessary for the darkening to take place. But in any case, even boiling, it is not less than ten to twenty minutes, and may be quite a long time, so that one has sufficient time for making an emulsion. If a small quantity of hydrogen peroxide be added, no discoloration takes place at 50°; but whether this is due to the oxidation of any aldehyde formed, to the acid, we cannot say at present. Citric acid also acts as a preventive of discoloration, but not so much so as hydrogen peroxide.

"Silver-ammonia-nitrate gives no reduction at 50°, only on boiling. The solution of agar which has been boiled for some time gives but little more reduction than that which has been freshly made.

"We find that our sample of agar does not form a peculiar compound with silver nitrate, similar to that produced with gelatine.

"Fehling's solution is not reduced by a fresh solution of agar; but by boiling with acids (such as sulphuric acid) the gelose is hydrolyzed to form a sugar which reduces Fehling's, and which gives a precipitate with phenyl hydrazine. This is being further studied, and the sugar is being identified.

"The distillate of a solution of agar boiled with dilute sulphuric acid, gives only a very slight colour with aniline acetate, so that no furfuraldehyde is formed, and there is no pentose group existing as such in the agar. It forms a very slight precipitate with phenyl hydrazine. The further study of these sugars and the products of hydrolysis are not of sufficient interest to the photographer to include here, but will be dealt with later.¹ It may be that agar is a glucoside, somewhat similar in constitution to fucose, a product also obtained from some varieties of sea-weed. Glucosides, on boiling with dilute acids, give one of the sugars as a product of hydrolysis.

¹ See Bauer: Jour. prakt. Chem. (2), 30, 367 (1884); and Muntz: Bull. Soc. chim. Paris (3), 37, 409 (1907).

"Sodium metaphosphate forms a gelatinous precipitate with a solution of agar, on boiling; gelatine gives no such precipitate.

"Tannin gives a precipitate with a solution of gelose when it is strong, but it dissolves on heating; the precipitate formed by tannin and gelatine is given in very dilute solution and does not dissolve on boiling in the presence of excess of tannin.

"Chromic acid seems to have no effect on agar, such as it has on gelatine; it does not form a precipitate, nor does it render it insoluble in water as it does with gelatine. Similarly potassium bichromate does not make it insoluble; neither does alum nor formalin. A mixture of agar and gelatine can be separated by adding formalin, evaporating to dryness, and extracting with hot water; the gelatine is insoluble, whereas the agar is dissolved. After being rendered insoluble in water, the gelatine may be dissolved in dilute acids and precipitated with tannin.

"Gold chloride does not give a precipitate with agar or gelatine solution; but platinum chloride gives a precipitate with gelatine and not with agar.

"It will be seen, therefore, that the difference between agar and gelatine is very marked. Agar gives no reactions with the colour tests for nitrogenous products; especially it gives no precipitate with picric acid, mercuric chloride, platinum chloride, chromic acid. Its reaction with iodine is distinctive, also that with hardening reagents.

Curves

"We have mentioned that many substances have a peculiar influence on agar in solution; it was also obvious that some chemicals had a greater effect than others; and we sought some method of ascertaining exactly what effect each of those we use would have on the solution. We considered that we should achieve our object by ascertaining the viscosity of the mixtures at varying intervals, since it is a property of great importance to the practical emulsion

maker; so we adopted the method and apparatus of Ostwald. This is the one most used for such purposes, both in physical work and in technical determinations of such substances as gelatine, glues, etc., and we had every reason to suppose that it was the best instrument to use for our purpose.

"We found, however, that there were several objections and difficulties. The solution of agar contains minute solid impurities, and we found that they were precipitated, and by blocking the capillary caused serious errors in the rates of flow. It is extremely difficult to be certain of the strength of the solution of gelose owing to the fact that, to get it into solution, the water must be boiled and kept boiling for some time, so that a considerable amount of water is evaporated off. At first we thought that it was necessary to use a 3 percent solution, which is very viscous, too much so for the experiments and the emulsion making; we adopted this strength because we did not know what viscosity the actual maker obtained with his gelatine emulsions; Mr. Gillard used a 3 percent solution of agar, and we concluded that this must be the best strength, so that we persevered with a 3 percent solution for a considerable time. Great care has to be taken not to get any part of the apparatus cooled when manipulating the agar, and adding the chemicals. These and other practical difficulties have shown us that the method is not well adapted to the object in view—at least, not without several modifications.

"We have our results, and though we must admit that owing to the practical difficulties they are inaccurate, yet they are sufficiently accurate to be of interest, inasmuch as they give a fair estimate of the relative effect of the chemicals; as these relative effects are of extreme importance practically, we consider that it is worth while showing them. The whole, however, is being undertaken afresh, with a modified and different apparatus, using perfectly clear agar of a 1 percent concentration.

"The viscometers used by us are made with a wider

capillary than usual and standardized with phosphoric acid, sp. gr. 1.5. In the most convenient ones, the time taken to run from the upper to the lower mark was about 60 seconds at 15°, or 24 seconds at 50°, that used for such chemicals as nitric acid took 383 seconds at 15°, and 113 seconds at 50°. In all experiments 3 grams of air-dried agar were dissolved in water and made up to a final weight of 103 grams. We consider that this is much too concentrated, and that a 1 percent solution would be better.

"The agar was soaked in running water overnight, dissolved in distilled water by boiling, boiled for a quarter of an hour, made up to the correct weight, strained, cooled to 50° C, then mixed with solutions of the chemical heated to 50° C, immediately placed in the viscometer and a reading taken.

"The curves, Fig. 1,¹ show the degelatinization, at varying intervals of time; we must repeat that they are not accurate owing to the difficulties of the work; but they illustrate the effects produced in actual work and so are instructive.

"In the case of nitric acid, deci-normal, it is seen that in ten minutes the solution is only 72 percent as viscous; after twenty minutes it is 64 percent; in sixty minutes it is 11 percent as viscous; if left longer it becomes only 8 percent as 'thick' as at the commencement.

"Tartaric acid, deci-normal, causes the solution to become only about 69 percent as thick, in twenty minutes; in time (about two hours) it will be 23 percent as viscous.

"The curve for acetic acid, normal, is very erratic; probably the capillary became somewhat choked after sixty minutes. But it certainly has a considerable effect.

"Citric acid, decinormal, has a small degelatinizing effect, and even after one hour it reduces the viscosity to no more than 80 percent.

"The effect of silver nitrate, normal, is marked at first,

¹ [The cuts referred to in the text are not reproduced in this article.]

but after ten minutes there is not much alteration. The manner in which the line rises after a lapse of time is curious. The same peculiarity occurs in the curve for sodium hydrate.

"Sodium hydrate, normal, has a very considerable degelatinizing power.

"Sodium chloride has no effect whatever. Ammonium chloride, however, makes it more viscous, and in thirty-two minutes the solution has become 8 percent 'thicker.' It gradually becomes less viscous, and in about eighty minutes it returns to its initial viscosity.

"The effect of borax has been mentioned already. The curve has not been determined, as the capillary of the viscometer became blocked up.

"The next set of curves, Fig. 2, taken more exactly, show the comparative effect of citric, tartaric, and nitric acids. The results are very similar to those shown in the previous diagram. Nitric acid has a great degelatinizing power; tartaric acid is almost as potent. The effect of citric acid is very much less than that of either of the other two, and is never very great.

"The practical application of these results can now be seen. In preparing emulsions, such chemicals as free tartaric or nitric acid should be avoided; similarly, combinations of chemicals which react to produce free nitric or tartaric acid cause degelatinizing. In such a reaction as that between silver nitrate and iodine in solution, wherever a grain of silver iodide is formed, there is a concentration of nitric acid round it; this causes local degelatinization; hence the granular appearance of some of Mr. Gillard's emulsions; also it would cause coagulation of the silver haloid by destroying the colloidal nature of the medium. We found, in making emulsions, that this coagulation was a common accident, and we ascribe it to this cause. It should be mentioned that Rochelle salt, which Mr. Gillard frequently used, has an effect similar to tartaric acid, in its power of degelatinization.

"Mr. Gillard, in mixing some of his chemicals with the solution of gelose, did not dissolve them, but added them

solid. This would cause excessive local concentration, and must have been responsible for the peculiar 'boiled rice' effect in his emulsions. We have repeatedly made emulsions to his formulae, quite successfully, but we dissolved the chemicals in water and added them gradually.

"An acid is required in a P.O.P. emulsion to make the paper keep, and preserve the whites. It will be seen from the curves that, of those examined, citric acid has less degelatinizing effects than others, and should be best adapted to that purpose. We have made many emulsions with it and have found it quite suitable.

"We are now in a position to discuss the failures of Mr. Gillard, mentioned previously, and to see how to avoid them.

"(1) The opacity was due to incorrect manipulation and can be overcome by filtering the solution of gelose at a strength of about one and a half percent.

"(2) The degelatinizing is due to the presence of certain chemicals in the emulsion, either added or formed by the reactions in emulsifying. The value of the curves will now be apparent. It has been shown that nitric acid, even in small quantities, has a very great degelatinizing effect; that tartaric and acetic acids are also detrimental; that citric acid does effect the viscosity, but not to any material degree. Therefore it is advisable to use citric acid, in preference to others, in order to make the paper keep.

"It should be noted that if tartaric acid is required in an emulsion, then the emulsion should be made very much thicker at first; so that the tartaric acid may reduce the viscosity to the required degree.

"(3) The difficulty of solution causes no trouble except in washing emulsions. We are told that one cannot dissolve the emulsion after it has been set and washed; but we show a sample of bromide paper, of about the same speed as 'Nikko,' also some lantern slides, all made with emulsion which has been washed and set, then dissolved. There was scarcely any fog at all in these during development.

"(4) The setting of the emulsion is due to careless ma-

nipulation. In pouring from one vessel to another, the second vessel must be heated to about 40° C. In coating also, the same point must be noted.

“(5) The reduction of the gold chloride was due to using the salt which reduces the gold most easily. In P.O.P. emulsions there is an excess of silver nitrate over the amount necessary to form the silver haloid, and this makes the reduction take place more easily. The notes on the reducibility of gold chloride should be of use here.

Apparatus for Drying Agar Coated Papers

“Since agar when once set is insoluble in water unless heated to boiling, it seemed to us that the paper off the coating machine could be dried very quickly by means of hot air. An experimental apparatus was made on a small scale. A long tubular wooden tube of rectangular section was made. The total length was 55 feet; it was about 10 inches wide and about 3 1/2 inches deep. Paper 8 inches wide was drawn through it. This paper was supported in the tube by glass rollers (made from glass tube) placed about 1 foot apart. The end into which the paper entered was open; the other end was closed by two pieces of wood covered with plush, pressed together. About 8 feet from the exit end a box was placed under the tube, and communication was made between the box and the bottom of the tube by means of holes bored through. At the same time, communication was made with the box and the top of the tube, by means of glass tubes. A large iron pipe leading from a blacksmith's bellows through a furnace opened into the box below the tube.

“The iron pipe was heated to redness, the air was blown through it by means of the bellows. The wooden tube having been made air-tight, the only exit from the air was at the open end where the paper entered. After blowing for some time the tube became heated up to temperatures shown in Fig. 4, the highest being 84° C, or 183° F. The temperatures were ascertained by means of thermometers let into the tube by means of corks.

"The solution was then put into the pan and the paper coated and drawn through the wooden tube as shown in Fig. 3, A and B. After running for a short time, the paper on the receiving roll was quite dry, and by tearing open the box at a distance of 36 feet from the paper-inlet end, it was seen that the paper was perfectly dry there; it may have been dry before it reached that point, but we could not ascertain this, as the tube was nailed up. The speed at which the paper was being drawn through was ascertained by taking the time for a mark to run through the tube, and was found to be 4 feet per minute. A wooden shuttle 3 feet long was used to pull the commencement of the paper through the tube and to lead it over the rollers. Two strips of tape drawn through the apparatus under the paper, served to support it and prevent it from breaking. Baffle plates were inserted in the tube to mix the air, and to keep it on to the upper and lower surfaces of the paper.

"It will be noticed that the hottest air met the driest part of the paper, so as to complete the desiccation, and that the paper was dried from both sides.

Rate of paper	4 feet per min.
Time taken to dry	11.5 per min.
Highest temperature	84° C. = 183° F.
Lowest "	43° C. = 109° F.
Distance at which the paper was dried	36 feet.

"From these figures it will be seen that the agar-coated paper can be dried quite readily in a short time.

"In conclusion it is hoped that though our work is necessarily incomplete, yet enough has been done to form the basis of future study and also to assist the practical user in the chief of his difficulties. Agar-agar has certain advantages over gelatine and we firmly believe that its use will be much more common in the future. Its cheapness is no inconsiderable item, the cost being less than gelatine and only about one-eighth the amount being used. Its insolubility in water under a temperature of 80°-90° C enables very hot

water to be used in washing; at the same time, prints can be dried with extreme rapidity over a naked flame. Certain chemicals can be used in agar which cannot be added to gelatine, such as platinum chloride. The pellicle of agar is very much thinner than that of gelatine—about one-eighth the thickness—so that toning, washing, and other manipulations can be carried out much more quickly.”

The change in the colour of an emulsion during ripening indicates qualitatively a change in the relative sensitiveness to light of different wave-lengths. The quantitative side of the matter has been brought out clearly by Eder¹ and I quote from him.

“It must not be overlooked that light is changed in composition by passing through silver bromide films. Unripe emulsions make the transmitted light reddish and therefore absorb chiefly the shorter wave-lengths, the blue and the violet. A highly ripened silver bromide appears bluish gray and is much more transparent for the blue and violet lights. Addition of silver iodide makes the film more yellow and causes a correspondingly greater absorption for blue. Of course the amount of the absorption depends on the thickness of the film.

“Gaedicke² has made measurements on the transparency of ripened films of silver bromide gelatine. Six films were placed in a pile. When the upper one received an exposure to the amount of 120 meter-candle seconds, only 33 M.C.S. came through to the second film, 9 M.C.S. to the third, and 2.6 M.C.S. to the fourth, while the fifth and sixth films received no perceptible light. Each film therefore absorbed $13/18$ of the light and let $5/18$ through. The absorption coefficient of these films is therefore $13/18 = 0.722$, while the transparency coefficient, or penetration coefficient, as Gaedicke calls it, is $5/18 = 0.278$. The absorption depends on the thickness of the film, on the size of the silver bromide

¹ Eder's *Handbuch der Photographie*, 5th Ed., 3, I, 79, 140-148, 149-150 (1902); *Akad. Wiss. Wien.*, 90, II, 1097 (1884).

² Eder's *Jahrbuch der Photographie*, 14, 5 (1900).

grain, and on the volume ratio of silver bromide to gelatine, which is usually 1 : 7.

"Abney¹ found somewhat different figures. He determined at the same time the spectral transparency of the silver bromide gelatine by placing six films in a pile, exposing them to the spectrum and developing. He discovered, and demonstrated by photographs of the spectrum, that a silver bromide gelatine film absorbed all the light from the edge of the violet and ultra-violet, about half the light in the blue, and very little in the yellow. It looks as though this gave us a means of determining the absorption factor of a silver bromide film and of explaining why and to what extent the maximum effect of the spectrum in a thick film is displaced from that in a thin film. The thicker the film, the easier it is for one to photograph the lower end of the spectrum. With a thin film it is very difficult to obtain photographs down through the yellow. It has often been noticed that the red end of the spectrum can be photographed better with a thick film than with a thin one."

"The action of the solar spectrum on the different silver emulsions is of real importance because it is only in such investigations that we get the effect due to a pure color.

I. Action of Solar Spectrum on Silver Bromide and Silver Chloride Gelatine without Development

"If a solar spectrum, produced by glass prisms, is allowed to act on silver bromide and silver chloride gelatine emulsions until these latter darken without a developer, the following phenomena may be noted. Both unripe and highly sensitive silver bromide show about the same decomposition as occurs when a developer is used, except that the exposure must be much longer in the former case. With highly sensitive silver bromide there is a slight action even in the red (Abney). When no developer is used, silver chloride gelatine is changed most along the stretch between blue and violet just as is the case when a developer is used. With

¹ Eder's *Jahrbuch der Photographie*, 14, 302 (1900).

pure silver chloride the action of the spectrum sinks very rapidly to nothing near the blue. An addition of silver citrate makes the silver chloride much more sensitive for blue, green and yellow. A mixture of silver chloride and silver citrate is therefore affected by a large number of different rays, which is advantageous when making copies. As a matter of fact, such mixtures are used for copying processes on glass, etc.

II. Silver Bromide in Gelatine Emulsion with Development

"Silver bromide behaves differently towards the solar spectrum according to whether it is emulsified in collodion or gelatine. The curve for the action of the spectrum has already been given.¹ Silver chloride and silver iodide show similar differences when emulsified first in one and then in the other substance.

"H. W. Vogel² pointed out:

"(1) Silver bromide collodion always shows a maximum sensitiveness at G (wave-length 410-438).

"(2) Silver bromide gelatine shows a maximum sensitiveness in the clear blue (wave-length 450 with variations from 420 to 460³). It makes no difference whether the bromide is precipitated hot or cold, whether the emulsion is boiled or not boiled, digested or not digested. Boiling, digesting or treating silver bromide gelatine with ammonia, has the effect only of increasing considerably the sensitiveness for the other colours, violet, ultra-violet, green and red, the increased being less for the less refrangible rays.

"(3) The so-called green silver bromide, obtained by addition of ammonia to collodion emulsion, is not identical

¹ Eder's *Handbuch der Photographie*, 2nd Ed., I, 241 (1892).

² *Phot. Mittheilungen*, 19, 33, 94, 108 (1882).

³ According to O. Lohse the maximum action of the solar spectrum, produced by a glass spectograph, is about $\lambda = 440-430$ for silver bromide gelatine plates. In the blue at F $\lambda = 470$, only about one-fourth the maximum effect can be observed while three-fourths of it can be obtained at $\lambda = 452$, Eder's *Jahrbuch der Photographie*, 8, 271 (1894).

with the green silver bromide of the ripened emulsion. It shows a maximum at G.

"(4) Silver chloride collodion shows a maximum of sensitiveness at the two Fraunhofer lines H and K (wavelength 309-403).

"Naming the silver bromide according to its color, white or green, does not give any definite information in regard to its nature, especially since an excess of potassium bromide or of silver nitrate affects the color. Consequently Vogel calls the silver bromide in the gelatine emulsion blue-sensitive silver bromide from the position of its greatest sensitiveness in the spectrum, and the silver bromide in the collodion emulsion indigo-sensitive silver bromide.

"We are most interested in the silver bromide gelatine emulsion. Eder¹ has published a long account of the action of the solar spectrum on silver bromide gelatine emulsions in different stages of ripening. In this work Eder used a 'large spectrograph' and a small direct-vision one, both from Steinheil. The latter gives almost no spectrum in the ultra-violet, the limit of visibility extending but little beyond H.

"The two instruments have a marked effect on the apparent chemical action of the solar spectrum. The combined flint and crown glass prisms in the direct-vision spectroscope weaken the visible violet very much. For this reason the spectrum obtained with this instrument has surprisingly little effect on silver bromide and silver chloride gelatine in the violet. This is most marked with silver chloride gelatine, developed with ferrous citrate. In the large spectrograph with flint glass prisms the maximum action is at H at the beginning of the ultra-violet. In the small direct-vision spectrograph the maximum lies between G and F. The difference between the two curves is so great that it is hard to believe that the two curves refer to the same silver salt.

"In my large spectrograph the maximum action is even

¹ Akad. Wiss. Wien., 90, II, 1097 (1884).

displaced noticeably when the blue-green is made to replace the extreme violet in the middle of the field of vision. Thus it is pretty unsafe to base conclusions as to modifications of silver bromide and chloride on determinations of the maximum of sensitiveness.¹ It is the more surprising therefore that the maxima for the sensitizing action of dyes in red-yellow and green are so strongly marked that, according to my observations, they appear in the same place quite independent of the instrument used, though they vary more or less in intensity with the distribution of light."

"The following experiments were all made with the large Steinheil spectrograph and the results are therefore comparable."

"If one mixes silver nitrate solution with an excess of ammonium bromide in presence of gelatine, there is formed a finely divided, pulverulent silver bromide which appears red by transmitted light. Plates covered with this emulsion² are dried and exposed for a short time to the solar spectrum produced by a spectrograph with glass prisms. When the plates were developed with ferrous oxalate or with alkaline pyrogallol, an action was obtained from the violet to the blue green (H nearly to F) with a maximum one-third of the way from G to F, at about $\lambda = 440$. With a longer exposure the action extends both ways to M and E. Curve 3, in Fig. 1, gives a graphical representation of the relative intensities of action for the different parts of the spectrum, with intensity as ordinates and the Fraunhofer

¹ For instance, Vogel's classification of silver bromide into blue-sensitive and indigo-sensitive modifications, a distinction which does not follow from Abney's observations.

² The following formula for making such an emulsion has proved practical: 30 g silver nitrate are dissolved in 250 cc water and just so much ammonia added as will dissolve the precipitate completely again. Then 20 g ammonium bromide and 30-45 g hard gelatine are dissolved in 250 cc of hot water and the two solutions mixed at 30°-35°, the silver solution being added in small portions to the bromide solution, and this latter being shaken vigorously. The emulsion is then poured into a flat dish standing in cold water. After the emulsion has solidified, it is cut into small pieces and washed with water.

lines as abscissas. The dotted line shows the blackening after a short exposure and the solid one the blackening after a long exposure.

"If the ammoniacal emulsion, mentioned in the last foot-note is digested at 30° – 40° for half an hour, the silver bromide changes to the finely-divided, granular modification. The grain of the silver bromide coarsens, and a thin film allows blue light to pass, and the total sensitiveness to white light increases. At the same time the sensitiveness to violet and to green increases, and the maximum sensitiveness is now about half way between G and F. The action is not so intense between G and F; the curve is flatter. With longer exposure the curve stretches out on one side to N and on the other side to D and beyond (Curve 4, Fig. 1). This curve represents the spectrographic behavior of most of the commercial dry plates.

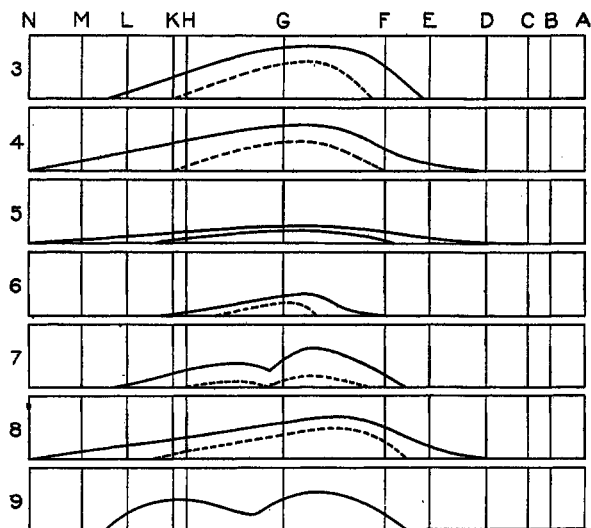


Fig. 1

3-5. Different modifications of silver bromide

6. Silver iodide

7. Mixed silver bromide and silver iodide

8. Ripened silver bromide

9. Mixed silver chloride and silver iodide

Dotted lines refer to short exposures, solid lines to longer ones

"When the digestion is carried on three to ten times as long as is necessary to obtain the results described in the preceding paragraph, the silver bromide is nearly ready to decompose. At the same time the curve of the spectrum action changes. It flattens more and more; there is no sharply marked maximum; and the photographic image lacks intensity. The sensitiveness to white light increases and also the sensitiveness to the less refrangible rays (Curve 5).

"We obtain Curve 5 if we digest for a long time the emulsion prepared according to the formula on page 231; but it can be obtained with greater certainty by keeping the gelatine content of the liquid very low, to one-half percent for instance, while the digestion is going on, adding the rest of the gelatine after the digestion is ended. Similar results are obtained by the method known as 'Henderson's cold emulsion.' The total sensitiveness of such an emulsion is very high and the details are well given in the shadows but the high lights are blurred¹ (Eder).

"These statements refer to glass spectrographs and sunlight. They therefore correspond to the results obtained by the usual methods of photography where glass lenses are used.

"Lenses and prisms of rock-crystal (quartz), fluorite, or Iceland spar are much more transparent than glass for ultra-violet.² With these the action of the spectrum is very uniform all the way from the blue-green to the extreme

¹ Photometric experiments with a scale photometer show that such silver bromide gelatine films give a developable image even with a very short exposure, but the intensity of the image does not increase proportionally to the amount of light and soon reaches a maximum which is not increased by a longer exposure. Such pictures therefore lack modelling in the high lights. This can be expressed more accurately if we make use of the conception of the "characteristic curve." We can say definitely that the characteristic curve is affected not only by the development, etc., but also by the modification of the silver bromide present in the emulsion. The results with the spectrograph are in harmony with this.

² For the transparency of different kinds of glass as compared with quartz, see Eder and Valenta. Eder's *Jahrbuch der Photographie*, 9, 310 (1895).

ultra-violet ($\lambda = 2200$ or 2000). Concave gratings give the same result. For ultra-violet of very short wave-lengths (λ less than 2000), the ordinary silver bromide gelatine plates are not much good because the gelatine film absorbs these rays too much and prevents their reaching the silver bromide (Schumann). Pure silver bromide is extremely sensitive, however, for rays of the shortest wave-length.

"The atmosphere also absorbs rays of short wave-lengths so that with ordinary gelatine plates in the air it is not possible to photograph the ultra-violet beyond $\lambda = 1850$. For still shorter wave-lengths, it is necessary to use a silver bromide, which is sensitive to the ultra-violet and a vacuum spectrograph.

III. Silver Iodide in Gelatine Emulsion with Development

"When silver iodide is precipitated in presence of an excess of potassium iodide it is several hundred times less sensitive to light than silver bromide. If the exposure is very long and if the development is done with alkaline pyrogallol, a weak image is obtained at G. With still longer exposure the image extends towards H and towards F, with a maximum one-third to one-half the way from G to F (Curve 6). On the other hand, it is very sensitive to the extreme ultra-violet,¹ $\lambda = 1900$.

"If washed silver bromide gelatine is mixed with 10-50 percent of washed silver iodide gelatine, there is a slight decrease in the sensitiveness of the mixture towards white light. The intensity of the image decreases a good deal; but the plates are clearer and show less tendency to form halos. Two maxima are found in the spectrum, one between G and H followed by a minimum² and another maximum, usually a stronger one, between G and F. This latter is caused by the silver iodide. An emulsion made up of mixed

¹ Schumann: Eder's Jahrbuch der Photographie, 11, 357 (1897).

² This minimum is also obtained when a little potassium iodide is added to a pure silver bromide gelatine and the plates are poured without any long digestion.

silver iodide and silver bromide gelatines is therefore quantitatively more sensitive in the blue than a pure, ripened silver bromide gelatine, such as is shown in Curves 4 and 5. Curve 7 represents the silver bromide and silver iodide mixed as an emulsion. The extension of the curve towards the ultra-violet and the green usually lies between Curves 3 and 4.

"This behavior of a mixed silver iodide and bromide was first noticed by Abney, whose results were confirmed by the observations of Eder. It was still a question whether these two maxima remained distinct when the emulsion was digested for a long time or whether they merged into one. Schumann claimed that they did, but it was denied by others.

"Eder's experiments showed that heating for half an hour to an hour actually caused the two maxima to change into one. The same result was obtained if silver nitrate was added to a mixture of potassium iodide and bromide so that silver iodide and silver bromide were precipitated simultaneously. The sensitiveness of such an emulsion to the less refrangible rays is greater than that of a pure silver bromide emulsion. The maximum action is displaced somewhat towards F and there is a distinct action even beyond F so that the correctness of Schumann's statements is established. Curve 8 shows the behavior of silver brom-iodide. The best results are obtained with a mixture containing one formula weight of silver iodide to eight to twenty formula weights of silver bromide. Emulsions containing more silver iodide are more sensitive to green but those with only small amounts of silver iodide¹ give stronger and handsomer pictures.

"The photographic action of silver brom-iodide emulsions seems to point to the existence of some sort of compound of silver iodide and bromide. This is the less improbable because a mixture containing equivalent weights of silver iodide and silver chloride shows a remarkable lowering of the melting-point.

¹ Not exceeding five percent of silver iodide.

IV. Silver Chloride in Gelatine Emulsion, with Development

"When silver chloride gelatine is developed with ferrous citrate or with ferrous oxalate and potassium bromide, it proves to be less sensitive to white light than silver bromide. The maximum sensitiveness is further over in the violet or ultra-violet than is the case with silver iodide and silver bromide. The maximum is near KH, about at the dividing line between the visible violet and the ultra-violet. The action extends to N and to F, though only to L, and to G when the exposure is short. When ten to thirty percent of a silver iodide emulsion is added to a silver chloride emulsion, two distinct maxima are obtained. The one due to the silver chloride is at H while the one due to the silver iodide lies about halfway between G and F (Curve 9). When the emulsions are digested or boiled, the two maxima become one, though not so readily as in the case of the silver bromide. With a chlor-iodide emulsion it is possible to use a stronger developer than with a silver chloride emulsion and yet not fog the plate. The sensitiveness of a chlor-iodide emulsion approximates that of silver bromide though without equalling it.

V. Effect of Colorless Substances on the Color-Sensitiveness of Silver Bromide Gelatine

"If silver bromide gelatine plates are bathed for a few minutes in dilute ammonia (say 2 cc ammonia in 100 cc water) and are then dried, the plates are about twice as sensitive to white light and give more intense pictures. Such plates are in general more sensitive to the solar spectrum without there being any increase in the sensitiveness towards special groups of rays. Since the ammonia evaporates during the drying, its action can only be due to a molecular change in the silver bromide."

"The solution of silver bromide in ammonia actually deposits microscopic crystals when evaporating, as Elsdon¹ has showed. They also are formed when silver bromide

¹ Photographic News, 1881, 17.

is precipitated in presence of much ammonia. Depending on the concentration of the solution, the crystals . . . vary in size from 0.02 to 0.2 mm. The thickness is about 0.001 mm. Crystals of this size are not formed by bathing silver bromide gelatine in dilute ammonia; but when ammonia evaporates from the moist plate, the silver bromide undoubtedly becomes crystalline and this may cause the increased sensitiveness to light."

"If a silver bromide gelatine plate is bathed in a dilute silver nitrate solution and is then tested in the spectrograph, we notice first an increase in the total sensitiveness. On closer examination we find that the relative sensitiveness for the less refrangible rays has also increased somewhat. Many dyes are more powerful colour sensitizers in presence of traces of silver nitrate (Eder, December, 1885). This is especially true of the eosine dyes and of others which form organic silver compounds or which are not decomposed by silver nitrate."

The general theory of optical sensitizers has already been discussed at length;¹ but there are some points in regard to the matter for which it is still necessary to quote from Eder.²

"If a photographic plate is to reproduce the colors with the same values as seen by the human eye, the orange at C and the clear blue at F of the solar spectrum should be about equal in intensity, while the yellow near D should be eight times as strong as the blue, the yellow-green near D about ten times as strong and the green at E approximately three times as strong; whereas the violet should be only about one-tenth as strong as the blue. As yet, no silver bromide gelatine process has been discovered which satisfies these requirements completely. By interposing yellow glasses or dyes, it is possible, however, to weaken the blue to such an extent that with stained silver bromide plates the yellow

¹ Bancroft: *Jour. Phys. Chem.*, 12, 318 (1908).

² Eder's *Handbuch der Photographie*, 5th Ed., 3, I, 149, 150, 153, 154, 168 (1902).

green is much more powerful than the blue and the violet. The action in the red and the orange is then lacking. Eder has proposed the name 'orthochromatic' for plates which, by optical or chemical means, give all the colors with the relative values as seen by the eye. This is now an accepted term along with 'isochromatic' and 'color-sensitive.' Everybody knows that, with the plates ordinarily used, orange and yellow come out almost black and much darker than dark blue and violet which act almost like white.

"The orthochromatic plates of commerce are usually sensitized for yellow green. In addition to the sensitiveness of the silver bromide in the violet and the blue, there is an increased sensitiveness for the green and the yellow, between the Fraunhofer lines E and D. With these plates it is possible to photograph the sodium (D) line with sufficient intensity. These plates are usually dyed with erythrosine, less often with eosine, quinoline red, or some other dye. Even though there is no real sensitiveness in the red, these plates are suitable for reproducing pictures and colored objects of all kinds, for taking landscapes in the mountains, and for cloud photographs. Pure reds, such as mercuric sulphide, only act slightly on erythrosine and therefore appear black when photographed. Since such colors only appear occasionally in paintings and elsewhere, one can help out by retouching. If one insists on the exact photographic reproduction of the red, one must use other sensitizers. . . . Lumière in Lyons makes plates which are sensitive in the red. When plates are simultaneously red-sensitive, yellow-sensitive, and green-sensitive, they are called panchromatic. They are usually less sensitive for any given color than plates which are sensitized especially for that color and which are of importance for three-color printing."

"The best concentration varies with the nature of the dye. It is well to start with an addition of 2-4 mg per 100 cc of emulsion or to dissolve this amount in water and to bathe the dry plate in this solution for two to five minutes. If the dye has a strong coloring power, a weaker solution

should be used. With some dyes, having only a slight coloring power, the concentration must be ten times as great. With eosine one ten-thousandth of one percent is enough to sensitize the emulsion perceptibly with the characteristic band in the yellow green, although the eye cannot detect any reddish color. The dye can apparently be removed completely from such gelatine emulsions by washing for many hours and yet its sensitizing action can still be detected by means of the spectrograph.

IX. Effect of the Degree of Ripening of the Silver Bromide Gelatine on the Ease with Which it is Sensitized by Dyes

"As a rule color-sensitizing is possible both with colloidal, unripe, pulverulent, silver bromide and with ripened, highly sensitive silver bromide, either in a gelatine emulsion or more readily in a collodion emulsion. It must not be overlooked that ripened, highly sensitive silver bromide is in itself somewhat, though not much, more sensitive to the less refrangible (red and yellow) rays than unripened silver bromide. Such a silver bromide can be sensitized for the red more readily than unripe silver bromide. The observation has often been made that different dry plates are not all sensitized equally readily.¹ These are points which are not yet properly understood.

X. Effect of Silver Bromide, Iodide and Chloride on the Color Sensitizing

"The nature of the silver salt in the photographic plate has an effect on the sensitizing action of the dye. As a rule, one can say that pure silver bromide plates are the most suitable for experiments with sensitizers. Silver chloride can also be used and the relative increase in sensitiveness is often greater than with silver bromide (Eder). Owing to the lesser absolute sensitiveness, silver chloride is not used much in ordinary negative processes. Pure silver iodide

¹ The author [Eder] always uses the silver bromide plates of Schleussner in Frankfort a.M. or of Schattera in Vienna.

gelatine cannot be sensitized to any extent by dyes even by such as eosine which have a powerful sensitizing action on silver bromide. Brom-iodide emulsions with more than two percent iodide are much less readily sensitized than pure silver bromide emulsions. It is practicable, however, to sensitize emulsions containing up to five percent of silver iodide. For spectrum analysis such plates are desirable on account of the sensitiveness near the line F.

"The presence of relatively large amounts of potassium bromide or of similar restrainers in the emulsion modifies the sensitizing action of dyes. The sensitizing band becomes surprisingly weaker and the orthochromatism of the plate suffers."

XIV. The Manner of Dyeing Silver Bromide Gelatine

"The sensitizers differ extraordinarily in the degree to which they make the silver bromide plates sensitive to the less refrangible rays, red and yellow. The result is also affected by the way in which the dyes are applied to the silver bromide plates. The dyeing of the silver bromide gelatine may be done in two ways: by adding the dye to the liquid emulsion or by bathing the finished, dry plate in an aqueous or an alcoholic solution of the dye. The alcoholic solution is usually not so satisfactory as the aqueous one because alcohol does not penetrate the gelatine readily.

"When making dry plates on a commercial scale it is usual to add the color-sensitizer to the washed and remelted emulsion and then to pour the dyed emulsion on glass plates by means of a pouring machine. Erythrosine and eosine plates can also be made by adding the dyes before the materials for the emulsion are mixed; in other words, to the bromide or to the ammoniacal silver oxide solution. If ammoniacal silver oxide is used, the dye must be stable in presence of ammonia. When the emulsion is dyed in this way, a good deal of the dye must be added because a good deal, though never all, of the dye is removed by the subsequent washing.

"When an emulsion is sensitized on a small scale, for

laboratory experiments, it is more convenient to bathe commercial dry plates in a solution of the dye. The bathed plates often work better than the others, especially if ammonia is added. The advantages of the bathed plates show in greater color-sensitiveness.¹ It is helpful to give the plate a preliminary bath in aqueous ammonia. When preparing orthochromatic plates, V. Schumann² recommends a preliminary bath of 200 cc water and 0.25–2.0 cc caustic ammonia, which makes the film more porous. After two minutes the plate is taken out, allowed to drip, washed for two to four minutes in a cyanine solution (100 parts water, 1–2 parts ammonia, 5–10 parts alcohol, 2–5 parts alcoholic cyanine solution 1–500), and then dried.

“A preliminary treatment with ammonia gives a similarly good effect with many other dyes, such as eosine, erythrosine, nigrosine, glycine red, etc. It has also been recommended to add alcohol to the ammonia bath in order to cause a more rapid drying (80 cc water, 20 cc alcohol and 2 cc ammonia).³ Under these circumstances it is well to add a corresponding amount of alcohol to the subsequent dyeing bath to prevent the formation of streaks.

“A mere surface contact of the dye with the silver bromide gelatine is enough to cause a distinct sensitizing. One can even sensitize silver bromide gelatine plates by superposing dyed collodion or alcoholic solutions, which do not go in very deep. This was first pointed out by Abney⁴ and was afterwards recommended by Ives;⁵ but this method of

¹ Finished plates, when bathed in an eosine solution, are four times as sensitive to yellow green as is the case when the dye is added to the melted emulsion (Schumann, October, 1885). The same thing is true for erythrosine and for the colors of the eosine and cyanine groups.

² Phot. Wochenblatt, 1885, 395; 1886, 49.

³ P. Ruh. Phot. Correspondenz, 35, 243 (1898).

⁴ Phot. News, 1888.

⁵ Ives proposed covering the gelatine plate with an alcoholic solution of the dye (1 : 1700), drying, washing with water, and drying again (Eder's *Jahrbuch der Photographie*, 4, 59 (1890)); but Bothamley found that there was no advantage in this.

sensitizing is usually quite insufficient.¹ The plates are not sensitive because the dye must be intimately mixed with the silver bromide if it is to produce the maximum effect.² Nevertheless, there are scattered cases where pure alcoholic solutions of dyes can be used successfully for sensitizing. Thus alcoholic cyanine solutions have but little sensitizing action if poured on silver bromide gelatine plates and then dried; but if the plate is then laid for a moment in water, the gelatine swells, some cyanine dissolves and penetrates a little way into the emulsion, with the result that the plate is quite sensitive to orange while wet.

"A distinct proof, that the sensitizing action of dyes on dry plates varies with the treatment, is furnished by Hinterberger's³ careful experiments on cyanine. He repeated the work of Weissenberger, Debenham and Schumann.

"Weissenberger recommended bathing the silver bromide gelatine plate in a very dilute cyanine solution (1:5000000), which is made colorless with a trace of acetic acid. When the plate was dried, the acetic acid evaporated and left the cyanine behind with its blue color. With this small amount of dye, the sensitizing action is so slight that it can scarcely be detected even in the orange. When the amount of cyanine is increased, the sensitiveness to blue decreases while there is an increase in the sensitiveness to orange yellow, yellow green, and red. When the amount of cyanine becomes very large, the screening effect causes the sensitiveness to those last colors to decrease with the exception of a small strip near A. The best form of Weissenberger's method is to bathe the plate for a couple of minutes in a solution made up of one liter of water, 2 cc alcoholic cyanine solution (1:500) and one drop of acetic acid. The plate is dried after the bath.

"Debenham recommended bathing the plate in a pure alcoholic cyanine solution (1:2000), drying in the air in an

¹ Wellington: Phot. News, 1885, 415.

² H. W. Vogel: Phot. Mittheilungen, 25, 117 (1888).

³ Eder's Jahrbuch der Photographie, 11, 379 (1897).

absolutely dark room (which takes several minutes), bathing in pure water for two or three minutes, and exposing the plate *while wet*.

"The conclusions which Hinterberger drew from his comparisons were:

"(1) Schumann's method is uncertain and usually gives impure and fogged plates.

"(2) Weissenberger's method is reliable. The plates are very clear and quite sensitive; but the sensitiveness only covers the blue and a narrow strip in the orange between C and D.

"(3) Debenham's method is reliable. The plates are fairly pure and very sensitive. The color-sensitiveness extends over red, orange, yellow, yellow green, and blue to dark blue and is only broken by minima in the red at *a* and in the green between E and F. The disadvantage is that the plate must be exposed wet."

One of the very important things about the medium forming the emulsion is the way in which it retards the action of the developer on the unexposed silver bromide. I quote from Lüppo-Cramer:¹

"When people have discussed the theory of the latent image, they have ignored entirely the fact that, when silver bromide is precipitated in aqueous solution, it is readily reduced by the developer even without exposure to light. This fact proves conclusively that it is not necessary to assume a reduction as the result of exposure to light. The following experiment shows that the mere enclosing of the silver bromide grain in a sheath of the medium is not the cause of a normal, emulsified silver bromide not being reduced unless it has been exposed to light. If silver bromide is precipitated from aqueous solution and is then suspended in a gelatine solution, it is reduced promptly and completely by a developer solution."

¹ Phot. Correspondenz, 38, 222 (1901).

In a later paper on "The Reducibility of Precipitated Silver Bromide," Lüppo-Cramer¹ returns to this subject.

"In the course of my papers on the latent image, I have often had occasion to call attention to the fact, first observed by Abney,² that silver bromide precipitated in the dark from aqueous solution by an excess of bromide, is reduced instantaneously by a developer solution. In this respect it does not differ from silver bromide which has been exposed to light for a short or a long time. Years ago Andresen³ established this fact by quantitative analysis and the author's work on bromhydroquinone (aduro) has confirmed the results obtained by Andresen under the conditions specified by him.

"At the Fifth International Congress for Applied Chemistry, the results of Andresen were called in question by Schaum. I therefore repeated the experiments and found that, with ordinary developer solutions such as Andresen used, the unexposed silver bromide was reduced instantaneously. No difference could be detected between the behavior of the unexposed silver bromide and that of silver bromide which had been exposed to light. Although the iron developer is usually slow during the first stages, yet it reduces at once silver bromide precipitated according to Andresen's directions. If one adds potassium bromide to the iron developer (1 cc KBr, 1 : 10, to 80 cc developer) a difference can be detected between the rate of reduction of an unexposed silver bromide and of one that has been exposed for a few seconds to daylight. The difference is more marked if one uses metol and sulphite without alkali. This solution causes an instantaneous reduction of silver bromide which has been exposed for a few seconds, while the unexposed silver bromide requires 30-40 seconds for reduction.

"The coarsely flocculent, precipitated silver bromide is therefore capable of photographic action though we must characterize it as fogging badly. The very much finer sil-

¹ Phot. Correspondenz, 40, 671 (1903).

² Eder's Jahrbuch der Photographie, 12, 420 (1898).

³ Ibid., 13, 143 (1899).

ver bromide, used by Schumann¹ in the plates sensitive to ultra-violet, fogged readily, which is probably the cause of Schumann's using a halide emulsified in a very little gelatine in his later work.

"At present we are not able to say how the colloidal media make exposed and unexposed silver bromide act so differently toward developer solutions that certain emulsions can be developed for hours without the unexposed silver bromide being reduced. The matter will be discussed in a later section."

According to Schaum² the matter is not so complex.

"We must say a few words in regard to the action of developers on silver bromide containing no binder. It has frequently been stated, even quite recently, that silver bromide containing no binder is reduced equally rapidly whether it has been exposed or not. The inaccuracy of this statement has been proved by Luther's experiments. We also have had no difficulty in showing by development the action of light on our silver bromide layers, which were obtained by precipitating from concentrated neutral solutions with an excess of bromide, while Luther used much more dilute solutions and an excess of hydrobromic acid. If one uses developers with the concentration usual for gelatine plates, many of them, such as ferrous oxalate or edinol, cause a complete blackening almost instantaneously. The complete reduction takes place somewhat less readily with adurol, hydroquinone, or Belitski's developer; metol acts the slowest. If one wants good gradation and freedom from fog, it can be obtained by taking one of these last developers and diluting to one-half with water. The gelatine is the cause of the slow reduction of silver bromide in the emulsion film as compared with the reduction of silver bromide containing no binder.

"The effect of the binder on the development, especially

¹ Sitzungsber. Akad. Wiss. Wien., 102, IIa, 994 (1893); Drude's Ann., 5, 349 (1901).

² Eder's Jahrbuch der Photographie, 18, 75 (1904).

in the case of gelatine, has been ascribed by Abney¹ to a mechanical retarding. This point of view is supported by our experiments. Precipitated silver bromide was suspended² in gelatine solution. Plates poured with this emulsion developed glass-clear with concentrated developers after exposure.

"Every trace of the organic matter was removed from a washed, ripened silver bromide taken from a ripened Schleussner emulsion; and the silver bromide was allowed to settle on a piece of ground glass. This silver bromide is reduced much more rapidly than the freshly-precipitated bromide. It is possible however to develop an image on this silver bromide by using a metol developer diluted to one-half and allowed to act only for a short time. After this silver bromide has been emulsified again in gelatine, a photographic image can be developed quite well even with concentrated developers. If a sedimentary silver bromide layer is merely coated with gelatine, the development is retarded considerably. If there are other differences—apart from differences in degree of ripening—between silver bromide precipitated in gelatine and silver bromide precipitated in water but afterwards suspended in gelatine, these seem to be that the suspended silver bromide is reduced more rapidly than the emulsified silver bromide. Quincke's³ explanation applies here, namely, that solutions of silver bromide and gelatine are formed which have very complicated properties. Such solutions occur of course to a much greater extent when an emulsion is formed than when silver bromide is suspended in gelatine. In these solutions the unexposed silver bromide is less readily reduced than when it is merely protected by a coating of gelatine, because a solution of silver bromide and gelatine has a lower bromine pressure than pure silver bromide. The formation and properties of such solutions should be suffi-

¹ Eder's *Jahrbuch der Photographie*, 12, 420 (1848).

² [It is not clear whether the author means suspended or emulsified. If he means the latter, the experiment proves nothing.—W. D. B.]

³ Drude's *Ann.*, 11, 1100 (1903).

cient to account for many other phenomena, such as the great differences between collodion and gelatine emulsions.

"The sensitiveness of silver bromide containing no binder depends on the nature of the precipitating bromide. This point is now being studied in detail.

"The phenomenon of ripening is usually referred to a coarsening of the grain and to the action of gelatine (slight reduction or, according to Quincke, the coagulating of turbid media). We found that our layers containing no binder show the phenomenon of ripening if they are heated to 65° either when moist or dry. At the end of 70 minutes we obtained an increase of sensitiveness from 5° Scheiner to 9° . After heating for five hours to 65° , the plate fogged at once in the developer. When heated under water, the sensitiveness increased though not to anything like the same extent. While the gradation is pretty bad with the unripened layers, it is quite good with the ripened layers."

While we are on the subject of silver bromide precipitated from aqueous solution, it is interesting to note that, according to Weisz,¹ the precipitated silver bromide is more sensitive to light, the finer the grain, which is the exact opposite of what is usually believed in regard to the emulsified silver bromide.

"The concentration for preparing the milky silver bromide was originally the same as Luther's: one volume of N/20 AgNO_3 to one volume N/10 HBr . Higher concentrations than these make the grain coarser and produce a less sensitive plate. A less excess of hydrobromic acid makes the grain finer and the plate more sensitive. When there is an excess of silver nitrate during precipitation and sedimentation, the layer does not hold together and floats off during the experiments. The slightest trace of thiosulphate on the surface of the glass has the same effect and it is therefore desirable not to clean spoiled plates with thiosulphate²

¹ *Zeit. phys. Chem.*, **54**, 322, 351 (1906).

² I avoided gelatinizing the exposed plates before development. Luther: *Zeit. phys. Chem.*, **30**, 628 (1899).

if fresh silver bromide is to be precipitated upon them.

"The temperature of the silver nitrate and hydrobromic acid solutions should be between 15° and 19° . During sedimentation, all jarring of the dish must be avoided as far as possible. In the summer I could not get any satisfactory plates, though I do not know why. Perhaps the temperature was too high during sedimentation.

"The time of sedimentation is of great importance. If the milk settles too rapidly, one can be certain of getting irregular, mostly insensitive, plates with a silver bromide layer which does not cling to the glass. If the sedimentation is allowed to go on too long, the plates fog in the developer. This is because the finest silver bromide particles settle too, as dust on the surface of the layer and cause the fogging. If such a plate is cleaned vigorously with a brush, it becomes much less sensitive to light and does not fog in the developer any more."

"I divided a precipitation of silver bromide . . . into three fractional precipitations. The liquid layer was seven centimeters deep and I allowed the bromide to settle for five days, then sucked off the supernatant milk and let that settle on fresh plates for six days. The third time, the mixture was allowed to stand for two months. I thus had three fractional sedimentations, T_1 , T_2 , T_3 , of which T_1 had the coarsest grain and T_3 the finest. There were four plates of each type. This experiment confirmed the opinion previously expressed; because the plates T_2 were about four times as sensitive as the plates T_1 Plates T_3 fogged completely in the developer, which was what was to be expected."

The special idiosyncrasies of a plate sensitive to ultra-violet are brought out clearly in a paper by Schumann¹ from which I quote:

"It is known that the sensitiveness to light and the intensity of the gelatine dry plate decreases considerably

¹ Drude's Ann., 5, 349 (1901).

as we pass from the wave-length $220\mu\mu$ to the shorter wave-lengths. I have previously shown¹ that the cause of this decrease is the insufficient transparency of the gelatine. Silver bromide itself shows no such decrease in sensitiveness. There is also no decrease in sensitiveness if the silver bromide is used in presence of very small amounts of gelatine. It is on this fact that I based my earlier process of preparing plates sensitive to ultra-violet, which enabled me to investigate the regions beyond $185\mu\mu$. As I have previously stated, this process had many faults. I have been busy until recently in attempts to overcome these faults. In this way I have gradually succeeded in making plates which surpass the earlier ones considerably in purity, in delicacy of gradation accompanied by sufficient intensity, and in reliability.

"The essential features of the improved process are as follows: A silver bromide emulsion is prepared which is very rich in silver. This is allowed to solidify and is washed thoroughly.² It is then melted in presence of a very large excess of water [in order to dilute the gelatine], is filtered, and is poured on plates laid horizontally. The silver bromide is allowed to settle for half an hour and the emulsion is then poured off. The fine layer of silver bromide remaining on the plate dries quickly because it is so thin. The plate may be used as soon as it is dry. Still better results are obtained if the heavier particles of silver bromide are removed before the emulsion is filtered. The formation of the layer on the plate takes place as before but requires several hours instead of half an hour."

"If, instead of silver bromide, the emulsion contains other silver halides or mixtures, the photographic properties are different. The following are the most important conclusions which I have reached in regard to this matter:

"(1) Silver chloride gelatine, prepared with an excess of potassium chloride, is moderately sensitive, lacks strength, has a tendency to fog, and yields a fine-grained picture.

¹ Sitzungsber. Akad. Wiss. Wien, 102, IIa, 415, 994 (1893).

² [Apparently no attempt is made to ripen the emulsion.—W. D. B.]

"(2) Silver iodide gelatine, prepared with an excess of potassium iodide, develops glass-clear and very intense, yields a coarse, black grain; but is distinctly less sensitive than silver bromide gelatine.

"(3) Silver iodide gelatine, prepared with an excess of silver nitrate, differs from the preceding in that it is nearly twice as sensitive. On account of its uncertain behavior in the developer, it is much less to be recommended than the silver iodide gelatine prepared with an excess of potassium iodide.

"(4) Silver chlor-iodide gelatine, prepared with an excess of potassium chloride, fogs very little and yields a very fine grain; but lacks intensity.

"(5) Silver chlor-iodide gelatine, prepared with an excess of potassium iodide, fogs easily, becomes a dirty, brick-red color when developed with pyrogallol and soda, and yields fine-grained pictures which are lacking in intensity.

"(6) Silver brom-iodide gelatine, prepared with excess of potassium bromide, is highly sensitive, excessively intense; it fogs readily to the point of complete opacity. The grain increases sometimes so much as to form small lumps. It is useless for spectrographic purposes.

"(7) A mixture of silver chloride gelatine and silver iodide gelatine, gives powerful negatives, free from fog, with soft half-tones and a fine grain. It is the only plate made by the improved process which ranks at all with silver bromide gelatine for the preparation of plates sensitive to ultra-violet light.

"(8) A mixture of silver bromide gelatine and silver iodide gelatine gives coarse-grained negatives of great intensity, and free from fog. The plates are only slightly sensitive.

"All the preceding statements in regard to size of grain refer to the plate after it has been developed and fixed. The grain of the emulsion and of the undeveloped plate is distinctly smaller on the average. The size of the grain of the developed plate depends on the silver iodide content of the

layer and also on the amount of potassium bromide added to the developer."

"The first few days after it is prepared, the plate is not very sensitive and it is also lacking in intensity. During this period it will stand extraordinarily strong developers, solutions of concentrations which could not be used on a dry plate without danger of fog. There is no danger of the layer coming loose from the plate. The layer shows an extraordinary power of withstanding certain chemicals. It is not attacked by fuming nitric acid, concentrated sulphuric acid, hydrochloric acid, or potash solution 1:3. Fuming nitric acid does not destroy either the latent or the developed image. Even though the greater part of the silver is dissolved in the latter case, the image remains in all its details. The acid merely decreases the intensity. This behavior of the light-sensitive coating is the more surprising because one of its constituents, gelatine, is readily soluble in nitric acid. From this we must conclude that in this case the degree of solubility of the gelatine depends on the thickness of the film.

"On standing, the sensitiveness and the intensity of the plate both increase. At the end of a couple of weeks the increase in both is quite marked. From then on, it is the intensity which increases the more rapidly. I have usually obtained the best results with plates which were one to two months old. In the third month fog begins to be noticeable. Glass-clear negatives can be obtained however by adding plenty of potassium bromide to the developer. Plates¹ kept in dry air have even given excellent results at the end of two years. The only change is a marked decrease in the sensitiveness. Since the clearness of the picture can

¹ To test the effect of moisture on the keeping properties of the film, I have placed a series of differently prepared plates in tightly closed vessels of glass and of zinc, using sulphuric acid in some cases as drying agent and phosphorus pentoxide in others. The plates were shielded from light and at the end of twenty-two months they were exposed to the aluminum spectrum from blue to the wave-length 185 $\mu\mu$. The results stated in the text were based on these experiments.

only be obtained in this case by increasing the amount of potassium bromide, whereby the time of development is increased considerably, the use of such old plates is not to be recommended."

"On account of the extraordinary fineness of the lines the spectrum on a plate sensitive to ultra-violet can stand a very high magnification. The spectra obtained with a very narrow slit give distinct line images when magnified a hundred fold. All the same, the grain of such a negative is by no means as fine as one might expect from this and from the size of the distinctly smaller emulsion grain. Since the ordinary dry plate will not stand so high a magnification, this can only be due to the greater (five-fold) thickness and the relatively much greater gelatine content of the light-sensitive layer.

"If an ultra-violet and a very slightly sensitive silver bromide gelatine plate are exposed to a uniform white light, the latter receives a developable image much sooner than the former. The ultra-violet plate is less sensitive to the visible rays. The same thing is true for most of the ultra-violet spectrum. It is only at about $231\mu\mu$ that the ultra-violet plate begins to accomplish more than the gelatine plate, the image then becoming more intense and also sharper. As we pass towards the still shorter wave-lengths, this difference becomes so marked that the energy distribution and the intensity undergo a complete change in the field between 220 and $200\mu\mu$, a region in which, as every observer knows, negatives are characterized by lack of intensity and of gradation. All photographs of this region of the spectrum are more valuable as showing the absorption spectrum of gelatine than as showing the sensitiveness of the silver bromide. It is much the same also with the stretch between $231\mu\mu$ and the green of the spectrum where intensity and sensitiveness also depend on the gelatine though in a different way for the gelatine here acts as a sensitizer and increases the sensitiveness of the silver bromide to a marked extent, as everybody knows. From this it follows at once that all

measurements of light intensity, which depend on differences in the density of the spectrum image, have only a relative value. Since the absorption effect and the sensitizing effect of the gelatine undergo marked fluctuations, it follows that the measurements hold strictly for the particular plate actually used and not for the dry plate in general. Plates from different makers may therefore give widely differing results. In spectroscopy this is more important than is usually supposed because the degree of brightness of the different rays is taken as proportional to the blackness of the photographed lines. As a matter of fact, equal differences of brightness in the visible spectrum and in the more refrangible ultra-violet correspond to different degrees of blackness and not to the same. It is not even necessary to prove the case by taking such extreme instances, by comparing remote portions of the spectrum. It will suffice to take the blue of the spectrum where very different degrees of sensitiveness to light will be obtained with plates of different makes, depending on the way the emulsion has been prepared. In addition to the gelatine, it is the silver iodide,¹ to be found in most plates, which determines by its amount the degree of sensitiveness to white light and also to green blue light. While silver bromide gelatine, for instance, is practically not sensitive to the hydrogen line H_{β} and to that portion of the spectrum, this region comes out strong in silver bromiodide gelatine because silver iodide displaces the maximum of sensitiveness towards the red so that H_{β} equals the brilliant H_{γ} in intensity.

“For these reasons a plate, having a uniform sensitiveness over the whole spectrum, would be a very important addition to our equipment for making spectrographic measurements. The ultra-violet plate comes the nearest to satisfying these requirements of any plate that we have on account of its sensitiveness to the rays which can be photographed

¹ Most manufacturers of dry plates add varying amounts of silver iodide to the emulsions. There are plates on the market which contain no silver iodide and which are very popular, especially in scientific circles.

only in a vacuum and because of its uniform reproduction of the remainder of the spectrum. To illustrate to what extent this latter is true I give two spectra¹ of the spark between aluminum terminals, photographed under the same conditions with increasing time of exposure. The first was taken on an ultra-violet plate and the second on a gelatine dry plate. A comparison of the two shows: how entirely differently they represent the energy from the same source of light; how poorly the commercial plate is adapted for photographing the more refrangible portion of the ultra-violet as far as $185\mu\mu$; and how slightly its sensitiveness to light corresponds with that of pure silver bromide, which my earlier experiments have shown to be not only sensitive to all the rays from the blue portion of the spectrum to the shortest wave-lengths but also to be nearly uniformly sensitive to all these rays. It is also worth noting that the extremely small amount of gelatine used increases the sensitiveness of the ultra-violet plate in general and gives it the power of reproducing gradations. It is this which makes it possible, in spectrum work, to obtain the soft half-tones which cannot be obtained with silver bromide alone. If one covers a glass plate with pure silver bromide, it gives all the lines, which can be developed at all, with approximately the same maximum intensity of which the layer is capable.

"A further advantage of the ultra-violet plate consists in its lack of sensitiveness to the diffused light in the photographic apparatus, which makes great trouble in certain cases, when using ordinary plates. For instance, if one tries to photograph the spectrum beyond $185\mu\mu$, using a gelatine dry plate, the plate fogs before the image has obtained sufficient strength; it fogs so completely that only the most active lines remain visible. This fog is caused by rays which are scattered inside the lenses and the prisms, and which reaches the plate as diffused light. Since the diffused light consists chiefly of rays which have been refracted less and therefore of the rays which have the most effect on the dry

¹ [Not reproduced in this article.]

plate, it is not surprising that they should have a very strong fogging effect. Owing to the lack of a suitable light filter it has not proved possible so far to keep this diffused light completely out of the spectrum apparatus. All that we can do is to weaken it. This can be done easily by cutting down the light coming through the slit by shortening the slit to about one-third of a millimeter. This is the only way to obtain photographs of electrical discharges from the wave-length, 185μ , to the limit of the ultra-violet action on the dry plate 182μ . Since the ultra-violet plates are only slightly sensitive to the visible rays and the adjacent ultra-violet rays, the diffused light does not trouble them. It is therefore possible to make the slit as long as may be desired without having to fear fogging, no matter how long the exposure."

"There is another peculiarity of the plate which I must mention briefly. With the intense illumination which we get with a wide slit, heavy electrical currents, and a prolonged exposure, I have repeatedly obtained solarized spectra. Under these conditions the lines appear as pale strips surrounded by an edge of increased blackness caused by irradiation in the layer. That we are not dealing with a plain case of spectrum reversal is shown by the form of the dark edges. They occur at the ends of the lines as well as at the sides. Since this phenomenon only occurs occasionally, it is of more importance photochemically than spectroscopically. These results conflict with the observations of Abney; and some rays will cause solarization of silver bromide without the intervention of oxygen. My exposures were all made in a vacuum or in a hydrogen atmosphere having an excess pressure of several centimeters. Since the reversal cannot take place during the development of the image, it follows that the fact discovered by Abney does not hold for ultra-violet plates and that it therefore depends on the photographic plates used by Abney.¹

"In 1893 I published an account of a process for mak-

¹ [If Schumann had tested this conclusion he would have been in a position to have worked out a satisfactory theory of solarization.—W. D. B.].

ing plates which were sensitive to ultra-violet light.¹ In this process I added a great deal of water to an emulsion containing relatively little gelatine and poured the solution into deep dishes, in which the silver bromide settled upon glass plates placed therein. Many hours were necessary to produce the light-sensitive deposit, after which the emulsion was decanted and the plates were dried in a horizontal position. It is clear that the old process and the new one are very similar. It would be quite wrong, however, to reason from this to the photographic nature of the two makes of plates. The two have nothing in common beyond the sensitiveness to ultra-violet, the rapid fixing and drying, and the behavior when potassium iodide is present in the developer. In other respects they differ, and very considerably in some points.

"The most remarkable difference is in the behavior towards silver iodide. The emulsion made by the old process could stand quite a good deal of silver iodide; but the improved plate fogs so as to be quite useless. Many efforts have been made to introduce silver iodide into the sensitive film, but they have all failed on account of the ease of reduction and the excessive intensity which results therefrom. After many futile experiments I have succeeded in getting soft negatives, fairly free from fog, by means of stand development lasting seven hours; but it is clear that so lengthy a process of development is of little value for spectroscopic work.

"The improved process is much more dependent on the quality of the gelatine than the older one was. A gelatine, which formerly could be used successfully, now gave rise to a series of unexpected irregularities. Besides spots of various kinds, the films had the unpleasant peculiarity of becoming covered with numberless cracks, shaped like the tails of comets and varying up to 2.5 cm in length. This occurred within a few minutes after the emulsion had been

¹ Schumann: Akad. Wiss. Wien, 102 IIa, 994 (1893).

poured off and while the plate was still wet. Of course this made the plate useless.

"In another case, one of our best German gelatines gave films which were so slightly sensitive that we could not even reach the wave-length 185μ , which can be obtained without any trouble with the ordinary dry plate. When these plates were bathed in warm water (38°) for ten minutes, their character changed completely and they became surprisingly sensitive to ultra-violet. In this case, the water therefore plays the part of a physical sensitizer. Its sensitizing action is due in part to the fact that the gelatine melts enough so that the upper portion of the sensitive layer is freed from the coating which absorbs the light. It is also due in part to the fact that the continued heating increases the tendency of the silver bromide to reduce. The sensitizing action of the water on such a plate exceeds anything which I have ever noticed in my years of work with emulsions sensitive to ultra-violet. Unfortunately this treatment causes spots and dry zones of varying sensitiveness so that plates of this type are not to be recommended. Another objection is that the keeping qualities of the plate are decreased by the sensitizing bath.¹

"Out of all the different kinds of gelatine which I have tried, only one has always given good results. This is the previously mentioned, soft, English gelatine, which is known to the photographic trade as Nelson's No. 1. I therefore advise anybody who wishes to make these plates to begin with this gelatine and no other.

"Plates made by the older method required dilute developers, while exceptionally concentrated developers could be used with the improved plates, at any rate so long as the plates were new. The chief merits of the improved plates are reliability and a more equal sensitiveness. This was ob-

¹ It is surprising that it is not possible, by this means, to increase the sensitiveness of the ordinary plate to the shortest waves of lights. Experiments along this line gave negative results. The half of the plate which had been bathed developed to the same wave-length as the unbathed portion.

tained by letting the coarser particles of silver bromide settle to the bottom of the dish and keeping them off the glass plate.

"The photographing of crowded groups of lines showing marked differences of energy is a very severe test of a plate. My earlier plates did not stand this test very well. In them the lines often spread out enough to give a band, in which only the most intense lines could be detected. This difficulty was due chiefly to a lack of half tones. Owing to the finer gradations of the negatives obtained by the improved process this trouble has disappeared.

"I have previously called attention¹ to the peculiar action of potassium iodide when added to the developer used for ultra-violet plates. I found that a few drops of a one percent solution brought the image out more quickly and increased its density but also tended to produce a heavy fog which, however, did not appear simultaneously over the whole film as is the case with other plates. This fog began at the edges and crept slowly in to the centre. I have tried to avail myself of the accelerating action of potassium iodide by bathing the improved plate before exposure in an aqueous potassium iodide solution and then drying. The result did not come up to my expectations. The troubles were the same as with the old plates.²

"When it is a question of representing accurately the total photographic energy of a source of light, the ultra-

¹ Schumann: Sitzungsber. Akad. Wiss. Wien., 102, IIa, 1014 (1893).

² The action of a potassium iodide bath on the film varies with the concentration. I have tried solutions running from 1 : 1000000 to 1 : 15 and have found that even the small quantity of potassium iodide in the first solution has a weak sensitizing action. This is not much more marked with the 1 : 100000 solution but increases distinctly as the concentration goes up to 1 : 25000. With a concentration of 1 : 12500 we get a heavy fog along the edge. With increasing concentration the fog spreads over the whole plate and finally a point is reached at which the silver bromide is dissolved. A solution of potassium iodide 1 : 1.5 fixes an ultra-violet plate three to four times as fast as a solution of sodium hyposulphite 1 : 3. Gelatine is also dissolved at ordinary temperature by a potassium iodide solution. This makes it seem possible to extend the fixing of an ultra-violet plate to include the gelatine itself, which would have certain advantages when it came to enlargements. I made some experiments of this sort but the results were not satisfactory.

violet plate is superior to all others from the blue to the shortest wave-lengths. When one does not care about the region beyond $220\mu\mu$, the gelatine dry plate is the best. The sensitiveness of the improved plate to the ultra-violet becomes striking at $220\mu\mu$ and increases rapidly as the rays become more refrangible. The gelatine dry plate gives out at $182\mu\mu$. It is not absolutely lacking in sensitiveness for the shorter waves; but the spectrum which it gives is a false one. In consequence of the absorbing action of the gelatine, all spectra, even though discontinuous, develop as a continuous, faint band which does not correspond in any way to the energy differences of the different waves of the source of light under examination. Therefore the ultra-violet plate is the only one that can be used for photographing the spectrum beyond $182\mu\mu$."

In these three papers I have tried to give a fairly complete account of our knowledge in regard to photographic emulsions so far as this can be obtained from a study of the literature. I have tried to give a fair statement of the arguments for and against each particular hypothesis. The subject has been considered under the following heads: methods of preparation; amount of silver in film; sensitiveness of film to light; methods of ripening; limits to ripening; inhomogeneity of emulsion; reducing action of some gelatines; question of reduction during ripening; theories of ripening; state of silver bromide in film; behavior of mixed emulsions; opacity; coarsening of silver bromide grains; effect of water content and of gelatine content; effect of chemical and optical sensitizers; effect of medium; increased sensitiveness to different lights; sensitiveness of precipitated silver bromide to development; the ultra-violet plate. While it will take a great many experiments and a great deal of time to establish a satisfactory theory of the emulsion, it should not be difficult to develop a working hypothesis which will bring order out of chaos and which can be extended, modified or corrected as may prove desirable. In the next paper I shall try to present such a working hypothesis.

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